A STUDY ON THE SOIL AND WATER QUALITY OF SELECTED SITES AROUND SOLID WASTE DUMPING AREAS IN KERALA STATE

Thesis

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By

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Under the guidance of

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2018

DECLARATION

I, **Jaseela C** do hereby declare that this thesis entitled **"A Study on the Soil and Water Quality of Selected sites Around Solid Waste Dumping Areas in Kerala State"** submitted by me to the University of Calicut for the award of degree of Doctor of Philosophy in Chemistry under the Faculty of Science is the result of the bonafide research carried out by me under the guidance of **Dr. P S Harikumar**, Senior Principal Scientist and Head, Water Quality Division, CWRDM, Kozhikode. I further declare that the results presented in the thesis have not been submitted previously for any degree.

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This is to certify that the thesis entitled "**A STUDY ON THE SOIL AND WATER QUALITY OF SELECTED SITES AROUND SOLID WASTE DUMPING AREAS IN KERALA STATE**" is an authentic record of research work carried out by **Mrs. Jaseela C,** under my supervision and guidance, in partial fulfillment of the requirements for the award of Doctor of Philosophy in Chemistry under the Faculty of Science, University of Calicut. The contents of this thesis, in full or in parts, have not been presented before for the award of any degree or diploma.

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Jaseela C

DEDICATED TO MY FAMILY

AND DEAR ONES

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LIST OF ABBREVIATIONS

AAS	Atomic Absorption Spectrophotometer
APHA	American Public Health Association
BCF	Bioconcentration Factor
BIS	Bureau of Indian Standards
BOD	Biochemical Oxygen Demand
CCME	Canadian Council of Ministers of the Environment
CEC	Cation Exchange Capacity
CEC	Cation Exchange Capacity
COD	Chemical Oxygen Demand
CPCB	Central Pollution Control Board
DO	Dissolved Oxygen
DTPA	Diethylene Triamine Penta Acetic Acid
EC	Electrical Conductivity
EF	Enrichment Factor
EF	Enrichment Factor
GC	Gas Chromatography
GIS	Geographical Information System
ICP-OES	Inductively Coupled Plasma-Optical Emission Spectroscopy
KR	Kelly's Ratio
KR	Kelly's Ratio
LPI	Leachate Pollution Index
MHR	Magnesium Hazard Ratio
MoEF	Ministry of Environment and Forest

MPN	Most Probable Number
MSW	Municipal Solid Waste
PCA	Principal Component Analysis
PLI	Pollution Load Index
PLI	Pollution Load Index
SAR	Sodium Adsorption Ratio
SEM	Scanning Electron Microscope
SSP	Soluble Sodium Percentage
TEM	Transmission Electron microscopy
TF	Translocation Factor
TOC	Total Organic Carbon
USEPA	United States Environmental Protection Agency
WHO	World Health Organization
WQI	Water Quality Index

ANNEXURE I
LIST OF PUBLICATIONS

Publications related to the topic of research:

- Jaseela, C., Kavya, P., & Harikumar, P. S. (2016). Application of GIS and DRASTIC modeling for evaluation of groundwater vulnerability near a solid waste disposal site. *International Journal of Geosciences*, 7, 558-571. doi: 10.4236/ijg. 2016.74043

- Jaseela, C., Kavya, P., & Harikumar, P. S. (2016). Geospatial and Statistical Assessment of Groundwater Contamination due to Landfill Leachate- a case study.*Journal of Water Resource and Protection*, 8, 121-134. doi: 10.4236/jwarp.2016.82010

- Jaseela,C., & Harikumar, P.S. (2018). Assessment of contamination risk in soils of Njeliamparamba municipal solid waste landfill site in India using pollution indicators, Pollution Research, EM International(communicated).

Other publication in the field of Chemistry

- Harikumar, P.S., Jaseela, C.& Megha, T. (2012). Defluoridation of water using Biosorbents. Natural Science, 4(4), 245-251. doi:10.4236/ ns.2012.44035

ANNEXURE II

- Jaseela, C., & Harikumar, P. S. (2015). *Impact of landfill leachate on groundwater quality around a solid waste dump site in Kozhikode district, Kerala.* Proceedings of the National Seminar on Issues, Challenges and Strategies in Sustaining Soil health, 10-11 December 2015, Kerala Forest Research Institute, Thrissur, Kerala.

- Jaseela, C., Priyanka, M., & Harikumar, P.S. (2014).*Assessment of Heavy Metal Contamination of Soil near a Solid Waste Dumping Site using Statistical Analysis and Contamination Factor*, Proceedings of the International Symposium on Integrated Water Resources Management, 19-21 February 2014, Centre for Water Resources Development and Management, Kozhikode, Kerala.

ABSTRACT

Solid waste generation have dynamically increased in urban localities all over the world due to the rapid urbanization and population growth. Hazardous wastes from residential and industrial chemicals that should be disposed off in hazardous waste landfills sometimes end up in municipal landfills. Once these wastes end up in the landfill, chemicals can leach into the soil and groundwater by means of precipitation and surface runoff. Leachate contains large amount of organic content, inorganic salts and heavy metals. Unscientific disposal of municipal solid waste (MSW) causes an adverse impact on all components of the environment and human health. There is a dire need to monitor leachate, groundwater and soil to assess the extent of pollution and to implement suitable remedial measures.

Deterioration of groundwater quality in the vicinity of MSW dumping sites was carried out by monitoring the various physico-chemical and biological parameters. A total of 59 groundwater samples were collected from the four selected MSW dumping sites (Njeliamparamba, Laloor, Pettipalam and Vellaramkunnu) in Kerala and the results of analysis indicated that Njeliamparamba was found to be the area with maximum contamination. Results obtained in Njeliamparamba revealed that, the quality of the

groundwater samples collected within 300 meter from the dumping site were determined to be highly polluted. The effect of leachate migration from the Laloor dumping site might have caused higher concentrations of nitrate and coliform bacteria. Presence of coliforms bacteria in the Pettipalam and Vellaramkunnu dumping site indicated the presence of microbial pollution of the groundwater. With the help of Piper diagram, the interpretation of hydrochemical facies of groundwater samples in Njeliamparamba, Laloor and Pettipalam indicated that, dominant ions comprised of (Na^++K^+) Cl^- type, and the type of water that predominates in Vellaramkunnu is calcium chloride type.

The impact of leachate on the surrounding groundwater quality in Njeliamparamba is a major environmental concern of the area. To evaluate the water quality issues associated with MSW, leachate and groundwater samples within 500 meter from the dumping site were collected and analyzed. The results of the physico-chemical and bacteriological analyses have confirmed the presence of various contaminants such as organics, inorganics and heavy metals. Spatial distribution of groundwater quality parameters was measured by Geographical Information System (GIS). The water quality status of groundwater samples indicated that, the samples collected within 300m distance from the dumping site were affected by leachate percolation. Leachate Pollution Index (LPI) and Water Quality Index (WQI) in the study area were applied to assess the overall quality of the leachate and groundwater. Since there is no natural or other possible reason for high concentration of the pollutants, it can be concluded that leachate has significant impact on groundwater quality in the area. Quality assessments for irrigation suitability of the groundwater samples were assessed using soluble sodium percentage, sodium adsorption ratio, Kelly’s ratio and magnesium hazard and the results showed that majority of the groundwater samples were found to be suitable for agriculture purposes.

Deteriorating soil quality is a grave consequence of MSW dumping which have resulted in growing public concern. To evaluate the soil quality and assessment of soil contamination at Njeliamparamba, a total of 50 soil samples were collected at the depth of 0-30cm and 30-60cm from 25 sites. The physicochemical characteristics of most of the samples revealed acidic nature and obtained mainly three types of texture (sandy loam, loam and clay loam). The mean value of the major ions (cations and anions) in soil samples follows the order: exchangeable calcium> sodium> potassium> magnesium > inorganic phosphorous and sulphate> chloride> alkalinity. The results revealed that the concentrations of all the physico-chemical parameters decreased from surface to sub-surface soil in all the stations, which confirmed the increased anthropogenic activities with time. The monitoring of pesticide residues indicated that out of twenty five sampling sites, only one sample showed the presence of lindane and three samples reported the presence of aldrin. The heavy metals such as Fe, Cu, Ni, Pb and Zn were detected in all the analysed soil samples and were found to be within the CCME soil quality limit except Pb. The results of the enrichment factor for surface soils revealed that most of the soils samples could be considered as deficiency or minimal enrichment for all the studied metals, while the values of Pb was found to have significant enrichment. The results of the contamination factor also found to have low contamination levels for Cu, Ni, Zn, Cd and moderate contamination levels for Pb. The pollution load index calculated for majority of the sampling sites were found to be low except one sampling site. The concentrations of available metals in the soils of Njeliamparamba were found to be above the critical limit for micronutrients. The results of the study indicated that the samples collected within the buffer zone had more contamination than those collected outside the zone.

The DRASTIC model in a Geograhic Information System environment was used to determine the groundwater vulnerability to contamination in the

vicinity of a two solid waste disposal sites, Njeliamparamba and Laloor, municipal dumping sites in Kozhikode and Thrissure district. DRASTIC is an index model composed of several hydrogeological parameters. The ArcMap 10.1 was used to prepare a vulnerability map for the study area. According to the vulnerability map in the Njeliamparamba, the study area was divided into moderate vulnerable, high vulnerable and very high vulnerable. The resulting vulnerability map was then validated using a chemical and bacteriological parameter analysed from nearby wells of the dumping site to assess the area which is of more potential risk to pollution. From the results of the study, it is clear that the concentrations of total dissolved solids and *E.coli* can be correlated in different vulnerable zones; which validated the results obtained. The vulnerability index map in the Laloor dumping site was identified into three categories of groundwater vulnerable zones corresponding to low, medium and high vulnerability zones respectively. The characteristics of groundwater samples from Laloor indicated that, the nitrate is the major contaminant; therefore the DRASTIC model was validated using the nitrate concentrations. The vulnerability map indicates that 80% of the nitrate contaminated samples were coming in the region of high vulnerable zone. The results revealed that the vulnerability index value was found to be higher in Laloor compared to Njeliamparamba; but more groundwater contamination was observed in Njeliamparamba due to high leachate percolation. The results provided a preliminary tool to identify potential areas or vulnerability zones with high risks of groundwater contamination due to the leachate percolation from solid waste dumping sites. The vulnerability map obtained from the DRASTIC method provides information about the locations that should be avoided waste dumping and also highlight the importance of showing high priority in terms of protection and prevention of contamination.

Electro-coagulation technology was employed for the removal of organic and inorganic contaminants in MSW landfill leachate. This study investigated the removal of nitrate, COD and heavy metals from MSW landfill leachate. Effects of different parameters including pH (3, 7, 9 and 12), electro-coagulation time (20, 40, 60, 80 and 100min), applied voltage (2, 4, 6 and 8V), supporting electrolyte, NaCl (0.20, 0.40, 0.60, 0.80 and 1.0g/L), electrode material (Fe and Al) and initial concentration of different parameters were studied in order to evaluate the efficiency of electro-coagulation. The highest removal efficiency of nitrate (75.1± 0.2%) was observed under the following conditions: pH: 9, voltage: 8V, electrolysis time: 80 minutes, NaCl concentration of 0.60g/L, initial nitrate concentration of 101.0±1.5mg/L and Al as sacrificial anode. For higher removal of COD, the optimal conditions are pH: 7, voltage: 8V, electrolysis time : 80 minutes, NaCl concentration of 0.60g/L, initial COD concentration of 3.40g/L, and Al as sacrificial anode. The highest removal efficiency for heavy metals was observed at pH 6, 8V, 30 minutes of EC time, NaCl concentration of 0.60g/L, initial heavy metals concentration of 5.0mg/L and Fe as sacrificial anode. In order to minimize the energy consumption while maintaining higher removal efficiency, the current density must not be higher than 1.8mA/cm^2, with EC time in the range of 15 to 30 minutes for heavy metals and 60 to 80 min for nitrate and COD. This process consumes low amount of energy, making the process economically feasible technique and possible to scale up. The results also demonstrated that the electro-coagulation is a feasible technique for treatment of multi-pollutants (organic, inorganic and heavy metals) removal from the landfill leachate.

Developing cost effective and environmentally friendly technologies for the remediation of wastewaters polluted with toxic substances is a topic of global interest. The treatment of wastewater using horizontal flow constructed wetlands vegetated with *Eichhornia crassipes* and *Marsileaceae* were investigated. The monitoring of CW shows that the performance of the system was good and it effectively removed high concentration of pollutants such as COD, TDS, TSS, oil and grease, nitrate, phosphate, sulphate, bacteria and heavy metals within a few days under local conditions. The percentage removal of heavy metals by constructed wetland in synthetic wastewater was 94.0%, 86.80% and 80.36% for Pb, Ni and Cd respectively within 12 days.

Phytoremediation technology uses plants to clean up contaminated environments. The phytoremediation using aquatic plant species such as *Salvinia molesta, Azolla Caroliniana* and *Marsileaceae* were used to remediate water contaminated with heavy metals. The study revealed that the *Salvania molesta* and *Marsileaceae* could remove Pb, Ni and Cd efficiently (>90.0%) within 21 days of treatment. Maximum bioconcentration factor were obtained for *Salvinia Molesta* and *Marsileaceae* compared to *Azolla Caroliniana*. TF of metals in the studied plants showed a root to shoot translocation factor of greater than one for all the metals*;* hence these plants are effectively transported metals from root to shoot.

Phytoremediation and enhanced phytoremediation was employed to investigate the capability of phytoremediation and enhanced phytoremediation techniques using nanoscale zero-valent iron particles (nZVIFe) and citric acid to remediate heavy metal contaminated soil. The terrestrial plant species such as *Catherathus rosaseus, Tradescantia spathacea* and *Alternanthera dentate* were selected. The removal removal efficiency of the tested plants was observed in the following order: treatment with citric acid > treatment with nZVIFe > phytoremediation. Within 45 days of citric acid enhanced phytoremediation study, removal efficiency of Pb, Ni and Cd (with an initial concentration of 100mg/kg of Pb, 55.0mg/kg of Ni & 50.0mg/kg of Cd) were 97.90%, 77.27% and 71.50%, respectively for *Catharathus rosaseus,* 93.20%, 74.18% and

73.60%, respectively for *Tradescantia spathacea* and 92.70%, 80.36% and 76.80%, respectively for *Alternanthera dentate*.

Among the methods, phytoremediation and constructed wetland technology proved to be an economical option for the treatment of contaminated water, soil and leachate. Electro-coagulation helped in the remediation of contaminants in wastewater within a short period of time.

JASEELA C.”A STUDY ON THE SOIL AND WATER QUALITY OF SELECTED SITES AROUND SOLID WASTE DUMPING AREAS IN KERALA STATE”. THESIS. CWRDM (CENTRE FOR WATER RESOURCES DEVELOPMENT AND MANAGEMENT), UNIVERSITY OF CALICUT, 2018.

Chapter 1

INTRODUCTION

The production of solid waste is an inevitable consequence of human activity, and its management has become a serious issue as it directly impacts the health of the people and environment surrounding it. The worlds' cities generate 2.01 billion tonnes of solid waste, amounting to a footprint of 0.74 kilograms per person per day. With an increasing population, economic growth, along with urbanization and industrialization, annual solid waste generation is expected to increase by 70% from 2016 levels to 3.40 billion tonnes in 2050 (World Bank, 2018). About 960 million tonnes of solid waste is being generated annually as byproducts during municipal, agricultural, industrial, mining and other processes in India. Out of this, 350 million tonnes is organic in nature, 290 million tonnes is inorganic in nature, and 4.5 million tonnes is hazardous in nature (Pappu et al., 2007).

1.1 Generation of municipal solid waste

Currently, the quantity of waste generated from urban centers of the world is about 1,300 million tonnes per year (1.2 kg/capita/day) which is expected to rise to 2,200 million tonnes per year by 2025 (World Bank, 2012).

The waste generated from South and East Asia corresponds to 33% of the world's total quantity. It is estimated that the generation of municipal solid waste in Asia will reach 1.80 million tonnes per day by 2025 (World Bank, 1999). India, the second most populous country intended to achieve an industrialized nation status by the year 2020, has experienced rapid urbanisation and industrialisation during the last few decades (Sharma & Shah, 2005). The waste generation in India, is more than 42 million tons annually, and the rate of solid waste generation varies from 0.20 kg/d to 0.80 kg/ d (Rana et al., 2015). It is reported from the literature study that the increase in the generation of municipal solid waste in India is around 5% annually (Sharholy et al., 2008), and the generation is 127,486 tonnes per day (TPD) in 2011 (Rana et al., 2017). Out of the total municipal solid waste generated in India, 89,334 TPD of waste was collected and 15,881 TPD was recycled (TERI, 2015). State-level statistics of municipal solid waste generation in India (2009 to 2012) is indicated in Figure 1.1.

Kerala State which has the highest human development index (0.790) in India due to the increasing urbanization, constraints of land availability and regular change in consumption pattern, the generation of municipal solid waste in Kerala has increased beyond the assimilative capacity of our environment and management capability of the existing waste management systems. The quantity of waste generated in the Kerala State is about 6506 TPD (Varma, 2013) and it is about 477 TPD in Kozhikode (Varma, 2013), which is the third largest city of Kerala.

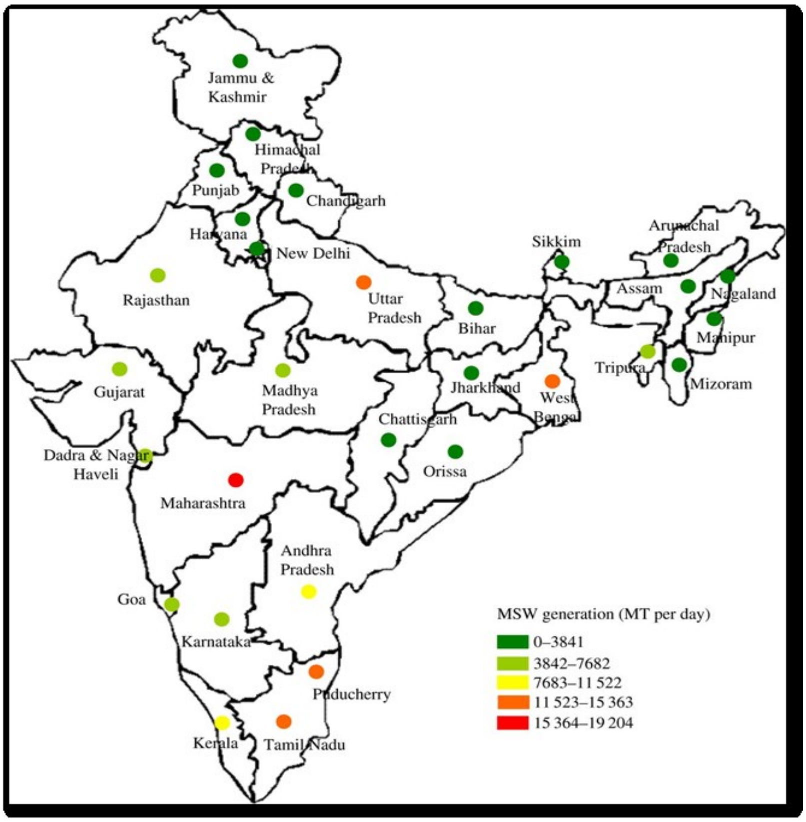

Figure 1.1: State level statistics of MSW generation in India (Adapted from Kumar et al., 2017)

1.2 Composition, characteristics and status of Indian municipal solid waste

Municipal solid waste (MSW) defined by the Ministry of Environment Forest and Climate Change as “the commercial and residential wastes generated in municipal or notified areas in either solid or semi-solid form excluding industrial hazardous wastes but including treated bio-medical wastes” (MoEF, 2000). The composition and characteristics of MSW is significantly influenced by many factors such as living standards, economic development, food habits, culture, literacy rate, and topographical conditions (Gupta et al., 2015). MSW includes compostable organic matter (food waste), recyclables (paper, plastic, metals, glass, etc.), toxic substances (paints, used batteries, pesticides, medicines), and soiled waste (disposable syringes, blood stained cotton, sanitary napkins) (Kausal et al., 2012). Table 1.1 shows the composition of MSW in

India and regional variation. Figure 1.2 illustrates the average composition of MSW produced by Kerala.

Table 1.1: Composition of MSW in India and regional variation (Annepu, 2012)

Region/City	**MSW (TPD)**	**Compostables (%)**	**Recyclables (%)**	**Inerts (%)**	**Moisture (%)**	**C.V. (MJ/kg)**	**C.V. (kcal/kg)**
Metros	51,402	50.89	16.28	32.82	46	6.4	1523
Other cities	2,723	51.91	19.23	28.86	49	8.7	2084
North India	380	50.41	21.44	28.15	46	9.8	2341
East India	6835	52.38	16.78	30.85	49	6.8	1623
South India	2343	53.41	17.02	29.57	51	7.6	1827
West India	380	50.41	21.44	28.15	46	9.8	2341
Overall urban India	130000	51.30	17.48	31.21	47	7.3	1751

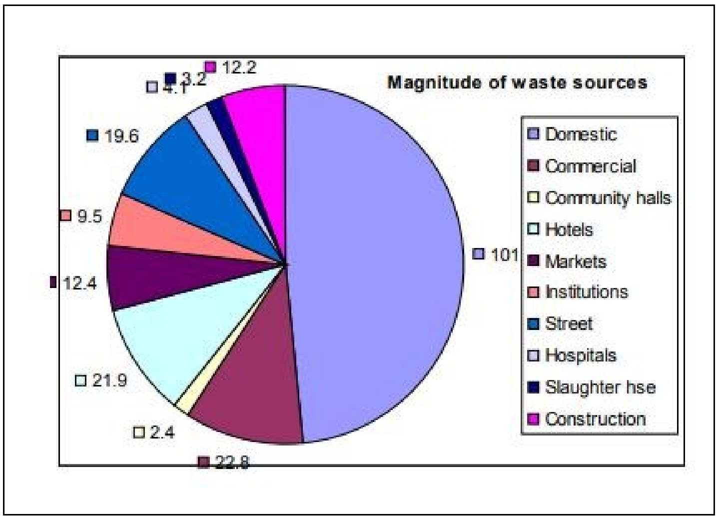

Figure 1.2: Average composition of MSW in Kerala (Adapted from Varma, 2013)

The Ministry of Environment Forest and Climate Change (MoEFCC), Government of India had issued MSW management and handling rules (2000) for scientific MSW management, ensuring appropriate collection, segregation, transportation, processing and disposal of waste and improve the existing amenities to prevent contamination of soil, groundwater and air. However, the current status of MSW management in India is not very satisfactory. MSW in India is generally disposed off in low lying areas or open dumps without necessary precautions (Srivastava et al., 2014). Usually municipalities are responsible for managing MSW in India, but they fail to manage it because of the lack of proper collection system, technical expertise and insufficient financial resources (Srivastava et al., 2014; Guerrero et al., 2013). The municipalities utilise major portion of their financial resources on collection of MSW and small amount is left thereafter for its management (Collivignarelli et al., 2004). Current systems in India cannot cope up with the volume of waste generated by an increasing urban population, and these impacts on the environmental and social imposed by MSW received attention in recent decades.

1.3 Municipal solid waste landfill

Disposal of MSW in landfills is the most common used method of waste management worldwide. Though, mostly at unlined landfills, leachate can contaminate soil and groundwater with potentially hazardous chemicals at concentrations that exceeded drinking water quality standards (Reyes-López et al., 2008). Lined or engineered landfills also deteriorate over time and eventually fail to prevent the migration of leachate into an aquifer (Banu & Berrin, 2015). The major environmental problem at landfills is the migration of leachates and the subsequent contamination of soil and groundwater.

1.4 Hydrological aspects of landfill process

Hydrological and hydrogeological characteristics play major role in selection of landfill sites, landfill design and its performance. In order to assess the potential landfill site, the factors such as availability of land area, soil conditions, topography, hydrology, geologic and hydrogeological conditions, environmental conditions, and climatological conditions have to be measured. Therefore, the hydrometeorological parameters such as surface storage, infiltration, soil storage, lateral drainage, leakage through liners, weather and also hydrogeological components and topographical features are necessary to be incorporated while monitoring plan is investigated. These parameters are helpful for estimating the quantity of percolated leachate periodically. Therefore, the movement of percolated leachate of the landfill depends on the characteristics of the surrounding materials. In the case of unlined landfills, transport of leachate occurs along with the groundwater flow and may ultimately reach streams or other sources (Ghosh & Sharma, 2006).

1.5 Landfill leachate: generation and characteristics

Wastes placed in landfills are subjected to groundwater underflow or infiltration from precipitation and as water percolates through the waste, it extracts variety of inorganic, organic compounds and other toxic components. The resulting liquid called ‘leachate’ accumulates at the bottom of the landfill and percolates through the soil, finally reaches the groundwater (Kumari et al., 2017; Mor et al., 2006). Figure 1.3 shows the schematic representation of the generation of leachate

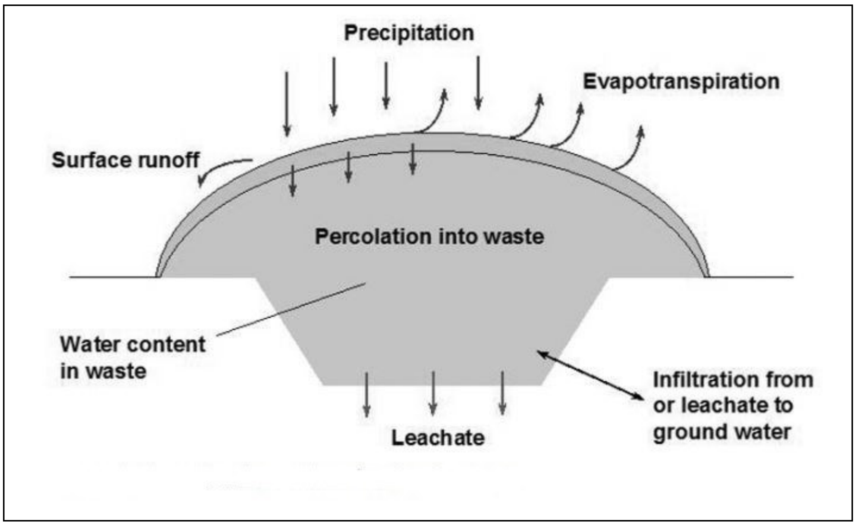

Figure 1.3: Schematic representation of the generation of leachate (Adapted from Sami Serti, 2000)

The rate and characteristics of landfill leachate depends on various factors like solid waste composition, hydrology of site, age of landfill, moisture and temperature conditions, particle size, degree of compaction, and available oxygen. Leachate are extremely concentrated complex effluents which contain mainly four groups of pollutants including dissolved organic matter (volatile fatty acid and refractory organic matter like humic substances), macro inorganic compounds (Na^+, K^+, Ca^{2+}, Mg^{2+}, NH_4^+, HCO_3^-, Fe), heavy metals (Fe, Pb, Ni, Cd, Zn, Cu and Mn), xenobiotic organic compounds (pesticides, aromatic hydrocarbons, phenols), and microorganisms (predominantly total and thermotolerant coliforms) (Yao, 2017). The young acidogenic landfill leachate is usually characterized by high concentrations of biochemical oxygen demand (4000–13,000mg/L) and chemical oxygen demand (30,000–60,000mg/L), moderately high concentration of ammonium nitrogen (500–2000mg/L), high ratio of BOD_5/COD (0.40 to 0.70) and pH value (as low as 4) with biodegradable volatile fatty acids present to be its main constituents (De Morais & Zamora, 2005). Heavy metals are one of the most hazardous components present in the leachate (Adeolu et al., 2011). Table 1.2 shows the classification of leachate according to the composition changes.

Table 1.2: Classification of leachate according to composition changes

Type of leachate	**Yong (0-5 years)**	**Intermediate (5-10 years)**	**Stabilised (10-20 years)**	**Old (>20 years)**	**Reference**
pH	3 - 6	6 - 7	7 - 7.5	7.5	Yao, 2017
TDS, (mg/L)	10,000-25,000	5000-10,000	2000-5000	<1000	Mukherjee et al., 2015
Chloride, (mg/L)	1000-3000	500-2000	100-500	<100	Mukherjee et al., 2015
Biodegradability	Important	Medium	Low		Yao, 2017
Ammonia Nitrogen, (mg/L)	<400	-	>400	<30	Mukherjee et al., 2015
BOD_5/COD	0.50-1.0	0.10-0.50	<0.10	<0.05	Yao, 2017
TOC/COD	<0.30	0.30-0.50	>0.50	-	Yao, 2017
Organic compounds	80% volatile fatty acids (VFA)	5–30% VFA+ humic and fulvic acids	Humic and fulvic acids	-	Foo & Hameed, 2009
Sulfate, (mg/L)	500-2000	200-1000	50-200	<50	Mukherjee et al., 2015
Heavy metals, (mg/L)	Low to medium	Low	Low	-	Yao, 2017

Leachate composition is influenced by a various factors such as climatic and hydro-geological conditions (rainfall, groundwater intrusion, snowmelt), operational and management issues at the landfill (compaction, refuse pre-treatment, liquid waste codisposal, vegetation cover, re-circulation), characteristics of dumped waste in the landfill (chemical composition, biodegradability, initial moisture content, particle size, density), internal processes inside landfill (decomposition of organic materials, gas and heat generation and their transport, refuse settlement), and age of the landfill (Christensen et al., 2001; Rodríguez et al., 2004).

1.6 Formation of leachate plume

Gravity causes the movement of landfill leachate to the bottom through the underlying soil and subsequently it reaches the aquifer system. When leachates move towards the subsurface, mix with groundwater held in the soil spaces and this mixture move along the groundwater's flow path as a plume of contaminated groundwater. The contaminants in the leachates come into the unsaturated zone initially and ultimately are transported to the groundwater table in the saturated zone. Both water and air fill the pores between soil particles in the unsaturated zone**.** The slow movement of leachates in the unsaturated zone causes attenuation of certain chemicals in the leachate. Positively charged Pb, Zn, Cd and Hg metals, are easily attenuated and while others (volatile organic compounds and acids) are not easily attenuated. As easily attenuated pollutants flows through soil, these pollutants adsorb to the soil and are removed from the leachate. When binding sites of the soil particles become occupied, they can hold no more chemicals and thus pollutants will move through the soil in to the groundwater.

1.7 Threats

Dumping of MSW without proper treatment imposes negative effect on different components of environment (soil, water and air), human health and aesthetic value. Various studies have been reported that the MSW leachate can be contaminate the surrounding environment, and subsequent contamination of the soil and groundwater quality.

1.7.1 Groundwater contamination

Leachate generated from municipal solid waste dumping site are considered to be significant sources of groundwater contamination due to the migration of leachate, a complex mixture of pollutants having high concentration of organic and inorganic contaminants and lasting toxicological characteristics (Bashir et al., 2009; Abd El-Salam & Abu-Zuid, 2014). After leachate reach the groundwater system, the contaminants in leachate can mix with the aquifers. Contamination of groundwater is a long-term problem where contamination can persist in aquifers for decades without treatment because groundwater travel times are comparatively slow. Therefore, the contaminants can persist for a long time in the groundwater environment, rendering groundwater unsuitable for consumption and other uses (Kelly & Wilson 2002). The unscientific disposal of MSW over large areas poses severe threat to the underground water resources, environment and community health (Ganiyu et al., 2016). The quality of groundwater depends on the quantity and quality of generated waste, quality of recharged water, sewage treatment and subsurface geochemical processes (Ganiyu et al., 2016; Rizwan & Gurdeep, 2010). Areas near MSW dumping site have higher possibility of groundwater contamination because of the pollution source of leachate originating from the nearby dumping site. This groundwater contamination results in a significant threat to the natural environment as well as the local groundwater resource user. The impact of landfill sites on groundwater quality has been studied by different workers in recent years (Mor et al., 2006; Ganiyu et al., 2016; Abd El-Salam & Abu-Zuid, 2014).

Several studies on the contamination of groundwater due to the transport of leachate have been reported. Han et al. (2016) reported that more than 96 types of pollutants have been detected in groundwater collected near the MSW dumping site, and 22 types of pollutants were considered to be the major pollutants in groundwater. Based on their distribution, these pollutants were designated as “widespread”, “local” and “point”. The groundwater pollutants such as ammonia, nitrate, nitrite, organic matter, chemical oxygen demand, total hardness, chloride, iron, manganese, total coliforms, volatile phenol and permanganate index are included in widespread pollutants. The local groundwater pollutants included total dissolved solids, fluoride, total phosphorus, sulfate, hexavalent chromium and bacterial count. The trichloro-benzene, lead, cadmium, mercury and iodide are included in point groundwater pollutants.

1.7.2 Contamination of soil

Soil is the main constituent of the earth system as it control the hydrological, biological, erosional, and geochemical cycles (Adamcová et al., 2016). Soil contamination caused by human activities has adverse effects on the environments and ecosystems worldwide (Thomaz & Luiz, 2012; Chen et al., 2015), and MSW is an emerging environmental problem. The soil is a significant component of landfill site is a media where polluted materials are deposited. The unscientific dumping of MSW on land is adversely affecting soil properties (both biotic and abiotic). Precipitation that infiltrates through the MSW leaches the constituents from the decomposed waste mass while moving down leading to contamination of subsurface soil. Leachate generated from the MSW dumping site has adverse effect on chemical properties as well as the geotechnical properties of the soil. As leachate penetrates through the soil stratum, it contaminates the ambient environment. The degree of contamination in the aquifers depends on the transport rate of contaminants and depository conditions at the site while the contaminants permeate through the soil media (Vasanthi et al., 2008). Thus, understanding the transportation of leachate within the soil depends on understanding the structures of the soil. The difference in soil porosity, hydraulic conductivity, particle size, permeability and surface area will lead to variation in contact time with the leachate.

Soil pollution by heavy metals has become a serious environmental problem due to its potential adverse ecological effects (Adamcová et al., 2016). Some heavy metals are carcinogenic, mutagenic, teratogenic and endocrine disruptors while others cause neurological and behavioral changes especially in children (Mahar et al., 2016; Cristaldi et al., 2017). Heavy metals occur naturally at low concentrations in soils, but they are considered as soil contaminants due to their toxicity, non-biodegradable properties, wide source, and their ability to accumulate for long period of time (Dong et al., 2011). Heavy metal pollution in soil is an irreversible process, once heavy metals enter the soil, they are difficult to extract from the soil environment, are hazardous to organisms and influence soil ecosystem (Zhou & Song, 2004). Table 1.3 discusses the some of the toxic effects of some heavy metals on human health.

The heavy metals pollution of soil near MSW dumping site has recently been the subject of extensive discussion (Kasassi et al. 2008; Kanmani & Gandhimathi 2013). Indeed, various studies have demonstrated that soils collected near the dumping site are seriously contaminated by heavy metals; therefore, the assessment of heavy metals is useful to assess pollution in the environment. Solid waste disposals methods also represent a significant source of heavy metals released into the environment (Waheed et al., 2010; Rizo et al., 2012). Due to migration of leachate, soils have been contaminated with heavy metals such as lead, copper, zinc, iron, manganese, chromium, and cadmium. The major sources of these heavy metals in MSW dumping sites are the co-disposed industrial wastes, incinerator ashes, mine wastes and household hazardous substances such as batteries, paints, dyes, inks, etc. (Erses & Onay 2003; Hong et al., 2002). The presence of humic substance in leachate might enhance the transportation of heavy metals, and also increase of ash content in landfill may increase the heavy metal and salts concentrations in leachates (Urase et al., 1997).

Table 1.3: Toxic effects of various heavy metals on human health (Dixit et al., 2015)

Heavy metals	Toxic Effects
Cd	Mutagenic, carcinogenic, endocrine disruptor, fragile bones and lung damage, affects calcium regulation in biological systems.
As	Affects essential cellular processes such as ATP synthesis and oxidative phosphorylation.
Cr	Excess of Cr^{6+} result in perforation of the nasal septum, bronchial carcinomas, dermatitis, allergic issues.
Cu	Brain and kidney damage, liver cirrhosis and chronic anemia, intestine and stomach irritation.
Hg	Brain damage, lung and kidney failure, autoimmune diseases, loss of memory, depression, drowsiness, fatigue, hair loss, insomnia, restlessness, disturbance of vision, tremors, temper outbursts.
Ni	Cancer of the lungs, nose, sinuses, throat through continuous inhalation, immunotoxic, genotoxic, neurotoxic, affects fertility, allergic skin diseases such as itching, hair loss.
Pb	Excess exposure in children causes risk of cardiovascular disease, impaired development, short-term memory loss, reduced intelligence, disabilities in learning and coordination problems.
Se	Dietary exposure of around 300µg day-1 affects endocrine function, gastrointestinal disturbances and hepatotoxicity, impairment of natural killer cells activity.
Zn	Dizziness, fatigue etc.
Ag	Exposure may cause breathing problems, lung and throat irritation and stomach pain, skin and other body tissues to turn gray or bluegray.
Ba	Cause cardiac arrhythmias, respiratory failure, high blood pressure, gastrointestinal dysfunction, and muscle twitching.

1.7.3 Contamination of air

In India, MSW is mostly characterised by high density that emulates high degree of biodegradable organic matter and moisture content, which when undergoes anaerobic decomposition in landfills, leading to generation of landfill gas. The landfill gas mainly consists of CH_4 and CO_2 together with little amount of volatile organic compounds and other trace gases (Hegde et al., 2003). Being greenhouse gas both methane and carbon dioxide have global warming potential, which is 25 times higher in methane than global warming potential of carbo dioxide with atmospheric residence time of 12±3 years (IPCC, 2007).

1.7.4 Health impacts

Due to continuous increase in the generation of MSW, its mismanagement, ever-changing composition and poor public attitude, people are directly exposed to health risks. There is direct and indirect relationship between health impact with every step of the handling, treatment, and disposal methods of waste (Giusti, 2009). Open burning, illegal transfer of biomedical and other hazardous waste to dumping place leads to health problems as well as pollution of air, soil and groundwater (Kathiravale & Yunus, 2008). People residing nearby landfill sites have been reported high risk of congenital birth defects, cancers, bronchitis, asthma-like symptoms, chronic obstructive pulmonary disease, neurological symptoms, and liver problems, skin irritation, eye irritation, anxiety or depression in those who lived near the landfill site (Sever, 1997; Ray et al., 2005; Narayana, 2009). In addition, parasitic infections such as dengue and malaria have often occurred as they used groundwater for domestic purposes (De & Debnath, 2016).

1.8 Managing waste in a sustainable manner

Various technologies are proposed to control the negative impacts of their waste and to find beneficial reuses for it. The two leading innovative mechanisms are adopted for disposing MSW, which includes Biogenic waste conversion technologies and non-biogenic waste conversion technologies, and these technologies are discussed in Table 1.4 and Table 1.5.

Table 1.4: Biogenic waste conversion technologies

Processes	Descriptions of processes	References
Composting	Composting is the decomposition of organic fraction of MSW carried out by microorganism in warm moist, aerobic and anaerobic environment. The compost thus produced (which contains plant nutrients utilized for the growth of plants) used as soil conditioner in agricultural and horticultural or landscaping applications.	(Gupta et al., 2015)
Anaerobic digestion	This process is carried out by anaerobic micro organisms which convert carbon containing compounds to a biogas (primarily methane and carbon dioxide). The produced biogas can be burned for electricity, and the obtained residue can be aerobically digested to produce compost.	De Baere, 2006
MSW to ethanol	It is a promising technology as it uses a ubiquitous feedstock (MSW) to produce a cleaner liquid fuel for a rapidly motorizing, carbon-constrained world.	Kalogo et al, 2006
Biochar production	Thermal treatment of biogenic waste in oxygen-deficient conditions produces biochar, a soil amendment that gives agricultural uses as well as enduring carbon sequestration.	Fowles, 2007

Table 1.5: Non-biogenic waste conversion technologies

Processes	Descriptions of processes	References
Incineration	Incineration processes takes place in the presence of air and at the temperature of 850°C and waste are converted to carbon dioxide, non-combustible materials with solid residue (bottom ash) and water. It is highly exothermic and the heat generated recovered and utilized for production of steam, heating water and generating electricity. Incineration method is the most practical method of disposing hazardous waste.	DEFRA, 2007
Pyrolysis and gasification	Pyrolysis and gasification process are endothermic process, which converts waste to energy by combusting solid waste in oxygen deficient condition. The end products of both processes are syngas (CO, CH_4, and H_2), liquid (containing acetic acid, acetone and methanol) and char (containing carbon with inert material. The syngas can be burned as a fuel, and char can be used as a fuel or a soil amendment.	NSCA, 2002
Recycling	Recycling refers to the reprocessing of discarded materials into new products. Recycling requires a supply (collected, separated materials) and a demand (a market for the recycled product). Various MSW materials that would be recycled are plastics, paper, glass, rubber, metals, leather, etc.	Christensen et al., 2009

1.9 Assessment of groundwater vulnerability

Groundwater vulnerability is foundation stone for evaluating the risk of groundwater contamination and developing management preference to preserve the quality of groundwater. The concept of groundwater vulnerability is based on the statement that the physical environment may perhaps to provide some degree of protection for groundwater against human activities as well as natural contamination (Prasad & Shukla, 2014). National Research Council (1993) was defined groundwater vulnerability to contamination as ‘‘the tendency or likelihood of contaminants to reach a specified position in the groundwater system after introduction at some location above the uppermost aquifer''. Some of the hydro-geologic factors are soil material, geological formations of unsaturated zone and aquifers, depth of groundwater table and recharge rate.

1.9.1 Vulnerability assessment methods

The vulnerability assessment methods can be classified into three main categories, which are process based-methods, statistical methods and overlay and index methods (Vrba & Zaporozec, 1994; Tesoriero et al., 1998; Gogu & Dassargues, 2000; Harbaugh et al., 2000, Dixon, 2004). Selecting a suitable method will depend on several factors such as the extent of the study area, data availability, and desired results.

1.9.1.1 Process-based models

Process-based models usually required a large amount of primary and secondary data to apply the mathematical models for generating the principal tool. Such methods appear more complex and difficult to use on a regional scale (Neshat, 2013). Process-based simulation models employ the mathematical relations that govern the most important processes significant to water and contaminants behaviour in the subsurface system. These simulation models have the capability to quantify, predict and validate processes; vulnerability is represented in terms of travel times, concentrations of leachate or critical loads which are a quantitative assessment of pollution risk. This tool assists resources managers to develop a shared conceptual understanding of complex natural subsurface systems. The process based methods utilise simulation models to calculate the pollutant movement, but this method are limited by data shortage and computational problems.

1.9.1.2 Statistically-based methods

Statistical methods utilize data on the known a real contaminant distribution and explain the contamination potential for a specified geographical region using the available data in the regions of interest. This method is applied to quantify the vulnerability of groundwater contamination by determining the statistical dependence or relationship between observed contamination and environmental conditions that characterize vulnerability. It determines connection between actual source of contaminants and spatial variables in the groundwater using statistics. But statistical methods have limitations such as insufficient water quality interpretation, collection of spatial variables and data precision.

1.9.1.3 Overlay and index methods

Overlay and index methods highlights the combination of different regional maps by assigning a numerical index. Both methods are easy to apply in geographic information systems particularly on a regional scale, therefore, these techniques are the most popular methods used in vulnerability evaluation. The most widely used overlay and index methods includes GOD (Foster, 1987), DRASTIC (Aller et al., 1987), IRISH (Daly & Drew, 1999), and AVI (van Stemproot et al., 1993).

Overlay and index methods are based on the assumption that some major hydrogeological parameters mostly contribute in groundwater protection or affect groundwater vulnerability, and that these parameters can be identified and evaluated. These methods are usually based on limited basic regional data and generally cover extensive and regional areas. The collected hydrogeological parameters are classified according to a certain scoring or ranking system. This index would recognize areas where parameters indicating high vulnerability and some indices will assign numerical scores based on several parameters. Overlay and index methods are used to determine the migration of contaminants from the ground surface into the saturated zone that gives different vulnerability indices at different sites (Al-Hanbali & Kondoh, 2008). It is favorable because some of the factors like depth to groundwater and rainfall can be accessible over a large area, which makes them suitable for regional scale assessments. The main drawback of overlay and index method is the subjectivity in assigning numerical values to the explanatory entities and relative weights for the different attributes. DRASTIC index is one of the accepted overlay methods used to assess groundwater vulnerability.

1.9.2 Groundwater vulnerability using DRASTIC

The DRASTIC model was introduced by the U.S. Environmental Protection Agency to assess the potential of groundwater contamination (Aller et al., 1987). The regions which are more vulnerable to contamination can be identified using vulnerability mapping based on the hydro-geological parameters that affect and control the movement of groundwater (Aller et al, 1987). The groundwater vulnerability methods can provide information that can be used to prevent further pollution of contaminated areas. DRASTIC index assesses the groundwater vulnerability based on the intrinsic hydro-geological characteristics of a certain subsurface system. The DRASTIC method has four assumptions as follows: the contaminant is introduced at the ground surface; contaminant is flushed into the groundwater by precipitation; contaminant has the mobility of water; the area being evaluated by DRASTIC is 100 acres or larger.

1.9.3 GIS in vulnerability assessments

Geographical Information System in environmental contamination utilizes GIS software in mapping using the spatial interpolation tools from GIS. It utilise spatial interpolations of contaminants in the water and soil, and allows for proficient approach to remediation and monitoring of environmental contamination. GIS is a computer based method that is designed to capture, store, retrieve, manipulate and integrate spatial data. The DRASTIC model in a geographical information system environment was used in various vulnerability studies to assess the vulnerability of the study area (El-Naqa et al., 2006; Prasad & Shukla, 2014; Khan, 2014).

1.10 Treatment techniques

Generally, the best way of controlling the pollution due to landfill leachate must be treated before discharging to environment. Once leachate enters the soil and groundwater resources, remediation methods will be very difficult and expensive. Various techniques such as adsorption (Foo et al., 2013), chemical precipitation (Zhang et al., 2009), chemical oxidation (Singh & Tang, 2013) coagulation/flocculation (Guo et al., 2010), and biological methods (Xu et al., 2010) have been applied for the treatment of leachate. Because its characteristics change with the age of landfill, these methods have difficulty as decreasing treatment efficiencies and increasing cost. Therefore, electro-coagulation and phytoremediation technology has been used as a feasible alternative for the treatment of contaminated water, soil and leachate.

1.10.1 Electro-coagulation techniques

Electrochemical processes (electrolysis and electro-coagulation) have been successfully demonstrated for removing pollutants in various wastewaters. Removal mechanisms reported in the electrolysis process generally include oxidation, reduction, decomposition, whereas the mechanisms in the electro-coagulation process include coagulation, adsorption, precipitation and flotation (Kobya, 2003). Electro-coagulation (EC) is one of the most innovative electro-chemical techniques for wastewater treatment (Safari et al., 2011). This process is characterized by a fast rate of pollutant removal, no chemicals requirements, high sedimentation velocity, simplicity in operation, compact size of the equipment, and low capital and operating costs (Gengec et al., 2012). This technology is effective to remove a wide range of pollutants such as organic and inorganic pollutant, toxic metals.

In an EC process, the coagulating ions are generated in situ and this occurs in three stages: (a) electrolytic reactions at electrode surfaces, (b) formation of coagulants in aqueous phase and (c) adsorption of soluble or colloidal pollutants on coagulants, which are removed by sedimentation or flotation (Kobya et al., 2003). Iron and aluminum have been extensively used as a sacrificial electrode in the EC process (Gengec et al., 2012, Kobya et al., 2006). Sacrificial electrode dissolves from the anode producing corresponding metal ions. These ions hydrolyze to polymeric iron (aluminum oxyhydroxides), which are the coagulating agents (Gengec et al., 2012). EC is a promising process for pre-treatment of different wastewater; moreover the buffering effect allows the wastewater to be discharged without pH adjustments.

1.10.1.1 Advantages and disadvantages of electro-coagulation techniques

1.10.1.1.1 Advantages of EC

- Its ease of operation, pH buffering ability, low sludge production, lower toxic content and easy handling.
- Flocs formed during the EC process are larger, acid resistant, more stable and hence easy to eliminate through filtration.
- The EC process avoids uses of chemicals, and therefore no problem of neutralising excess chemicals and no possibility of secondary pollution caused by chemicals added at high concentration.

- Sludge formed by EC process tends to be readily settable and easy to de-water, because it is mostly composed of metallic oxides/ hydroxides. It is a low sludge producing technique.
- This technique can be conveniently used in rural areas where electricity is not available, since a solar panel attached to the unit may be sufficient to carry out the process.

1.10.1.1.2 Disadvantages of EC

- The 'sacrificial electrodes' are dissolved into wastewater as a result of oxidation (corrosion of electrode occurs), and need to be frequently replaced.
- The use of electricity may be expensive in many places.
- Formation of an oxide layer on the cathode with time resulting in a decrease in the removal efficiency.
- High conductivity of the wastewater suspension is required.
- Gelatinous hydroxide may tend to solubilise in some cases.
-

1.10.2 Phytoremediation

Phytoremediation is the innovative and cost effective technology using green plants for the degradation, removal, and detoxification of chemical pollutants from contaminated soils, sediments, or waters (Clayton, 2007). The U.S. Environmental Protection Agency (EPA) seeks to protect environment and the human health from danger associated with hazardous waste sites, whereas encouraging development of innovative technologies like phytoremediation for decontaminating these sites. The concept of phytoremediation method to clean and restore soil and wastewater has been employed for over 300 years (USEPA, 2000). This remediation method can be used to clean up organic and inorganic pollutants (metals, pesticides, persistent organic pollutants) from contaminated soil, sludge, sediments and water (Bhatia & Goyal, 2014; Bauddh et al., 2015).

The success of phytoremediation depends on various environmental factors such as soil structure, texture, and organic matter, water and oxygen availability, nutrients, solar radiation, temperature, and weathering. These factors directly enhance the bioavailability of contaminants and capability of plants to take up, translocate, and accumulate contaminants in shoots and plant–microbe interactions (Hooda, 2007). The hyper-accumulating plant species can concentrate heavy metals such as Cu, Zn, Co, Mn, Ni, Pb from 100 to 1000 times in comparison to non-accumulator plants (Sheoran et al., 2010). Each plant species have specific role in phytoremediation process and could be different mechanism which includes accumulation, exclusion, translocation, osmoregulation and distribution. Generally, accumulation, translocation and concentration of heavy metals in the aerial parts of hyper-accumulator plants occurred (Bhargava et al., 2012)

1.10.2.1 Mechanisms of phytoremediation

There are several processes associated with phytoremediation depending on the contaminant (both organic and inorganic) to be treated and site specific conditions. The major phytoremediation processes includes phytoextraction, rhizofiltration, phytostabilization, phytodegradation, rhizodegradation, and phytovolatilization (Clayton, 2007). Figure 1.4 describes the major processes of phytoremediation involved in the treatment of wastes. The summary of different phytoremediation techniques are discussed in Table 1.6.

Table 1.6: Different phytoremediation techniques

Technique	Application	Contaminant	Mechanism	Description	Accumulation part	Referene
Phytofiltration/ rhizofiltration	Water	Organics/ Inorganics/ heavy metals	Adsorption / absorption	Pollutants uptake from contaminated waters by aquatic plants	Aerial parts/root	Sharma et al., 2015 Thakur et al., 2016
Phytoextra-ction/ phytoaccumulation	Soil/ rarely in water	Inorganics/ heavy metals	Hyperaccumulation	Accumulation of pollutants in by root and translocate them to upper part	Shoots	Ali, et al., 2013 Sharma et al., 2015
Phytostabilization	Soil/ water	Inorganics/ heavy metals	Sorption, precipitation and complexation	Mobility limitation pollutant accessibility in soil by plant root	Reduction in rhizosphere	Sharma et al., 2015 Thakur et al., 2016
Phytovolatilization	Soil/ water	Organics/ some heavy metals	Volatilisation by leaves	Conversion of pollutants to volatile form	Release to the atmosphere	Sharma et al., 2015 Ali, et al., 2013
Phytodegra-datio/ phytotransformation	Soil/ water	Organics	Degradation in plant rhizosphere	Organic degradation by plant enzymes	Within plant tissues	Thakur et al., 2016 Cacador et al., 2015
Rhizodegradation	Soil	Organics/ Inorganics	Rhizosphere accumulation	Degradation of organic by rhizospheric microorganisms	Rhizosphere	Mackova et al., 2009
Phytodesalination	Soil	Organics (salt)	Reduction of salt by conversion	Removal of salts from soils by halophytes	Within plant tissues	Zorrig et al., 2012

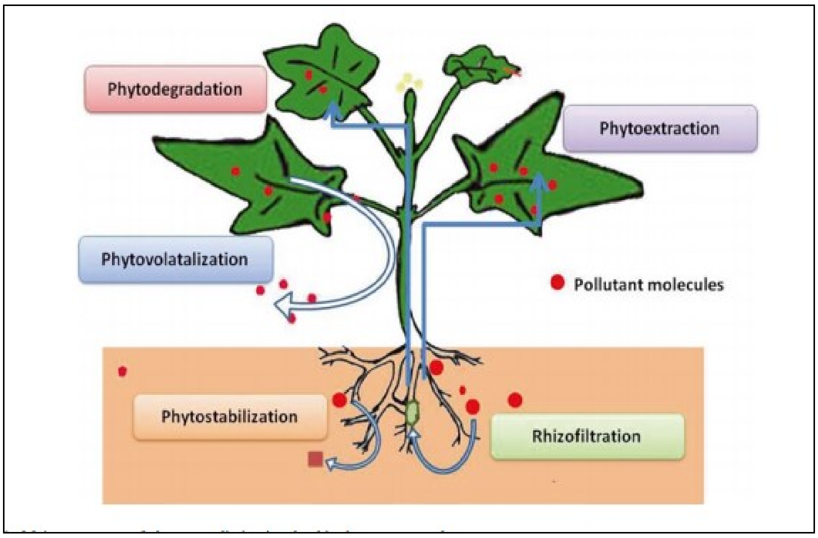

Figure 1.4: Major processes of phytoremediation techniques (Adapted from Herath & Vithanage, 2015)

1.10.2.2 Phytoremediation of heavy metals from wastewater using aquatic plants

Heavy metal contamination of the aquatic environment is a severe environmental problem, which threatens aquatic ecosystems and human health (Sasmaz et al., 2008). Heavy metals are persistent in nature and have the potential to accumulate in various sediments of the environment (Mishra & Tripathi, 2008). Conventional metal removal and mobilization techniques include adsorption, complexation, sedimentation, ion exchange, reverse osmosis, and electrodialysis. The majority of these technologies are relatively expensive, energy intensive and metal specific (Mishra & Tripathi, 2008). Consequently, the use of plants for removal of heavy metals from wastewater offers a promising technology (Miretzky et al., 2004; Mishra & Tripathi, 2008). Aquatic plants have enormous potential to accumulate metals within their body from the liquid environments (Singh & Singh, 2006). Therefore these plant species have been widely used for the removal of heavy metals from contaminated water bodies (Mishra et al., 2009). In order to enhance the phytoremediation efficiency of plants for decontaminating the environment, these are frequently used in combination with other technologies.

1.10.2.3 Phytoremediation by constructed wetland technology using wetland macrophytes

The use of constructed wetlands (CWs) for phytoremediation has been developed as a cost-effective and environmentally friendly method for the remediation of wastewater. CWs are considered to be complex ecosystems due to variable conditions of hydrology, plant species diversity, soil and sediment types, growing season, and water chemistry. This technology are being particularly designed to remove variety of pollutants including nutrients (ammonia, nitrate, phosphate), suspended solids, metals and metalloids, volatile organic compounds, pesticides, bacteria, enteric viruses, organohalogens, TNT, petroleum hydrocarbons and additives (Herath & Vithanage, 2015).

The classification of constructed wetlands is based on vegetation type (free floating, floating leaved, submerged, emergent), hydrology, and flow direction. Based on wetland hydrology, CWs are classified into free water surface and subsurface system, whereas the subsurface-flow CWs could be classified according to the flow direction (horizontal subsurface flow and vertical subsurface flow) (Vymazal, 2010). Currently, various types of constructed wetlands are being combined into hybrid systems, in order to attain better treatment performance.

1.10.2.3.1 Chemistry of constructed wetlands

Wetland chemistry is mainly influenced by physico-chemical variables that interacted with various elements such as oxygen, nitrogen, phosphorus, sulfur, aluminum and iron. The main mechanisms by which wetlands remove pollutants includes sedimentation, sorption, filtration, biological processes, and biochemical interactions are the. Plants also play an important role in the functioning of wetlands. The concentration of oxygen within sediments and the overlaying water is an important factor. The lack of oxygen conditions affects the aerobic respiration of plant roots and plant nutrient availability (Scholz & Lee, 2005). Wetland plants can live in anaerobic soils showing large adaptations for their survival. The nutrient availability and toxicity of a wetland is determined by the state of oxidation and reduction of ions such as, nitrogen, phosphorus, iron and manganese which are present within waterlogged soil and sediments in wetlands. The decomposition or oxidation of organic matter take places in the presence of some electron acceptors including O_2, NO_3^-, Mn^{2+}, Fe^{3+}, and SO_4^{2-}, however the oxidation is rapid in the presence of oxygen compared to other ions (Scholz & Lee, 2005). In addition, sulfur cycle is also involved in the degradation of organic matter. In the conversion of sulfate in to sulfide, low-molecular weight organic compounds which result from the fermentation are used as organic substrates by sulfur-reducing bacteria (Bradley, 2001). Phosphorus within wetland soils exists as soluble, insoluble, organic and inorganic complexes and characteristics of a wetland depend on the reactivity and solubility of different forms of phosphorus. In aerobic conditions, an insoluble phosphate is precipitated and reduces the availability of phosphorus to plants. The reducing the bioavailability of phosphates can also occurs by adsorbing onto clay particles, organic peat, and ferric/ aluminum hydroxides and oxides and bound up in organic matter through incorporation in bacteria, algae, and vascular macrophytes (Scholz & Lee, 2005). Nitrogen within different oxidation states is also significant to the biogeochemistry of wetlands. Oxidation of organic matter can be carrying out its various oxidation states. The anoxic condition in CWs environments leads to the release of gaseous nitrogen from the lithosphere and hydrosphere to the atmosphere through denitrification (Bradley, 2001).

1.10.2.3.2 Wetlands function as nutrient transformers

Various physical, chemical and biological processes are involved in the transformation of nutrients within the wetland. The most important physical process is the settling of suspended particulate matter. The reduction in the particulate organic matter is the main reason of reduction in BOD of wastewater. The chemical processes such as adsorption, chelation and precipitation which are responsible for the removal of phosphorus and heavy metals. The important biological process which is mediated by microorganism includes the oxidation and reduction of carbon, nitrogen and sulphur depending on the availability of oxygen. The main principles of the constructed wetlands are the continuous oxygen supply to the upper layer only, anaerobic conditions in the lower part of the filter and roots of plant provide favourable environment for bacteria diversity.

1.10.3 Nano-phytoremediation

Metal nanoparticles have been emerged as an important branch of nanotechnology in the last decade. Nanotechnology is an innovation method which has numerous toxic remediation applications. The nano-structured materials can be used as adsorbents or catalysts to remove toxic and harmful substances from wastewater and soil. Phytoremediation is an effective and eco-friendly method to decontaminate the environment, but the proposed technology is a long term (time consuming) process. Various methods were introduced to overcome the limitations of phyto-technology and nano-technology, and to combine together to form nano-phyto technology. Nano-phytoremediation is a combined technology involving nano-technology and phyto-technology (Jiamjitrpanich et al., 2013), and this method is simple, cost effective and less time consuming. When the remediation is carried out by nano-phytoremediation plants play a significant role in soil remediation.

Nanomaterials, including engineered nano-sized iron oxides, titanium oxides, or zinc oxides, manganese oxides and cerium oxides provide specific affinity for metal adsorption and their application is being rapidly extensive for environmental management. Their significant surface area, high adsorption capacities, and high number of active surface sites make this technology very promising as cost-effective amendments for decontamination of soils. The mitigation of the toxicities of metal/metalloids by their immobilization in the soil stimulates the growth and development of plants during phytoremediation.

Nanoscale zero-valent iron (nZVI) has been investigated as a new tool for the remediation of contaminated water and soil and this technology has been applied worldwide in recent years (Patil et al., 2016). The determined contaminant removal pathways of nZVI include adsorption, complexation, (co)precipitation and surface mediated chemical reduction (Miehr et al., 2004). The removal mechanism by nZVI mainly involves adsorption/surface complexation for metal ions such as Zn^{2+} and Cd^{2+} which have the standard electrode potentials (E^0) for reduction to a metallic state that are very close to, or more negative than Fe^0 (20.44 V). For metal ions such as Hg^{2+} and Cu^{2+} whose E^0 are much more positive than that of Fe^0, removal of metal ions is mainly realized via surface-mediated reductive precipitation in comparison. While metal cations are only slightly more electropositive than Fe^0, the removal is mainly realized via the adsorption with partial chemical reduction (Li & Zhang, 2007).

1.10.4 Chelate enhanced phytoremediation

Chemicall or chelate enhanced phytoremediation is based on the fact that the application of chemicals or chelating agents to the soil significantly enhances the bio-availability and hence increases the metal accumulation by plants (Garbisu & Alkorta, 2001). Chelating agent is a multidentate ligand, which has an ability to desorb toxic metals from soil solid phases by forming strong water-soluble complexes. After complex formation, it can be removed from the soil by plants during enhanced phytoextraction or by using soil washing techniques. In chelate enhanced phytoextraction process, initially the chelant can desorbs metals from the soil matrix, and the mobilized metals move to rhizosphere for uptake by plant roots (Tahmasbian & Sinegani, 2013). The amounts of bio-available metals in soil solution are generally determined by the properties of the soil and applied chelant. The successful application of chelate enhanced phytoremediation mainly depends on the use of the extracting agent. The EDTA (ethylene diamine triacetic acid), NTA (nitrilo triacetic acid), citrate, acetate, oxalate, malate, tartrate, succinate, phthalate, salicylate etc. have been used as chelators for rapid mobility and uptake of metals from contaminated soils by plants. Chelating agents can be classified in to synthetic and organic chelate agents.

1.10.4.1 Synthetic chelating agents

Synthetic chelating agents, such as ethylene diamine tetraacetic acid (EDTA), diethylene triamine pentaacetic acid (DTPA) and ethylene glycol tetraacetic acid (EGTA) have been used successfully for induced phytoremediation (Singh & Prasad, 2015; Tahmasbian & Sinegani, 2014; Alkorta et al., 2004). However, the application of such synthetic chelating agents introduces an environmental risk due to their high mobility in the soil, which can result in the transport of the contaminant to uncontaminated surrounding areas; this movement can potentially become a problem due to the high solubility and persistence in the soil of the chelate-heavy metal complex.

1.10.4.2 Organic chelating agents

The soil mobilizing agents which are much less harmful to the environment is the use of natural organic chelating agents, also called low-molecular-weight organic acids (LMWOA), such as citric acid, oxalic acid, malic acid and acetic acid. These molecules can form complexes of low to moderate stability with metals. LMWOA present an advantage because of their high rate of biodegradation in the soil, which means they do not cause the negative effects potentially caused by the application of the synthetic chelating compounds. In addition, the toxicity effect on plants, such as growth reduction, is not observed when citric acid is applied, in contrast to EDTA (Evangelou et al., 2007).

1.11 Significance and Objectives of the study

Rapid urbanisation, industrialisation, growing population and changing life style are the root causes of increasing solid waste generation in developing countries. Being the world's second most populous country, the MSW generation in India is estimated 127,486 tonnes per day in 2011. Kerala State is enriched by natural resources and a good environmental condition is being through the phase of urban development. The severe constraints of land availability and dense populations in Kerala leads to increase in the generation of MSW and the social issues related to improper management is increasing at an alarming rate. Open dumping or landfilling is the most common method used to dispose the waste due to its favourable economics. Leachate generated from waste dumping sites is one of the main sources of soil and groundwater contamination if it is not properly collected, treated and safely disposed as it may percolate through soil reaching water aquifers. Areas near the dumping site has greater possibility of soil and groundwater contamination if the leachate emanated from decomposed solid waste infiltrates and pollutes the water table.

Therefore, it is important to consider this problem as one of the main environmental concerns as it may lead to many adverse impacts in future. This current scenario makes the study related to monitoring soil and groundwater quality in the vicinity of MSW dumping area is highly significant. It is essential to monitor the contaminated sites to assess the extent of pollution and to develop methods for the removal from contaminated environments.

Groundwater samples were collected in the vicinity of selected MSW dumping sites (Njeliamparamba, Laloor, Pettipalam and Vellaramkunnu) of Kerala were monitored to find out the effect of leachate percolation on groundwater quality. The results of analysis indicated that Njeliamparamba was found to be highly contaminated, thus a detailed study on the monitoring of groundwater and soil samples in Njeliamparamba were continued. The physico-chemical and bacteriological parameters of leachate and groundwater samples were collected and analysed. Leachate Pollution Index and Water Quality Index in the study were also applied to assess the overall quality of the leachate and groundwater. Spatial distribution of groundwater quality parameters was measured by GIS. Assessment of groundwater vulnerability to contamination in the vicinity of MSW dumping site was carried out using DRASTIC modeling in a geographical information system environment. Thus, it is still valuable to remediate the groundwater and soil contamination in the vicinity of MSW dumping site and to prevent from secondary pollutions. Based on the results of monitoring, studies for the treatment of contaminants using electro-coagulation, phytoremediation, nano-phytoremediation and chelate-assisted phytoremediation were conducted. The results of monitoring and the methods are well explained in the thesis. This context, it is recommended to construct suitably engineered waste disposal facilities to improve public health and avoid environmental resources including soil and groundwater from being polluted.

The main objectives of the study are:

- To assess the pollution status of selected sites around municipal solid waste dumping sites in Kerala with respect to water and soil.
- To monitor the contaminated sites spatially and temporarily.
- To identify the area vulnerable to pollution using suitable model.
- To develop suitable remedial methods to decontaminate soil and water.

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Chapter 2

REVIEW OF LITERATURE

Rapid growth in industrialization and urbanization coupled with ever increasing population of the world, billions of tons of municipal solid waste (MSW) is generated every day worldwide. Management of MSW is a global problem and is faced by all developing countries. In most of the developing countries, especially in high population density areas, high production of solid waste and scarcity of sufficient land for dumping have caused the main problem of waste disposal. India is one of the least urbanized countries of the world, however its urban population is second largest amongst the countries of the world. The quantity of MSW is expected to increase considerably in the years to come as India strives to attain an industrialized nation status by the year 2020 (Kumari et al., 2017).

Municipal solid waste management has become a foremost environmental issue in India during the last few decades because of rapid increase in its quantity and complexity of generated waste (Panwar et al., 2017). The management of MSW in India is going through a critical phase, due to unavailability of appropriate methods to treat and dispose of the larger quantities of waste generated daily in urban cities (Gupta et al., 2015). Generally, municipal solid waste in India is disposed off in low-lying areas without taking any precautions or operational controls. Unscientific disposal of MSW causes an adverse impact on all components of the environment and human health (Sharma et al., 2018). Kerala state has the highest human development index in India, is also going through the phase of urban development and the state faces critical issues related to improper management of solid waste due to severe constraints of land availability, dense population and environmental fragility (Varma, 2013). Treatment of municipal solid waste in Kerala is more difficult due to the high average moisture content and low average calorific value (Pawels & Tom, 2013). The most of the existing technologies for the treatment of MSW in the state are unsuccessful which increases the adverse effects.

Leachate generation from municipal solid waste dumping site is a major envirornmental concern. Leachate contains elevated concentration of organic matters and inorganic ions, including heavy metals (Baun et al., 2000). The quantity and the quality of leachate are site specific and related to the age of the dumping site. The quality of leachate produced is mainly depending on the type of waste being dumped, moisture content, site hydrology, the degree of solid waste stabilization, climatic conditions, landfill age, and the stage of decomposition in the landfill (Abood et al., 2013). As the age of the landfill increases, stabilization of waste takesplace due to continuous degradation. Leachate generated during early stages (young leachate) is characterized by elevated concentration of biodegradable organic matter which is anaerobically fermented into volatile fatty acids (Renou et al., 2008). These fatty acids contribute to the characteristic low pH and high concentration of biological oxygen demand and chemical oxygen demand (Kjeldsen et al., 2002). As the landfill matures (methanogenenic stage), acids accumulated during the anaerobic phase are converted to CO_2 and CH_4 by methanogenic bacteria (Renou et al., 2008). Leachate generated during this phase is characterized by low COD concentration, high ammonium nitrogen and methane concentrations. Moreover, the BOD_5/COD ratio reduced as the amount of carboxylic acid decreases and amount of recalcitrant organic molecules increase (Kjeldsen et al., 2002).

The Leachate Pollution Index (LPI) provides an important method for evaluating the leachate contamination potential of different landfill sites at a particular time. It also gives an overall pollution potential of a landfill site. Kumar & Alappat (2005) investigated the LPI of two active and two closed landfills sites in Hong Kong and results concluded that leachate generated from the closed landfills have equal or more contamination potential than active landfill sites. Thus remediation actions and post-closure monitoring should be ensured at the closed landfills till no further threat to the environment. Huan-jung et al. (2006) studied the landfill leachate quality of three types of landfills and their results indicated that leachates had high concentrations of the chemical oxygen demand, total dissolved solids, volatile suspended solids, total organic carbon, electrical conductivity and heavy metals such as Fe, Ni and Cr.

Municipal solid waste dumping sites are considered to be significant sources of soil and groundwater pollution due to the leakage of leachate, a complex mixture of pollutants having high organic and inorganic content and lasting toxicological characteristics (Han et al., 2016; Sharma et al., 2018). Moreover, the waste deposited in dumping site generates leachate, which migrates from the dumping site and joins the hydrologeological system, and thus contaminating the soil and groundwater resourses. Gravity causes the movement of leachate to the bottom through the underlying soil and subsequently it reaches the aquifer system. These pollutants have accumulative, detrimental effect on the existance of aquatic life forms, ecology and food chains leading to various problems in public health including carcinogenic effects, acute toxicity and genotoxicity (Gajski et al., 2012).

Studies conducted in different regions of developing countries had reported groundwater contamination due to leachate migration; these landfills include the Matang landfill in Malaysia (Zawawia et al., 2012), Mediouna landfill in Morocco (Smahi et al., 2013), Henchir El Yahoudia landfill in Tunis (Marzougui & Mammou, 2006), Matuail landfill in Bangladesh (Azims et al., 2011), Ondo landfill in Nigeria (Akinbile, 2012), and the Guizhou landfill in China (Yang et al., 2013). Groundwater contamination due to MSW dumping has been a concern in many developed countries as well since the 1970s. About 75% of the 55,000 landfills in USA have contaminated the water resources close to them (Jones-Lee & Lee, 1993). In addition, the groundwater in the vicinity of some landfills has been contaminated by nitrate, nitrite and ammonium in Spain (Regadío et al., 2012), Denmark (Milosevic et al., 2012) and Greece (Fatta et al., 2002).

Groundwater in India is not free from contamination by landfill leachate. Mor et al. (2006) investigated the quality of groundwater in the vicinity of Gazipur landfill site in Delhi, and their results showed that the presence of high concentration of EC, TDS, Cl^-, SO_4^{2}, NO_3^-, Na^+, Fe and coliform bacteria in groundwater samples deteriorates its quality for drinking and other domestic purposes. Concentration of most of the water quality parameters in the vicinity of three unlined landfill site of Erode city exceeded the limit prescribed by the Bureau of Indian Standards (Nagarajan et al., 2012). Groundwater contamination near landfills was also reported in most provinces in India, such as in Suchi (Gunjan et al., 2012), Delhi (Jhamnani & Singh, 2009), Dhapa (Maitia et al., 2016) and Raipur (Agrawal et al., 2013).

Particularly at unlined landfills, leachate can contaminate groundwater with potentially hazardous chemicals at concentrations that exceeded drinking water quality standards (Reyes-López et al., 2008). Though, lined landfills also cause threat to groundwater quality because the liners fail ultimately (Banu & Berrin, 2015). Many studies have reported that the major groundwater pollutants from landfills include chloride, total dissolved solids, ammonium, organic matter, chemical oxygen demand, sodium, potassium, total hardness, heavy metals and phosphate (Rahim et al., 2010; Azims et al., 2011; Akinbile, 2012; Ganiyu et al., 2016).

The DRASTIC index model is a very useful tool for groundwater vulnerability prevention. It is also used to recognize areas that are more vulnerable to contamination, or give priorities to areas that require more groundwater monitoring. The DRASTIC index model is applicable in humid climates (Babiker et al., 2005) and in semi-arid to arid climates (Werz & Hötzl, 2007). Some studies have tried to correlate the DRASTIC index with contaminant parameters (Awawdeh & Jaradat, 2010; Neshat et al., 2013). Moreover, several researchers have attempted to modify the DRASTIC vulnerability index, producing models such as DRARCH (Guo et al. 2007), vector-DRASTIC (Pacheco & Fernandes, 2013).

Currently Geographic Information Systems (GIS) have been extensively used in groundwater vulnerability mapping (Al-Hanbali & Kondoh, 2008; Boughriba et al., 2010; Hallaq & Elaish, 2012; Jasmin & Mallikarjuna, 2015) studied the groundwater vulnerability to contamination in the Dead Sea groundwater basin using DRASTIC model and human activity impact (HAI). Their results showed that the impact of vadose zone, aquifer media, and recharge parameters have a significant impact on the DRASTIC model, whereas depth to water table and hydraulic conductivity parameters have no significant impact on the model. The result of DRASTIC and HAI indices indicated that human activity is affecting the groundwater quality and increasing its pollution risk.

The Geographic Information System (GIS) and Water Quality Index (WQI) methods provide useful information for water quality assessment, and also give spatial distribution of groundwater quality. Selvam et al. (2013) studied the GIS based evaluation of WQI of groundwater resources around Tuticorin coastal city, south India. The categories of water quality evaluated by Canadian Council of Ministers for the Environment Water Quality Index (CCME WQI) values of major part of the study area fall under fair category during pre-monsoon and good category during the post-monsoon period.

Municipal waste dumping sites, which are placed on permeable soil, create greater possibility of groundwater contamination. Type and quantity of pollutants migrating from dumping site to groundwaters mainly depends on the type and quantity of dumped waste, physical condition of the substratum, soil type, topography, and thickness of the aeration zone (Nowak et al., 2016). Mass of the pollutants migrating from the aeration zone to groundwater sourses can be assessed by the application of various models (Koda et al., 2009; Wysocka, 2015).

Land degradation caused by human activities has significant adverse effects on the environments and ecosystems worldwide (Chen et al., 2015), and solid waste dumping is an emerging environmental problem (Adamcov et al., 2016). The presence of humic substance in leachate might increase the transportation of heavy metals in soil (Urase et al., 1997). Various studies have demonstrated that soils from municipal solid waste dumping site are dangerously contaminated by heavy metals (Kanmani & Gandhimathi, 2013; Aydi, 2015). A study by Ogundiran & Afolabi (2008) reported that unscientific dumping of municipal and industrial waste can potentially contribute to high levels of heavy metals in the environment, and these metals accumulate in soil and have long persistence time through interaction with soil component and consequently enter food chain through plants or animals.

There are many factors which control the mobility of heavy metals in soils profile such as soil pH, soil texture, organic matter, cation and anion exchange capacity, type of clay minerals, amount of rainfall and soil drainage. Many studies also revealed relationships between elements (major and trace) and other soil physico-chemical properties such as pH, clay content, cation exchange capacity, soil texture and carbonates in non-contaminated soils. Soil pH has a major role in contribution of metal bioavailability, toxicity and leaching capability into the surrounding areas (Adamcová et al., 2016). At initial stages, the concentration of heavy metals in landfill is usually higher, because of the high metal solubility due to the production of organic acids (low pH) (Kulikowska & Klimiuk, 2008). As a result of increased pH at later stages, a decrease in metal solubility occurs resulting in a decrease in the heavy metal concentrations except Pb because it is known to produce complex with humic acids (Harmsen, 1983).

Many studies reported the correlation between exposure to dumping site and health problems. People residing or working nearby solid waste dumping sites have been reported to have high risk of congenital birth defects, respiratory illness and cancers (Sever 1997; Ray et al., 2005). Ray et al. (2009) reported that the impairment of lung function of landfill workers of Okhla landfill site in Delhi is more than 62% when compared to the control site. According to the World Health Organization (WHO, 2007), the evidences that links waste dumping and incinerators to health problem mainly cancer, reproductive outcomes and mortality is scarce. The landfill workers are more vulnerable to tissue damage and cardiovascular diseases due to activation of leukocyte, platelets and airway inflammation (Ray et al., 2009). Rag pickers are more susceptible to toxocariasis (Alvarado-Esquivel, 2013).

The best way of controlling the environmental pollution and health problems due to leachate is treating the leachate to remove the toxic contaminants before it enters the water system (Ngo et al., 2008). Various treatments including physical, chemical and biological methods have been studied for the treatment of leachate.The biological treatment method of nitrification and denitrification perhaps the most effective and cheapest method to remove nitrogen from leachate. Though, biological treatment is hampered by the specific toxic substances such as adsorbable organic halogens, polyaromatic hydrocarbons, polychlorinated biphenyls, and by the presence of bio-refractory organics such as humic substance or surfactants. The efficiency of denitrification is decreased due to the low amount of biodegradable organics, especially in stabilised landfills. Conventional treatment methods such as air stripping, coagulation, flocculation and settling are frequently costly in terms of energy requirements, frequent use of chemicals and expense of plant equipment. The treatment methods like reverse osmosis and active carbon adsorption, only transfer the pollution and do not mitigates the environmental problem. In the recent years, advanced oxidation processes (AOPs) such as UV/H_2O_2, UV/O_3, UV/TiO_2 and UV/FeII$^+$$H_2O_2$ have been proposed as an effective option for mineralization of refractory organics in landfill leachate. But, application of this techniques for the treatment of large scale effluents are not economically feasible (Wiszniowski et al., 2006).

According to USEPA (1999), the combination of different physico-chemical and biological processes occurring in nature, which can effectively reduce contaminants concentration, toxicity, and mobility, and can be defined as natural attenuation. Constructed wetlands (CWs) technology is environmentally friendly, economical, and sustainable engineering systems for the treatment of wastewater due to its characteristic properties like utilization of natural processes, simple construction, easy operation and low maintenance, process stability and cost effectiveness (Harikumar, 2010). Many studies reported that CWs could be efficient for removing various pollutants such as nutrients, organic matter, trace elements, and pathogens from various wastewaters (Cui et al., 2010; Saeed & Sun, 2012). Moreover, a variety of pollutant removal of processes such as filtration, sedimentation, adsorption, precipitation, volatilization, plant uptake, and various microbial processes are directly or indirectly influenced by the different internal and external environment conditions such as pH, organic carbon source, temperatures, availability of dissolved oxygen and operation strategies, and redox conditions in constructed wetlands (Saeed & Sun, 2012).

The wetlands provide appropriate environment for rapid natural attenuation of organic contaminants due to the presence of various microorganisms, nutrients in the discharging groundwater and redox conditions in the surrounding groundwater and surface water interfaces (Lorah et al., 2009). Microbial communities present in constructed wetlands can remove the complex organic compounds in wastewaters (Calli et al., 2006). Fluorescence results reveal the predominance of bacteria in constructed wetlands, which are responsible for the removal of biological oxygen demand (Sawaittayothin & Polprasert, 2007).

Harikumar (2010) investigated the potential of constructed wetlands vegetated with *Scripus Lacustris*, *Phragmites, Acorus calamus* and *Lagenandra meeboldi* for the treatment of biological oxygen demand (COD), chemical oxygen demand (COD), total Kjeldahl nitrogen (TKN) and total suspended solids (TSS) in wastewater. The percentage removal were found to be 84%, 72%, 40%, 90% for BOD, COD, TSS and TKN respectively. The comparison of horizontal and vertical constructed wetland systems planted with *Typha latifolia* for the treatment of organic, ammonia and heavy metal contaminats in wastewater was investigated by Yalcuk & Ugurlu (2009). The effect of different bedding material such as gravel and zeolite surface was also studied. The results showed that the maximum removal of NH_4–N was obtained for vertical system with zeolite layer, while horizontal system was more effective for COD removal.

Phytoremediation is emerging as an environmental friendly technology for the removal of heavy metal and has attracted more attention recently (Miretzky et al., 2004). The mechanisms involved in phytoremediation includes extraction of contaminants from groundwater or soil, immobilization of contaminants in the root zone, degradation of contaminants by various biotic or abiotic processes, concentration of contaminants in plant tissue, volatilization of volatile contaminants from plants to the air (USEPA, 2000). Each plant species have different heavy metal uptake mechanism which includes: accumulation, translocation, exclusion, osmoregulation and distribution. In those methods, the plants (hyper-accumulator) used for the phytoremediation accumulates metals mostly in their shoot than root (Singh et al., 2011). The mechanism of heavy metal uptake in aquatic plants mainly depends on the type of plant and wastewater through the direct absorption from the water to the plant surface. This process was followed by active or passive transport across membranes and by root uptake in a small extent (Nyquist & Greger, 2007). This mechanism is particularly observed in submerged species and free floating plants due to their poorly developed root system. The plant growth rate and heavy metal concentrations in plant tissues have direct effect on metal removing capacity of plants (Giripunje et al., 2015).

Various studies revealed that application of chelating agents in soil markedly increases metal accumulated by plants (Garbisu & Alkorta, 2001; Souza et al., 2013). Synthetic chelators such as critic acid, ethylene diamine tetraacetic acid (EDTA) and ammonium molybdate were proven to be effective in enhancing the bioavailability of metals in soils, therefore facilitating their plant absorption and translocation (Quartacci et al., 2005). Komárek et al. (2007) investigated the effect of addition of EDTA on metal contaminated soil. The results indicated that the addition of 9 mmol/kg of EDTA resulted in 100, 188, 121, and 61-fold increase of water soluble Cd, Cu, Pb and Zn concentrations, respectively than control soil. The amphoteric-immobilization and mobilization effect of ammonium molybdate on uptake of toxic metals from soils by *Medicago sativa L.* plants was investigated by Qu et al., (2011) and concluded that chromium and zinc were precipitated by ammonium molybdate, but the cadmium, nickel, and copper were chelanted with ammonium molybdate and formed soluble fractions. Thus ammonium molybdate is a half-stabilization agent, half-extracting agent and amphoteric agent.

Nanotechnology has many applications in environmental remediation. Nanomaterials, including nano-sized iron oxides, titanium oxides, zinc oxides, manganese oxides and cerium oxides provide specific affinity for metal adsorption and their application is being rapidly extensive for environmental management. Their significant surface area, high adsorption capacities, and high number of active surface sites make this technology very promising as cost-effective amendments for decontamination of soil and water (Liu & Lal, 2012). In addition, nano-particles can be used to increase the supply of elements to plant shoots and foliage, increasing seed germination and seedling growth. Thus, nanoparticles can facilitate enhanced ability of water and fertilizer absorption by roots, and increase antioxidant enzyme activity such as superoxide dismutase and catalase, and ncan increase plant resistance against different stresses (Morteza et al. 2013).

Nano zero valent iron (nZVI) was found to be very effective for the remediation of contaminated soil and groundwater. Franco et al. (2009) reported that 97.5% of hexavalent chromium (Cr^{+6}) in a contaminated soil could be reduced to trivalent chromium (Cr^{+3}) by nZVI, which significantly reduced the chromium toxicity in the soil. Similar reductive immobilization of hexavalent chromium in soils by nZVI was reported by other researchers (Xu and Zhao, 2007; Ponder et al., 2000). Nano zero valent iron is also able to remediate other toxic metals (Hg^{+2}, Ni^{+2}, Ag^{+1}, Cd^{+2}, As^{+3}, and As^{+5}) in water and soil (Li & Zhang, 2007). The decontamination mechanisms comprise reduction of metal ions to zero valent metals on the nZVI surfaces or adsorption of the ions on the nZVI particle shells which consist of a layer of iron oxides (iron oxidation products).

Nano-phytoremediation technology is identified as a promising treatment method for the decontamination of water and soil than either nanoremediation or phytoremediation. Harikumar & Jesitha (2016) studied the combined effect of phytoremediation and nanoscale zero valent iron for the removal of endosulphan from contaminated soil using *Alpinia calcarata* plant. The nano-phytoremediation completely removed endosulphan from contaminated soil within 30 days (initial concentration of 1200 µg/Kg of endosulphan). A study by Harikumar & Megha (2017) reported the enhancement of phytoremediation capacity of heavy metal in wastewater by *Eichhornia crassipes* and *Salvinia molesta* using titanium dioxide nanoparticles. The application of TiO_2 nanoparticles for the treatment of cadmium exposed *Eichhornia crassipes* and *Salvinia molesta* showed 99.06% and 89.57% respectively, within 3 days. The results also indicated that, plants applied with TiO_2 nanoparticles exhibited significant increase in physiological response like relative growth and the production of chlorophyll content compared to control.

The electro-coagulation is a promising technologies for the removal of organic and inorganic contaminants from wastewater due to its simple and easy operated equipment, no addition of chemicals, less operation time, and low sludge formation. Furthermore, advantages of the electro-coagulation compared to conventional chemical coagulation include low dosage of coagulant, superior coagulant dispersion, reduced wastewater salinity and acidification, and intrinsic electroflotation separation potential (Gengec et al., 2012). It is a modern technology in which sacrificial metal anode and cathode produce electrically active coagulants and tiny bubbles of hydrogen and oxygen in water (Erabeea et al., 2017). Al-Shannag et al. (2015) reported that more than 97% heavy metals such as Cu^{2+}, Cr^{3+}, Ni^{2+} and Zn^{2+} were removed from metal plating wastewater by using steel electrodes at current density of 4 mA/cm^2 within 45 min. El-Shazly et al. (2011) studied the removal of nitrate ions from wastewater using monopolar vertical aluminum electrodes in a batch electrochemical unit. The results showed that 90% of nitrate was obtained within 80 minutes of treatment time.

Leachate characterization along with soil and groundwater quality analysis is essential to assess level of contamination in the area. Several studies have reviewed the leachate characterization and its effects on groundwater quality, but little information is available on the effect of MSW dumping on soil quality, and also influence of hydrogeological parameters that transport contaminants from surface sources to groundwater. Moreover, there is lack of data available on the effect of MSW leachates on soil and groundwater quality as per the conditions prevailing in Kerala. Hence it is desired to study the effect of MSW dumping on soil and groundwater quality and identify vulnerable zones in the study area, also to develop remedial measures.

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Chapter 3

MATERIALS AND METHODS

3.1 Water Quality Assessment

The sampling and analysis of physico-chemical and bacteriological analysis of collected water samples were carried out as per the standard procedure reported by American Public Health Association (APHA, 2012)

3.1.1 Collection and preservation of water samples

Global positioning system (GPS) was used to obtain accurate sampling location data in terms of latitude and longitude for further reference. The sampling containers and equipments were thoroughly cleaned before collection of samples. The containers were labelled with proper information such as sample type, sample code and date of sampling. Details of the sampling locations and peculiar characteristics of the samples were noted. The water samples for the analysis of physico-chemical parameters were collected in 1litre clean plastic containers. For the estimation of dissolved oxygen and biochemical oxygen demand, glass containers were used for the collection of samples. The containers were rinsed with two or three times with the sample to be examined. The in-situ parameters such as pH, temperature, electrical conductivity were determined in the field. Samples for the bacteriological analysis were collected in the sterilized containers to avoid external contamination, and samples were transported to the laboratory in cool box with ice packs.

The samples for the analysis of pesticides were collected in 1litre clean amber glass bottles with teflon stopper. The collected samples were transported to the laboratory in cool box with ice packs and subsequently stored under refrigeration (at 4°C) until further analysis. Suitable preservation methods were used to avoid the physico-chemical and bacteriological change which may affect the intrinsic quality of the sample. Samples for heavy analysis were immediately preserved by acidifying with concentrated nitric acid (1.5ml con HNO_3/L sample) to pH<2. For organic constituents, the sample were immediately analysed because preservatives often interfere with the tests.

3.1.2 Analytical methods of water and wastewater

3.1.2.1 pH

Electrometric method (APHA, 2012 Part 4500 H^+ B) was used for the determination of pH of water samples. pH value was analysed using multi-parameter PCSTestr35. The pH meter was calibrated using calibration buffers, pH 4, 7 and 9.2.

3.1.2.2 Electrical Conductivity (EC)

Electrical conductivity of water sample was measured using multi-parameter PCSTestr35. The instrument was calibrated using standard conductivity solution (KCl, 0.01 M) of 1412 µS/cm at 25^0C.

3.1.2.3 Total Dissolved Solids

Gravimetric technique (APHA, 2012 Part 2540 C) was adopted for the determination of total dissolved solids. The sample was filtered through a standard glass fiber filter (Whatman grade 934AH) and the filtrate was evaporated to dryness in a weighed dish and dried to constant weight at 180^0C. The increase in weight of the dish represents total dissolved solids.

$$\text{Total dissolved solids, mg/L} = \frac{(A - B) \times 1000}{\text{Sample volume, ml}}$$

Where:

A = weight of dried residue and dish, mg
B = weight of dish, mg

3.1.2.4 Total Hardness

Complexometry was the principle used for the determination of total hardness and calcium hardness (APHA, 2012 Part 2340). Total hardness was estimated using standard EDTA solution (0.01 M) using Eriochrome Black-T as the indicator in the presence of NH_4Cl-NH_4OH buffer of pH 10.

$$\text{Total Hardness as, mg } CaCO_3\text{/L} = \frac{\text{Molarity of EDTA x vol. of EDTA x 100 x 1000}}{\text{Sample volume, ml}}$$

3.1.2.5 Calcium and Magnesium

For the determination of calcium hardness, the sample was titrated against standard EDTA (0.01M) solution in the presence of NaOH buffer and murexide indicator. Magnesium hardness was calculated from the difference between total hardness and calcium hardness. Concentration of calcium and magnesium were estimated using the following equation,

$$\text{Calcium hardness as, mg } CaCO_3/L = \frac{\text{Molarity of EDTA x vol. of EDTA x 40.08 x 1000}}{\text{Sample volume, ml}}$$

Where:

Calcium, mg/L = Calcium hardness ×0.4

Magnesium, mg/L = (Total Hardness–Calcium Hardness) ×0.243

3.1.2.6 Total Alkalinity

Alkalinity of the water sample was estimated using the principle of acid-base titrations (APHA, 2012 Part 2320 B). Total alkalinity was estimated by titrating the sample against standard H_2SO_4 (0.02 N) with methyl orange as indicator. The end point was indicated by a colour change from golden yellow to orange red. Reagent blank value was also determined.

$$\text{Alkalinity as, mg } CaCO_3/L = \frac{\text{A x N x 50000}}{\text{Sample volume, ml}}$$

Where:

A = ml standard acid used

N= normality of standard acid

3.1.2.7 Chloride

Argentometric method (APHA, 2012 Part 4500 Cl^- B) was adopted for the estimation of chloride concentration in water samples. The sample was titrated against standard silver nitrate solution (0.0141N) after the addition of potassium chromate indicator solution. The end point was indicated by a colour change from yellow to reddish orange.

$$\text{Chloride, mg/L} = \frac{\text{(A- B) x N x 35.45 x 1000}}{\text{Sample volume, ml}}$$

Where:

A= ml of $AgNO_3$ used for the titration of sample

B= ml $AgNO_3$ used for the titration of blank, N= normality of $AgNO_3$

3.1.2.8 Sulphate

Turbidimetric method (APHA, 2012 Part 4500-SO_4^{2-} E) was used for the determination of sulphate concentration of the samples by using Systronics Digital Nephelo-Turbidity meter 132. Sulphate ion was precipitated in an acetic acid medium with barium chloride so as to form barium sulphate crystals of uniform size. Light absorbance of the $BaSO_4$ suspension was measured using Nephelo-Turbidity meter and the SO_4^{2-} concentration was determined by comparison of the reading with a standard curve.

3.1.2.9 Sodium and Potassium

Alkali metals sodium (APHA, 2012 Part 3500-Na) and potassium (APHA, 2012 Part 3500-K) were analysed using Flame Emission Photometric method using Systronics Flame Photometer 128. Potassium was determined at a wavelength of 766.5 nm and sodium at 589 nm. The instrument was calibrated using standard solutions of sodium and potassium. The filtered samples were aspirated in to the flame and the concentrations were read in digital display.

3.1.2.10 Nitrate-N

Cadmium reduction technique (APHA, 2012 4500-NO_3^- E) followed by spectrophotometry was used for the estimation of nitrate. When the water sample was passed through a column containing amalgamated cadmium (commercially available Cd granules treated with copper sulphate and packed inside a glass column) nitrate was reduced almost quantitatively to nitrite. The NO^{2-} thus produced was determined by diazotizing with sulphanilamide and coupling with N (1- Naphthyl) - ethylenediamine dihydrochloride to form a highly coloured azo dye. The amount of azo dye formed was measured colorimetrically, which is proportional to the initial concentration of Nitrate–N over a wide range of concentration. The estimation of the azo dye was made at 543nm using UV–Visible spectrophotometer (Thermo Scientific- Evolution 201).

3.1.2.11 Phosphate- P

Stannous Chloride method (APHA, 2012 4500-P D) was used for the estimation of Phosphate-P. Ammonium molybdate reacts with phosphate under acid conditions to form a heteropoly acid, molybdophosphoric acid which was reduced to blue coloured complex ‘molybdenum blue' by the addition of stannous chloride. The colour intensity was measured using UV Visible Spectrophotometer (Thermo Scientific- Evolution 201) at 690nm and compared with a calibration curve, using a distilled water bank.

3.1.2.12 Heavy Metals (APHA, 2012 Part 3111 B)

The Atomic Absorption Spectrophotometer (M-series, Thermo AAS) was used for the determination of heavy metals. Pre-treatment of the water samples prior to elemental analysis was necessary because of the probability of such samples containing suspended particles along with metals. Pre-treatment involved filtration (Whatman no. 42) and addition of few drops of concentrated nitric acid to preserve the sample, destroying organic matter, minimize absorption on the walls of the containers and bringing all metals into solution.

3.1.2.13 Organochlorine pesticides

Liquid-liquid extraction method was adopted for the extraction of the pesticide residues in water. One litre of water sample was taken in a separating funnel and 30 g of NaCl and 50 ml of n-hexane was added in to it. The hexane layer was separated after shaking the sample. This process was repeated thrice and hexane portions were pooled together. The co-extractives were removed from the concentrated extract by passing through an alumina column overlaid with 1g anhydrous sodium sulphate to remove any remaining water molecules. The extract was concentrated to 10ml by using a rotary evaporator. The concentrated extract was transferred to air- tight, amber coloured GC vials and stored at 4°C until analysis (APHA 2012; USEPA 1989). The concentrated extract was analyzed using Gas Chromatograph with Electron Capture Detector which is specific and highly sensitive for halogenated compounds. Varian make CP-3800 Gas Chromatograph equipped with Ni 63 ECD (electron capture detector) was used to analyze the pesticides.

3.1.2.14 Dissolved Oxygen (DO)

Iodometric method was used for the analysis of dissolved oxygen. Samples were collected in narrow-mouth glass stopper BOD bottles of 300 ml capacity with tapered and pointed ground glass stoppers. To the collected samples, 1ml $MnSO_4$ solution followed by

1 ml alkali-iodide-azide reagent was added. The bottle was closed carefully to exclude air bubbles and mixed by inverting bottles for few minutes. When precipitate was settled sufficiently, 1 ml conc. H_2SO_4 was added and restoppered the bottle and mixed by inverting several times until dissolution was completed. The sample was titrated with 0.025M sodium thio sulphate solution and the starch indicator was added when the sample become pale straw colour. The titration was continued until the disappearence of blue colour.

$$\text{Dissolved Oxygen, mg/L} = \frac{N \times V \times 8000}{\text{Sample volume, ml}}$$

Where:

N= Normality of $Na_2S_2O_3$

V = ml of $Na_2S_2O_3$ used for the titration

3.1.2.15 Biochemical Oxygen Demand (BOD)

5-day BOD test (APHA, 2012 Part 5210 B) was used for the estimation of biochemical oxygen demand in water sample. The method consists of filling with diluted and seeded sample, to overflowing, an air tight bottle of specified size and incubated at 20± 1^0C for 5 days. The amount of dissolved oxygen present in the sample was measured initially and after incubation, and the BOD was estimated from the difference of initial and final dissolved oxygen (DO). For the dilution, dilution water was prepared by the addition of calcium carbonate, ferric chloride, magnesium, sulphate and phosphate buffer solutions into distilled water. Domestic sewage was used for seeding as per the requirements.

3.1.2.16 Chemical Oxygen Demand (COD)

Open reflux method (APHA, 2012 Part 5220 B) was used for the estimation of COD concentration in water samples. Most types of organic matter are oxidized by a boiling mixture of chromic and sulphuric acid. A sample was refluxed in strongly acid solution with a known excess of potassium dichromate ($K_2Cr_2O_7$). After digestion, the remaining unreduced $K_2Cr_2O_7$ was titrated with ferrous ammonium sulfate (FAS) to determine the amount of $K_2Cr_2O_7$ consumed and the oxidisable matter was calculated in terms of oxygen equivalent. H_2SO_4 was added to eliminate the interference of chloride and $AgSO_4$ used as catalyst for enhancing the rate of reaction.

For the determination of COD, the sample was refluxed with 0.25N potassium dichromate solution and sulphuric acid for two hours. Then cool to room temperature and titrate excess $K_2Cr_2O_7$ with FAS using ferroin as the indicator. The end point was indicated by a colour change from bluish green to reddish brown. Reagent blank value was also established.

$$\text{Chemical Oxygen Demand, mg/L} = \frac{(A-B) \times M \times 8000}{\text{Sample volume, ml}}$$

Where:

A= ml FAS used for blank

B= ml FAS used for sample

M= Molarity of FAS, and 8000= milliequivalent weight of oxygen x 1000 ml/l

3.1.2.17 Total Suspended Solids (APHA, 2012 Part 2540 D)

A well mixed sample was filtered through a weighed standard glass-fiber filter and the residue retained on the filter was dried to a constant weight at 103 to 105^{0}C. The increase in weight of the filter represents the total suspended solids.

$$\text{Total suspended solids, mg/L} = \frac{(A - B) \times 1000}{\text{Sample volume, ml}}$$

Where:

A = weight of dried residue and filter, mg

B = weight of filter, mg

3.1.2.18 Oil and Grease

Solid-phase, partition-gravimetric method (APHA, 2012 Part 5520 G) was used for the estimation of oil and grease concentration in the sample. Dissolved or emulsified oil and grease is extracted from water by passing a sample through a solid-phase extraction disk where the oil and grease are adsorbed by the disk and subsequently eluted with n-hexane. The oil and grease of the sample was calculated using the following equation

$$\text{Oil and grease, mg/L} = \frac{Wr}{Vs}$$

Where:

Wr = total weight of flask and residue - tare weight of flask, mg

Vs = initial sample volume

3.1.2.19 Microbial Analysis

The standard test for coliform group was carried out by multiple tube fermentation technique. Results of examination of replicate tubes and dilutions were reported in terms of the Most Probable Number (MPN) of organism present in100ml of the sample. MPN value for a given sample was obtained by the use of MPN index chart. Mac Conkey broth, Brilliant Green Lactose Broth (BGLB) and Peptone water were used as the media for total coliform, faecal coliform and *E. coli* respectively. For total coliform estimation 10, 1, and 0.1 ml of samples were inoculated in to the Mac Conkey broth and incubated at 37.50C for 48 hrs. Tubes with gas bubbles and colour change were taken as the positive tubes and count was noted. The positive tubes were gently shaken and with a sterile loop, three loopful of culture was transferred to a fermentation tube containing BGLB broth. This was then incubated at 44.5^0C for 24 hrs. In a similar manner numbers of positive tubes were noted. In both the above cases the count was determined using MPN index chart. The previous positive tubes were gently shaken and with a sterile loop transferred one loopful to a fermentation tube containing peptone water. The inoculated tubes were incubated at 44.5^0C for 24 hrs. After the incubation, 2-3 drops of Kovac's reagent were added. Formation of cherry red ring indicated the presence of Escherichia coli.

3.2 Assessment of soil quality

The sampling and analysis of soil samples were carried out as per the procedure reported by Black (1965), Hesse (1971), USEPA (1999), and Central Soil Analytical Laboratory (2007).

3.2.1 Collection and preprocessing of samples

Soil samples were collected with minimal disturbance, using a stainless steel augur (motorised) boring. Samples were collected from soil surface layer down to a depth of 0-30cm and 30-60cm soil layer. This method is the best for collection of soil samples from different depths of research field, the following points were noted while sampling: i) used screw type auger on dry or hard soil while post-hole auger was used for sampling in extremely wet area, ii) for composite sample, small portions of soil up to the desired depth was collected at least 10-15 well distributed spots, moving in a zig-zag manner from every individual sampling site after scrapping off the surface litter, if any, without removing soil, iii) stainless steel augers was used for micronutrient analysis. Plant materials, roots, undecomposed organic matter present on the surface were removed before sampling. Large lumps of soil were crushed and roots of plants were removed and the fine soil was used for soil analysis. After mixing well the gross soil sample, about 1 to 2 kg was transferred into a clean plastic bag. Bags was properly labeled with proper information such as sample number, depth, and date of sampling should be written on the bag from outside, and on a sample card placed inside the bag. Collected soil samples were spread in trays to dry the soil in air. The air dried soil was sieved through 2 mm sieve for the physico-chemical analyses. Soil rich in the clay were sieved before they were completely dried.

Soil pH and electrical conductivity was measured electrometrically with glass electrode pH meter in water using soil/water ratio of 1:10. Alkalinity, chloride and sulphate were estimated using the filtrate of the soil water suspension of 1:10 (w/v) ratio. The organic carbon content in the soil samples was determined using Walkley and Black wet oxidation method and soil organic matter content was determined from organic carbon. Exchangeable cations (Ca^{2+}, Mg^{2+}, K^+ and Na^+) were extracted using 1N neutral ammonium acetate, Na and K concentrations were determined using Systronics Flame Photometer 128, exchangeable Ca and Mg by Complexometric titration method. The soil texture was determined by hydrometer method. Extraction of the soil samples with 1M HCl was used for the analysis of inorganic phosphorous and was determined by using the UV Visible spectrophotometer (Thermo Scientific -Evolution 201). For the heavy metal analysis, the digestion of soil samples was performed with a mixture of HNO_3 and $HClO_4$ acid (USEPA, 1999).The digested samples were analyzed for heavy metals by Thermo M5 series Atomic Absorption Spectrophotometer. Ammonium saturation displacement method was used for the determination of cation exchange capacity of soil. Diethylene Triamine Penta Acetic acid (DTPA) extracting solution was used for the estimation of available metals (micronutrients) of soil. The procedure for the determination of soil quality characteristics is explained below in detail.

3.2.2 Soil quality characteristics

3.2.2.1 Soil Moisture

Soil moisture content is determined by drying a known quantity of soil samples in an electric oven at 105^0C to 110^0C and finding out the loss in weight.

3.2.2.2 pH

The pH of the soil samples was measured electrometrically with glass electrode pH meter in water using soil/water ratio of 1:2.5 (digital Systronics pH system 362). The pH meter was calibrated using pH 4, 7, 9.2 buffer solutions.

3.2.2.3 Electrical Conductivity (EC)

The EC of the soil was determined using 1:10 soil-water (w/v) suspension and the extract is determined using multi-parameter PCSTestr35. The instrument was calibrated using standard conductivity solution (KCl, 0.01 M) of 1412 µS/cm.

3.2.2.4 Alkalinity

Alkalinity was estimated by the principle of acid-base titration. The filtrate of the soil water suspension was titrated against 0.02 M hydrochloric acid with methyl orange indicator, the end point being colour change from golden yellow to orange red.

3.2.2.5 Chloride

Argentometric method was used for the estimation of chloride by titrating the filtrate of the soil-water suspension against silver nitrate solution (0.0141 N) after adding potassium chromate indicator .The end point was indicated by the colour change from yellow to orange red with the formation of a curdy precipitate.

3.2.2.6 Sulphate

The concentration of sulphate in the filtrate was determined by Turbidimetric method using Systronics Digital Nephelo-Turbidity meter 132. Nephelometer was standardized before the measurements were carried out and the SO_4^{2-} concentration was determined by comparison of the reading with a standard curve.

3.2.2.7 Organic Carbon and Organic matter

The organic matter content was estimated by Walkley and Black rapid titration method. In this method the soil organic matter was extracted by digesting the soil with chromic acid and sulphuric acid making use of heat of dilution of sulphuric acid. The excess chromic acid which was not reduced by the organic matter of the soil was determined with standard ferrous ammonium sulphate solution in presence of sodium fluoride, phosphoric acid and diphenyl amine solution indicator. At the end point, the colour of the suspension changed from violet through blue to bright green.

$$\%\ \text{organic carbon in soil} = \frac{(X-Y) \times N_1 \times 0.003 \times 100 \times f}{(N_2 \times S)}$$

Where:

X = Volume of FAS used in the blank

Y= Volume of FAS used to oxidize soil organic carbon (ml)

N_1 = Normality of FAS

N_2 = Normality of potassium dichromate

f =1.33 Correction factor

S = Weight of soil taken (g)

% of organic matter in soil= % organic carbon x 1.724

3.2.2.8 Exchangeable Sodium

Estimation of sodium was conducted by extracting the soil samples with neutral 1N ammonium acetate solution. The concentration of sodium in the filtrate was determined using flame photometer (Systronics Flame Photometer 128).

3.2.2.9 Exchangeable Potassium

Potassium was also determined by extracting the samples with neutral 1N ammonium acetate solution. The potassium ions in the exchange sites are replaced with NH_4^+ which release K^+. The concentration of potassium ions in the solution was determined by Flame Photometer (Systronics Flame Photometer 128).

3.2.2.10 Exchangeable Calcium

Complexometric titration method was employed for the estimation of calcium. Sample was extracted with neutral ammonium acetate solution (1M) and the filtrate was titrated against ethylene diamine tetra acetic acid (0.01 M) after adding sodium hydroxide buffer and murexide indicator. The end point was indicated by a colour change from pink to purple.

3.2.2.11 Exchangeable Magnesium

Exchangeable Magnesium was estimated by complexometric titration method. The filtrate of the sample after extraction with neutral ammonium acetate solution was titrated against ethylene diamine tetra acetic acid (0.01 M) in the presence of ammonium acetate buffer and Eriochrome black-T indicator. The end point was indicated by a colour change from wine red to blue.

3.2.2.12 Inorganic Phosphorous

The inorganic phosphorous content of the soil and sediment was determined by using the UV Visible spectrophotometer (Thermo Scientific Evolution 201). Air dried sieved sample was extracted using hydrochloric acid (1N). The phosphate was measured in UV-Visible spectrophotometer at 690 nm after adding ammonium molybdate and stannous chloride reagents. Ammonium molybdate reacted under acid conditions to form a heteropoly acid, molybdophosphoric acid which was reduced to blue coloured complex ‘molybdenum blue’ by the addition of stannous chloride. The colour intensity was measured and compared with a calibration curve.

3.2.2.13 Heavy Metals

The extraction of heavy metals from the soil, the digestion was performed with a mixture of concentrated nitric acid and perchloric acid (USEPA, 1999). The powerful oxidizing and dehydrating properties of hot, concentrated $HClO_4$ were extremely effective in decomposing organic matter and sulphides. HNO_3 dissolves the majority of the metals occurring in nature, with the exception of gold and platinum. HNO_3 was added far in excess of $HClO_4$, so that much of the oxidation was carried out before the action of perchloric acid was initiated. For the extraction of heavy metals 0.2g of soil was added with 20 ml with concentrated HNO_3 and 5 ml distilled water and heated on a hot plate for 2 hrs. After some time, 10 ml $HClO_4$ was added and evaporated the samples to fumes over a hot plate. The mixture was heated until the white fumes come and the soil become white. Then the solution was filtered and made up to 50 ml. The filtrate was analyzed for heavy metals like iron, manganese, lead, cadmium, mercury, nickel, copper and zinc using Atomic Absorption Spectrophotometer (Thermo M5 series).

$$\text{Concentration of metal in soil, mg/kg} = Y \times V/X \times 1000$$

Where:

Y = concentration of metal in the filtrate (mg/L)
V = total volume of the extract (ml)
d = dilution factor
X = weight of the soil (g)

3.2.2.14 Available metals (Micronutrients)

Diethylene Triamine Penta Acetic Acid (DTPA) extractant was used for the estimation of available Fe, Cu, Mn and Zn. DTPA forms stable complexes with Fe, Cu, Mn and Zn, and its capacity to complex each of the micronutrient cation is 10 times its atomic weight. For the extraction of available metals, 10g of air dried soil samples was added with 20ml of DTPA extractant solution (13.3ml of Triethanolamine (TEA), 1.97g of AR grade DTPA and 1.47g of $CaCl_2$ in 100ml distilled water) taken in stoppered conical flask and shaken for 2 hours in a mechanical shaker and filter through whatman No.42 filter paper. The filtrate was analyzed for available metals by Atomic Absorption Spectrophotometer (Thermo M5 series).

$$\text{Available micronutrients (AM)} = \frac{(RXV)}{W}$$

Where:

R= ppm micronutrient in the aliquot

V=Volume of extractant used

W=Weight of soil taken

Available micronutrients (AM), Kgha^{-1} = AM ppm x 2.24

3.2.2.15 Pesticide residues

For the extraction of pesticide in soil samples, 10 g of sample was taken in 100 ml conical flask containing 25ml acetone. The mixture was shaken well and kept the flask overnight in the electric shaker. The supernatant was transferred into a separating funnel of 1L capacity. Acetone (25 ml) was added to the sample and shaken well for about 10 minutes and kept for sedimentation. The supernatant acetone extract was transferred into the same separating funnel. To the separating funnel, 300 ml of deionised water, 15 g of sodium chloride, 20 ml n- hexane were added. The mixture was shaken well for 10 minutes and kept for layer separation. The aqueous layer was collected in a beaker. The n-hexane layer was transferred to a standard flask from the separating funnel. Again 20 ml n-hexane was added to the aqueous layer and shaken well for 10 minutes. Then the aqueous layer was discarded and the n-hexane layer was transferred from the separating funnel to 100 ml conical flask. Anhydrous sodium sulphate (3g) was added into n-hexane layer for dehydration and left the sample undisturbed for 20 minutes and then concentrated to 10 ml. The clean up was done on an alumina column overlaid with 1 g anhydrous sodium sulphate. The extract was stored in air tight amber colored vials at 4^{0}C until analysis (USEPA 1989). After processing the samples through the different extraction steps, the final concentrated and cleaned up sample was analyzed using Varian make CP-3800 Gas Chromatograph equipped with Ni 63 ECD (electron capture detector).

3.2.2.16 Soil texture

Soil texture was determined by hydrometer method. The hydrometer method is based on the change of density of a soil and water suspension upon the settling of the soil particles. It is based on the principle of Stokes law, which states that the rate of decrease in density at any given depth is related to settling velocities of the particles.

$$V=\frac{2gr^2 (d_1-d_2)}{g\eta}$$

Where:

V = velocity of fall cm/sec

r = radius of particles (cm)

d1 = density of particles g/ml

d2 = density of liquid g/ml

η = viscosity of the liquid (in poises)

g = acceleration due to gravity m/sec^2

40g of oven dried soil samples was taken in to 500ml beaker containing 30ml distilled water and mixed. Hydrogen peroxide (5 ml) was added to the sample to oxidize the organic matter and then the beaker was kept on a sand bath. H_2O_2 was added to the sample until the frothing no longer continued. The soil was transferred completely to a beaker containing 100 ml Calgon solution and 300ml distilled water, and then the soil solution was mixed for 5 minutes using an electric mixer. Then the soil suspension was completely transferred to a sedimentation cylinder and made up to the mark with distilled water. The mixture was shaken well and started the stop watch. Take the hydrometer reading and temperature reading after 5 minutes and 120 minutes. The same procedure was done for blank also (using calgon solution). For temperature correction, each ^{0}C above or below 20^{0}C added or subtracted 0.0004 graduation (g/cc) on the hydrometer.

$$\text{\% of suspension after 5 minutes} = \frac{\text{(Corrected hydrometer reading at 5 min - Corrected 5 min blank reading) x 1000x 100)}}{\text{Weight of sample}}$$

% Sand=100-% of suspension after 5 minutes

$$\text{\% of suspension at 120 minutes (Clay \%)} = \frac{\text{(Corrected hydrometer reading at 120 min - Corrected 120min blank reading) x 1000 x 100)}}{\text{Weight of sample}}$$

% of Silt = 100- % Sand+ % Clay

3.2.2.17 Cation exchange capacity

Cation exchange capacity was determined by leaching a known amount of soil by neutral ammonium acetate and estimated by distilling the quantity of NH_4^+ ions – cations adsorbed by the soil. Cation exchange capacity measures the total quantity of negative charges per unit weight of soil. The cation exchange capacity is expressed in terms of milliequivalents of negative charge per 100 g of oven-dried soil (meq/100 g).

5g of soil sample was taken in a 500ml beaker containing 25ml neutral ammonium acetate solution, stirred well and kept it overnight covering with watch glass. The soil solution was transferred into filter paper, leached it with 15ml ammonium acetate solution for six times. Add a pinch of solid ammonium chloride into the filter paper containing the soil and again leached with 60% alcohol until the filtrate runs free of chloride. Removed the filter paper along with the soil cautiously and placed it in a 500ml distillation flask. To the distillation flask, 250ml deionised water, and 12.5ml of 0.1N sulphuric acid and 2 drops of methyl red indicator were added into a 500ml ice tumbler and added. Placed the ice tumbler below the delivery end and ensured that the delivery end was completely immersed in 0.1N sulphuric acid. Then 5ml of 40% sodium hydroxide solution were added into the flask containing the soil. The flask immediately was stoppered and started distillation. Collected the ammonia liberated in the acid taken in the ice tumbler. The end of the delivery tube was washed with distilled water into the same ice tumbler when the distillate runs free of ammonia. Removed the ice tumbler and titrated the excess acid against 0.1N potassium hydroxide, the end point being the appearance of light or straw yellow colour.

$$\text{CEC (milli equivalents/100g soil)} = \frac{(V-V_1) \times 0.1 \times 100}{W}$$

Where: V= volume of 0.1N H_2SO_4 taken

V_1= volume of 0.1N KOH consumed

W= weight of soil taken, g

3.3 Statistical Analysis

The Statistical Package for Social Sciences (SPSS version 19.0 and 20.0) and SYSTAT 12 were used for the statistical interpretation of the analytical data. Maximum, minimum and mean values were calculated and reported. Different statistical analyses were explored to meet various objectives of the study. Pearson correlation coefficients were calculated in order to study inter-elemental relationship among the parameters. Principal component analysis (PCA) has been used for evaluation and characterization of analytical data. The PCA was performed using varimax normalized rotation on the dataset. Correlation analysis is useful to find out similarity groups between the sampling stations. The principal component analytical method, which is widely used to detect the hidden structure of sediment sources and to distinguish natural and anthropogenic inputs, was applied here to explore the origin and geochemical factors influencing their distribution.

JASEELA C.”A STUDY ON THE SOIL AND WATER QUALITY OF SELECTED SITES AROUND SOLID WASTE DUMPING AREAS IN KERALA STATE”. THESIS. CWRDM (CENTRE FOR WATER RESOURCES DEVELOPMENT AND MANAGEMENT), UNIVERSITY OF CALICUT, 2018.

Chapter 4

ASSESSMENT OF GROUNDWATER QUALITY IN THE VICINITY OF SELECTED MUNICIPAL SOLID WASTE DUMPING AREAS IN KERALA

4.1 Introduction

Groundwater has long been considered as an important water source owing to its relatively low susceptibility to pollution and large storage capacity. Groundwater is comparatively safe and reliable when compared with surface water (Gupta, 2014). However, deterioration of groundwater quality has become a serious problem in recent years. The unscientific disposal of municipal solid wastes over vast areas poses a serious threat to the underground water resources, environment and community health (Soupios et al., 2006; Ganiyu et al., 2016). The groundwater quality depends on the quantity and quality of generated waste, quality of recharged water, sewage treatment and subsurface geochemical processes (Rizwan & Gurdeep, 2010; Ganiyu et al., 2016). Open dumping or landfilling is the most common method used to dispose the waste due to its favourable economics (Wijesekara et al., 2014). Leachate generated from waste dumping sites is one of the main sources of groundwater contamination if it is not properly collected, treated and safely disposed as it may percolate through soil reaching water aquifers (Abd El-Salam & Abu-Zuid, 2014). Areas near the dumping site has greater possibility of groundwater contamination if the leachate emanated from decomposed solid waste infiltrates and pollutes the water table (Nagarajan et al., 2012). In Kerala, groundwater or dug wells are the most reliable water sources and 63% of the population depend on groundwater for their drinking, domestic, and agricultural needs (Census of India, 2001). So, it is important to consider this problem as one of the main environmental concerns as it may lead to many adverse impacts in future. Therefore, the assessment of groundwater quality near the MSW dumping area must be monitored carefully.

4.2 Materials and Methods

4.2.1Study area details

The four selected municipal solid waste dumping sites are Njeliamparamba from Kozhikode district, Laloor from Trissure district, Pettipalam from Kannur district and Vellaramkunnu from Wayanad district. The base maps for generating the location maps were collected from the Soil Survey Department of Kozhikode, Thrissur, Kannur and Wayanad districts. The maps were digitized and various findings were spatially represented using the ArcMap 10.1 software. The site details are discussed below.

4.2.1.1 Njeliamparamba

Njeliamparamba, a municipal solid waste dumping site of Kozhikode Corporation, India is situated 9 km from the city. Njeliamparamba, operational since 2004, is dumped an average of 200 tonnes of waste per day in 18 hectare area. The dumping site is located at 11^0 13′ 30″ N to 11^0 11′ N and 75^0 48′ E to 75^0 50′30″ E. Figure 4.1 shows the location map of Njeliamparamba dumping site showing the sampling stations.

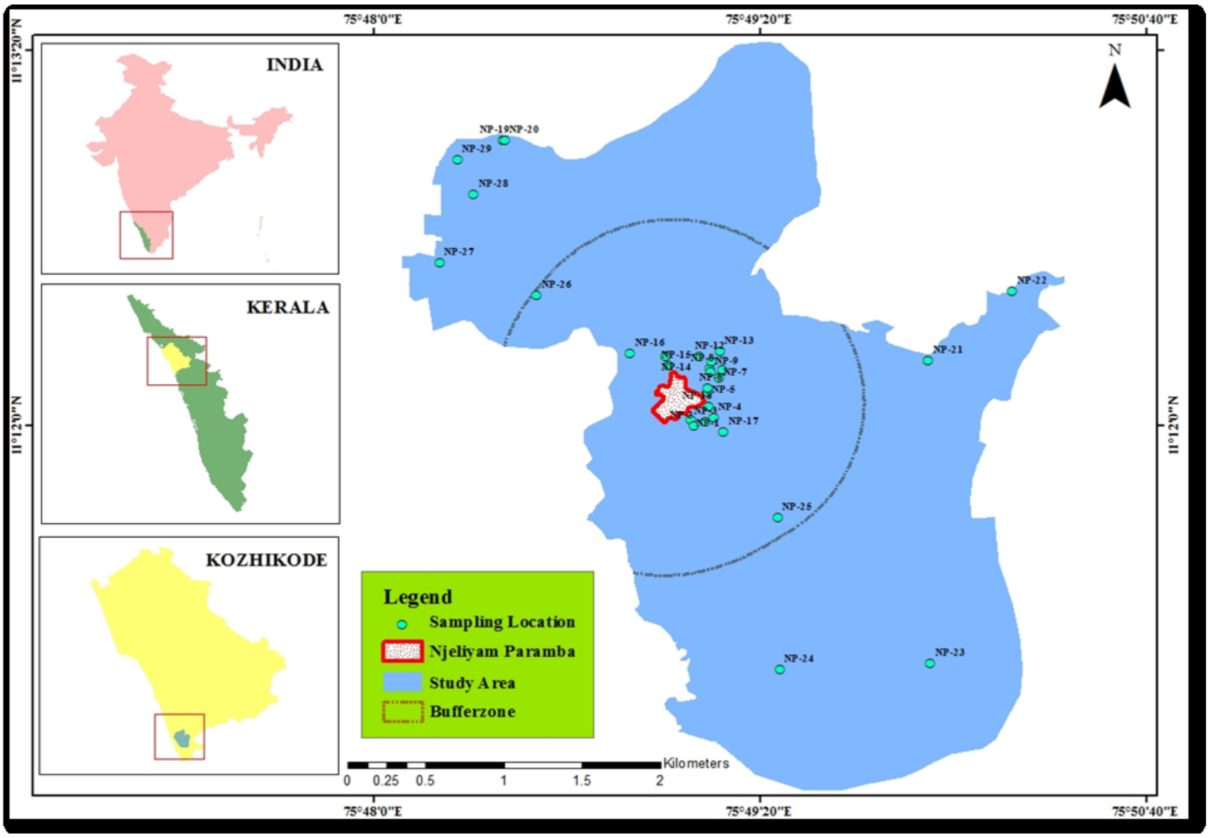


Figure 4.1: Location map of Njeliamparamba dumping site showing the sampling stations

The study area is characterised by a humid tropical climate with high rainfall. The average annual rainfall recorded in the area during the study period is 2777mm (IMD, 2013). The mean maximum temperature is 31.67^{0}C and the minimum is 22.97^{0}C. The relative humidity ranges from 74 to 92% during morning hours and 64 to 89% in evening hours. Physiographically the area lies in the middle portions of the Kozhikode district with an elevation ranging from 15 to 50m above the mean sea level. The area is one of the primary industrial areas of the Kozhikode district. A number of small, medium and large industrial units on clay, agro-forestry, chemical and metals are located in and around the site. The height of the dump is about 3 to 4m above ground level and average of 60-80 tones of organic waste (vegetable, meat and fish waste) from markets and households are deposited daily in the dumping yard. The landfill originally accepted only non-hazardous solid wastes but now receives both degradable and non-degradable waste including hazardous waste. Organic solid wastes are treated at the waste treatment plant at Njeliamparamba. Windrow composting method is used to convert the organic waste into compost. It is the controlled, heat dependent, microbiological process of decomposing organic materials into a biologically stable, humus-rich material. However, there is no leachate treatment facility in the dump yard. The leachate from the plant and trench yard is collected in a pond on the north east side of the plant. The general overview of Njeliamparamba dumpsite is indicated in plate 4.1.

Plate 4.1: General overview of Njeliamparamba dumping site

The geological formations of Njeliamparamba primarily consist of porous laterite and forms potential phreatic aquifers; it comes under the midland terrain of Kozhikode district (CGWB, 2009). Lateritic soil is derived from laterite under a tropical climate with alternating wet and dry conditions. The soil is reddish in colour, moderately permeable with an infiltration rate that enables absorption of most of the rain. Groundwater occurs under phreatic conditions in weathered crystalline rocks and under confined to semi-confined conditions in deeper crystalline formations. Dug wells are the principle water supply for drinking and other purposes in the study area. The average groundwater level during the pre-monsoon period is 2 to 16 mbgl (metres below ground level), whereas the water table level in post-monsoon is 0.38 to 9 mbgl. The effects of leachate percolation are observed in many nearby dug wells in the form of a brown oily appearance and unpleasant foul smell.

4.2.1.2 Laloor

The study area is a prominent landfill site located at Laloor in Thrissur district, central part of Kerala, India. The dumping site is located at $10^0$32’39”N to $10^0$29’21”N and $76^0$12’19”E to $86^0$9’33” E. The map showing the sampling stations is indicated in Figure 4.2.

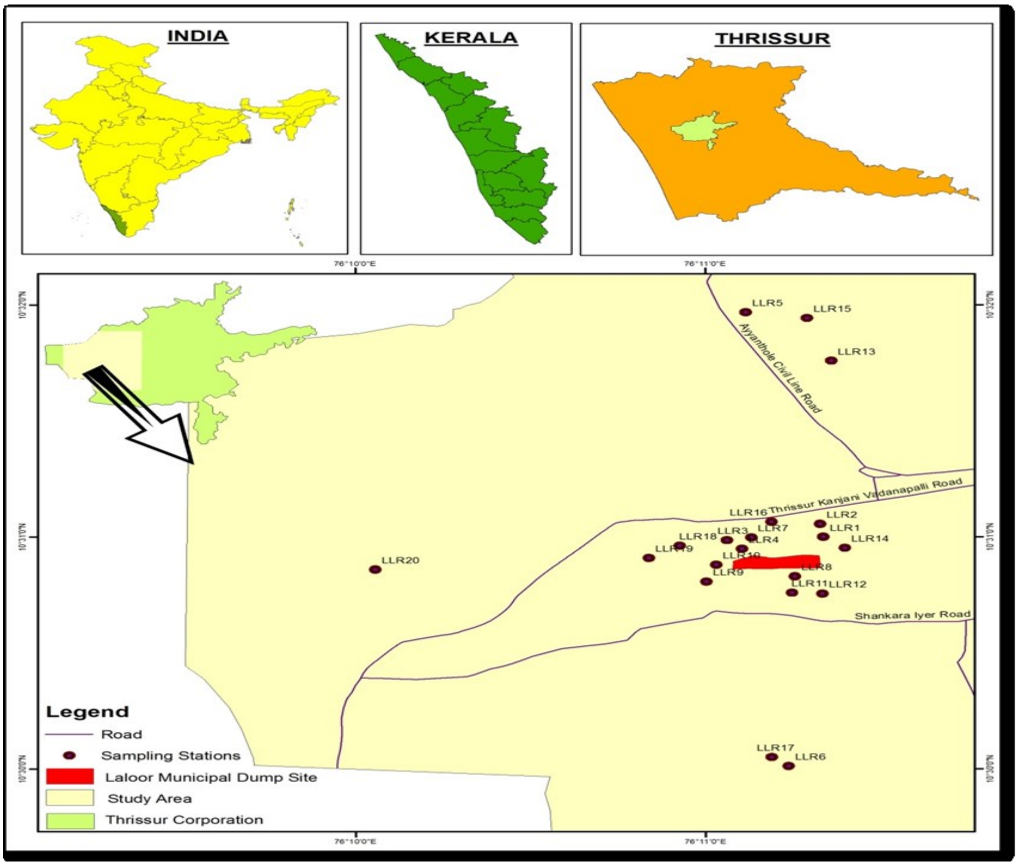


Figure 4.2: Location map of Laloor dumping site showing the sampling stations

The Laloor municipal waste dump site is situated at a distance of 4 km from the city centre, spreading over an area of 4.53 hectares. The site is being used by the municipal co-corporation for the past two decades, for waste processing and disposal. Open land filling is the method used in waste disposal. Due to public protest, there is no dumping in this site for the past seven years. The area has a humid tropical climate with mean annual temperature of 27.49^{0}C and average annual precipitation is 2488 mm. The general slope of the area lies between 1-25% with an average groundwater level during pre-monsoon is 1.40 to12.90 mbgl, where as the water table level in post monsoon is 0.59 to 10.86mbgl. The average annual rainfall ranges between 2310.1 and 3955.3 mm in the district with mean annual rainfall of 3198.133 mm (CGWB, 2013). Hydrogeology of the aquifer system in the study area can be broadly divided into hard rock aquifers, laterite aquifers and sedimentary aquifers. The hard rock and laterite aquifers constitute major aquifer system while the sedimentary aquifers are seen along the coast and river courses. Groundwater occurs under phreatic, semi confined to confined conditions in the weathered and fractured portions of the crystalline formations and occurs semi-confined and confined condition in deep seated fractured and sedimentary formations (CGWB, 2013). The general overview of Laloor dumpsite is indicated in plate 4.2.

Plate 4.2: General overview of Laloor dumping site

4.2.1.3 Pettipalam

Punnol Pettipalam municipal solid waste dumping site is located in Thalassery, a commercial town on the Malabar cost in Kannur district. The dumping site is located at 11° 43' 9.0264" N to 11° 43' 17.2416" N and 75° 31' 2.406" E to 75° 31' 13.35" E. It is situated in an altitude ranging from 2.5m to 30m above mean sea level. The map showing the sampling stations is indicated in Figure 4.3.

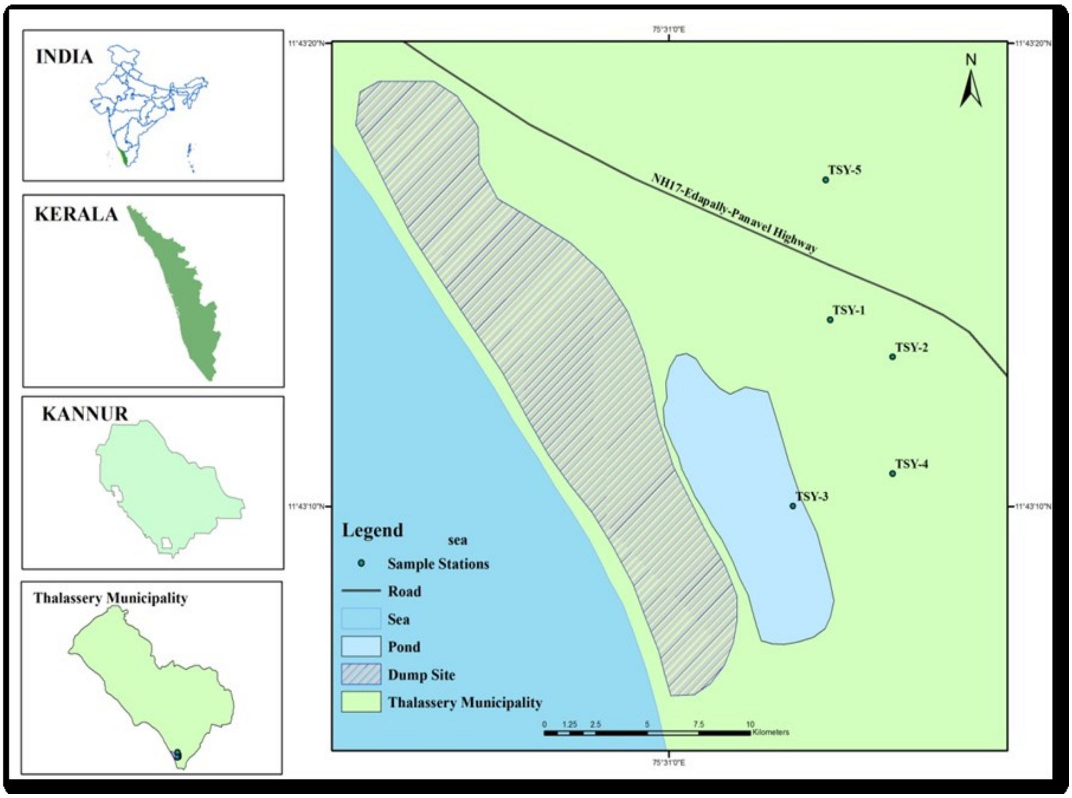


Figure 4.3: Location map of Pettipalam dumping site showing the sampling stations

Open land filling is the method used in waste disposal. An average of 24 tonnes of municipal solid waste per day is dumped in this area which includes wastes from adjacent vegetable market, fish market, kitchen, paper, plastic, glass, cardboard, clothes, and also construction and demolition waste. The western side of the dumping yard is the sea and eastern side is a pond. Due to public protest, there is no dumping at that site for the past six years. The average annual rainfall recorded in the area during the study period was 3438mm. The depth of the wells in the study area ranged from 5 to 20mbgl. Hydrogeology of the study area is encountered by phreatic conditions in weathered mantle of the crystalline rocks, laterites and unconsolidated coastal sediments. The soil observed in the area consists of lateritic soil, brown hydromorphic soil, coastal and river alluvium and forest loamy soil (CGWB, 2013). The general overview of Pettipalam dumpsite is indicated in plate 4.3.

Plate 4.3: General overview of Pettipalam dumping site

4.2.1.4 Vellaramkunnu

Vellaramkunnu, a municipal solid waste dumping site located at Kalpetta in Wayanad district, centre of tourism activities in Kerala. It is situated at an altitude of about 780m above sea level. The dumping site is located at 11° 35' 51.576"N to 11° 35' 52.98"N and 76° 3' 22.5"E to 76° 3' 19.404"E. The map showing the sampling stations is indicated in Figure 4.4.

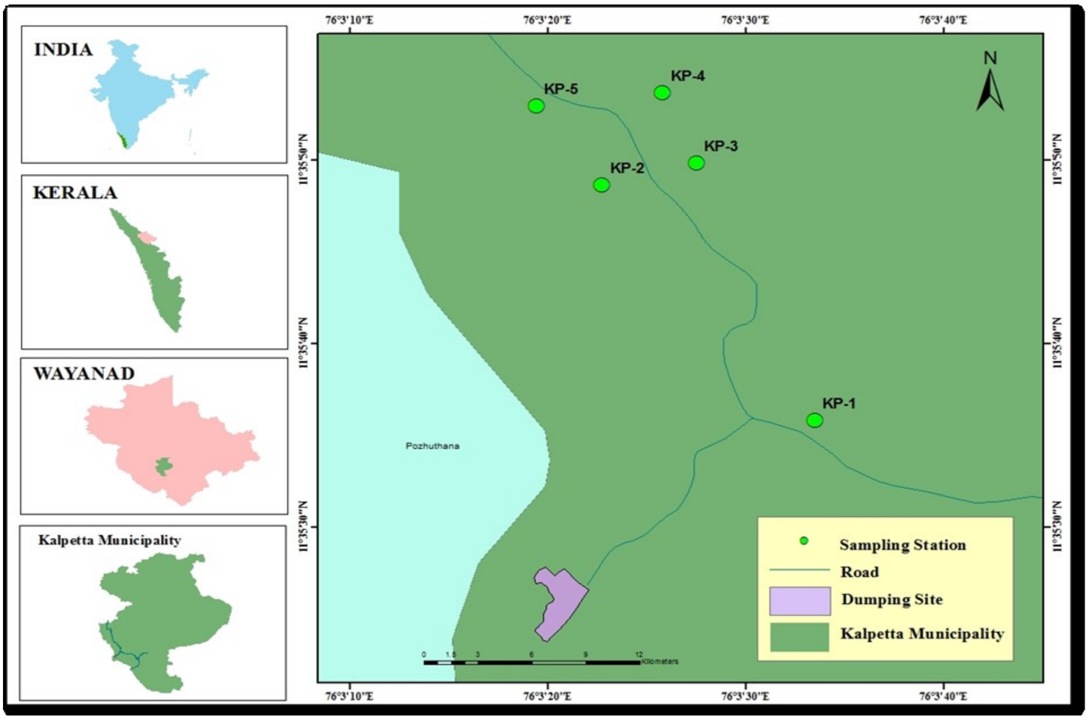


Figure 4.4: Location map of Vellaramkunnu dumping site showing the sampling stations

Plate 4.4: General overview of Vellaramkunnu dumping site

The average annual rainfall recorded in the area during the study period is 2786mm. Average of 9 tonnes of waste per day is dumped in 10 hectre area. The waste generated from markets, shops, households etc are collected by the municipality and carried to the dumping yard using trucks. Open trenching is the method used for disposal of waste, which is quiet unscientific. The landfill accepts biodegradable and non- biodegradable wastes, but these are not segregated especially the plastic waste. At present, the municipality doesn't have any facility for the treatment of waste, which may possesses serious threat to public health and environmental quality. Hydrogeology occurs in weathered, crystalline and alluvial formations. Phreatic conditions exist in weathered formation and are mostly developed by dug wells for domestic and irrigation purposes. Semi-confined conditions exist in deep fractures and storage and movement of groundwater is mainly controlled by the fracture system. The soil present in the study area is mainly consisting of laterite soil, brown hydromorphic soil, forest loam and riverine alluvium (District Survey Report, Wayanad District, 2016). The general overview of Vellaramkunnu dumpsite is indicated in plate 4.4.

4.2.2 Sampling and analytical methods

As a part of groundwater quality assessment, 59 groundwater samples were collected during February 2013 from the four selected MSW dumping sites in Kerala. The sampling wells were selected based on the availability of the wells around the landfill sites. Groundwater samples were analysed for various physico-chemical parameters as per the standard procedure (APHA, 2012). pH, electrical conductivity and dissolved solids were measured in situ with a multi-parameter PCSTestr35. Titrimetric method was adopted for the estimation of total hardness, calcium, magnesium, chloride and total alkalinity. The concentrations of sodium and potassium in groundwater samples were determined by Flame Photometric Method. The concentrations of sulphate, nitrate and phosphate were analyzed using UV-VIS Spectrophotometer (Thermo Evolution, USA). For the analysis of heavy metals, the samples were filtered (Whatman no. 42) and preserved using concentrated HNO_3 for further analysis (APHA, 2012). Concentrations of heavy metals in water samples were determined with Atomic Absorption Spectrophotometer (Thermo M5 series) with a specific lamp for particular metal. Organochlorine pesticides in the samples were analyzed using Gas Chromatography with Electron capture Detector (Varian CP-3800). Bacterial analysis, i.e. the presence of total coliforms and *E.coli* from the water samples was done as per the procedure described in APHA (2012). All the results were compared with the Bureau of Indian Standards (BIS, 2012). The detailed procedures were discussed in detail in chapter 3. All chemicals used in this study were of analytical reagent grade and glassware used for analysis was washed with acid solution followed by distilled water. Hydrogeochemical facies of the analysed groundwater samples was done with the aid of Piper tri-linear diagram using groundwater modelling software- Aqua Chem 5.0.

4.3 Results and Discussion

4.3.1 Physico-chemical and bacteriological characteristics of groundwater samples at Njeliamparamba

The physico-chemical and bacteriological characteristics of groundwater samples was statistically analyzed and the results are given in Table 4.1 to Table 4.4. Table 4.5 shows the descriptive statistics of the groundwater quality, acceptable limits for various parameters as per the BIS (2012), and the well no's exceeding the limit.

Table 4.1: Physico-chemical and bacteriological characteristics of the groundwater samples at Njeliamparamba

Sample ID	**NP-1**	**NP-2**	**NP-3**	**NP-4**	**NP-5**	**NP-6**	**NP-7**
pH	5.40±0.06	5.84±0.02	5.34±0.03	6.20±0.05	5.20±0.01	5.24±0.02	6.05±0.02
EC, µS/cm	1250.0±52.7	1230.0±10	1145.0±12.0	850.0±13.23	1420±23.0	1415.0±7.64	960±3.61
TDS, mg/L	887.50±11.3	873.3±8.70	813.66±5.0	603.50±3.60	1008.0±5.0	1004.65±6.0	681.6±3.53
Sulphate, mg/L	80.60±1.5	65.60±2.0	64.0±2.0	20.50±2.06	75.0±1.50	47.40±3.06	45.0±1.53
Chloride, mg/L	200.0±5.0	190.50±3.0	185.0±4.50	115.0±2.65	252.60±4.73	252.50±3.29	170.0±3.16
Total Alkalinity, mg/L	210.0±3.10	251.0±5.78	147.0±3.20	106.0±4.64	181.50±6.15	189.50±2.80	109.80±2.06
Total Hardness, mg/L	420.0±2.0	371.0±2.43	351.0±4.20	441.0±3.53	287.0±3.62	231.0±3.21	168.0±3.51
Calcium, mg/L	101.50±1.50	76.0±1.10	90.0±1.10	73.0±2.62	96.70±1.70	76.50±1.01	65.0±1.71
Magnesium, mg/L	50.50±1.50	46.0±1.10	40.0±1.53	52.0±0.78	40.0±1.21	28.50±0.76	25.60±1.27
Sodium, mg/L	111.0±1.60	130.0±2.42	145.0±2.89	87.0±2.80	101.60±2.6	75.50±1.32	96.0±1.69
Potassium, mg/L	50.0±2.50	25.0±1.53	16.50±1.66	40.0±1.74	51.50±1.0	34.50±2.08	40.0±2.52
COD, (mg/L)	70.0±2.50	50.0±2.73	85.0±2.52	85.0±2.52	255.50±2.5	250.0±2.52	85.0±2.08
BOD, (mg/L)	8.0±1.20	7.0±0.60	4.50±1.30	3.60±1.0	8.50±5.60	9.0±4.90	4.20±2.0
Phosphate-P,(mg/L)	0.20±0.01	0.15±0.01	0.05±0.01	0.10±0.03	0.05±0.02	0.10±0.02	0.16±0.01
Nitrate, (mg/L)	3.50±0.67	18.50±0.75	20.50±1.56	11.50±0.53	90.6±1.06	51.50±0.90	40.0±3.06
Iron, (mg/L)	0.35±0.02	0.40±0.02	0.35±0.01	0.34±0.02	0.29±0.02	0.35±0.03	0.25±0.02
Copper, (mg/L)	0.02±0.001	0.03±0.001	BDL	0.01±0.001	0.06±0.002	0.045±0.001	0.01±0.001
Zinc, (mg/L)	0.04±0.002	0.03±0.001	0.10±0.002	0.01±0.001	BDL	BDL	0.01±0.001
Manganese, (mg/L)	0.05±0.02	0.04±0.09	0.04±0.01	0.02±0.02	0.04±0.02	0.06±0.02	0.12±0.02
Cadmium, (mg/L)	0.003±0.001	0.001±0.009	BDL	0.003±0.008	BDL	BDL	BDL
Lead, (mg/L)	0.02±0.001	0.015±0.001	0.008±0.002	0.008±0.003	0.02±0.002	0.025±0.001	0.009±0.002
Nickel, (mg/L)	0.01±0.003	0.006±0.001	0.009±0.002	BDL	0.01±0.001	0.015±0.001	BDL
TCF, (MPN/100ml)	≥2400	1100	460	1100	≥2400	≥2400	23
E.coli	Present	Absent	Present	Absent	Absent	Present	Absent

BDL-Below Detection Limit, COD- Chemical Oxygen Demand, BOD- Biochemical Oxygen Demand, TCF-Total Coliforms

Table 4.2: Physico-chemical and bacteriological characteristics of the groundwater samples at Njeliamparamba

Sample ID	**NP-8**	**NP-9**	**NP-10**	**NP-11**	**NP-12**	**NP-13**	**NP-14**
pH	5.36±0.02	5.84±0.02	5.45±0.10	5.30±0.04	6.80±0.10	6.56±0.01	6.45±0.04
EC, (µS/cm)	1626.0±10.4	1538.0±9.0	560.0±6.0	890.0±8.1	440.0±5.6	300.0±6.5	553.0±6.10
TDS, (mg/L)	1154.0±9.0	1092.0±9.6	397.60±5.0	631.90±5.53	312.0±4.53	213.0±2.0	392.63±2.50
Sulphate, (mg/L)	70.0±1.0	78.0±1.53	22.0±1.0	17.50±1.65	18.0±2.08	1.05±0.79	35.60±0.65
Chloride, (mg/L)	252.0±4.93	260.5±4.04	80.30±2.5	180.0±4.62	101.0±2.65	85.0±4.36	95.40±2.69
Total Alkalinity, (mg/L)	201.0±4.18	251.0±2.39	48.0±1.3	90.9±2.17	11.80±3.27	22.58±0.64	45.90±3.41
Total Hardness, (mg/L)	371.0±9.13	280.0±2.46	100.0±3.2	220.0±1.32	70.20±1.06	45.0±0.76	95.80±0.99
Calcium, (mg/L)	98.7±1.80	60.50±1.10	30.20±1.0	45.60±1.31	42.30±0.42	18.09±0.45	33.60±1.0
Magnesium, (mg/L)	55.6±0.95	40.30±1.69	13.70±0.80	20.50±1.50	11.90±0.26	11.58±0.12	12.50±0.72
Sodium, (mg/L)	102.0±6.86	171.0±5.50	50.50±2.0	110.50±3.33	44.50±1.26	26.80±1.42	75.50±1.50
Potassium, (mg/L	66.50±6.25	142.0±2.35	20.0±1.20	35.0±2.42	18.50±1.63	3.60±0.44	25.0±3.30
COD, (mg/L)	252.6±2.52	40.0±2.08	82.50±3.0	80.50±3.21	40.50±2.71	23.40±2.08	41.50±3.06
BOD, (mg/L)	10.0±6.0	9.50±0.90	3.0±0.90	3.60±1.0	1.50±0.50	1.80±0.20	1.60±0.60
Phosphate-P,(mg/L)	0.01±0.01	0.10±0.04	0.25±0.40	0.20±0.03	0.30±0.03	0.15±0.02	0.15±0.03
Nitrate, (mg/L)	50.5±1.80	20.60±1.31	35.60±1.20	30.0±1.53	10.5±1.27	5.50±1.76	10.40±1.53
Iron, (mg/L)	0.24±0.02	0.52±0.02	0.30±0.01	0.12±0.01	BDL	0.09±0.001	0.012±0.01
Copper, (mg/L)	0.02±0.001	0.003±0.01	BDL	BDL	BDL	0.01±0.002	BDL
Zinc, (mg/L)	0.01±0.001	0.01±0.001	BDL	0.01±0.002	0.03±0.02	0.02±0.003	0.01±0.002
Manganese, (mg/L)	0.15±0.02	0.15±0.02	0.08±0.10	0.07±0.001	BDL	0.01±0.01	0.02±0.001
Cadmium, (mg/L)	0.002±0.008	0.001±0.009	BDL	BDL	BDL	BDL	BDL
Lead, (mg/L)	0.022±0.001	0.02±0.001	BDL	0.008±0.002	BDL	BDL	BDL
Nickel, (mg/L)	0.016±0.001	0.008±0.002	BDL	0.009±0.001	BDL	BDL	BDL
TCF, (MPN/100 ml)	≥2400	≥2400	≥2400	≥2400			≥2400
E.coli	Present	Present	Absent	Absent	Absent	Absent	Absent

BDL-Below Detection Limit, COD- Chemical Oxygen Demand, BOD- Biochemical Oxygen Demand, TCF-Total Coliforms

Table 4.3: Physico-chemical and bacteriological characteristics of the groundwater samples at Njeliamparamba

Sample ID	**NP-15**	**NP-16**	**NP-17**	**NP-18**	**NP-19**	**NP-20**	**NP-21**
pH	6.01±0.03	6.54±0.01	6.42±0.02	5.40±0.10	6.67±0.01	6.85±0.01	5.02±0.02
EC, (µS/cm)	870.0±7.6	305.0±5.0	600.0±14.0	1398.0±10.0	367.0±6.5	181.3±3.1	1290.0±10.50
TDS, (mg/L)	617.70±2.65	216.55±4.40	426.0±4.0	992.58±4.04	260.57±2.30	128.72±2.0	916.0±7.6
Sulphate, (mg/L)	58.20±1.51	23.50±1.74	50.50±7.64	90.0±3.06	12.80±0.8	1.76±0.40	60.0±1.0
Chloride, (mg/L)	158.20±2.89	50.30±2.21	95.60±5.50	250.5±2.50	78.95±1.0	54.72±0.80	251.20±2.50
Total Alkalinity, (mg/L)	110.50±2.35	40.80±1.63	100.90±6.30	102.8±2.01	55.68±1.0	12.24±0.70	135.60±1.30
Total Hardness, (mg/L)	370.50±2.02	49.90±1.52	109.502.36	371.0±5.51	50.0±1.20	30.50±0.90	130.0±1.0
Calcium, (mg/L)	89.60±2.31	20.50±0.85	36.80±1.10	80.56±2.03	19.20±0.6	14.80±0.20	78.50±2.0
Magnesium, (mg/L)	30.50±1.0	10.60±0.15	18.75±1.14	39.6±1.20	12.92±0.50	2.97±0.20	35.50±1.0
Sodium, (mg/L)	85.60±2.0	21.50±2.65	56.0±1.53	80.50±2.08	36.80±0.80	10.20±0.10	105.0±3.80
Potassium, (mg/L)	35.0±2.31	22.60±0.70	18.9±0.50	35.50±4.70	13.60±0.60	4.50±0.80	36.50±1.30
COD, (mg/L)	35.0±1.53	15.60±2.65	30.0±5.52	251.0±3.61	15.70±0.80	18.5±0.50	101.50±3.56
BOD, (mg/L)	4.0±0.90	1.0±0.35	2.30±0.65	10.0±6.50	1.30±0.20	1.0±0.01	6.50±2.10
Phosphate-P,(mg/L)	0.1±0.02	0.10±0.03	0.30±0.03	0.35±0.02	0.15±0.01	0.10±0.001	0.09±0.001
Nitrate, (mg/L)	0.75±0.10	1.0±0.15	1.50±0.15	55.60±1.21	6.55±0.01	BDL	5.50±0.60
Iron, (mg/L)	0.1±0.02	0.10±0.03	0.10±0.03	0.15±0.02	BDL	BDL	0.25±0.05
Copper, (mg/L)	BDL	BDL	BDL	0.03±0.002	BDL	BDL	0.03±0.005
Zinc, (mg/L)	0.04±0.02	0.10±0.03	0.01±0.02	0.04±0.02	BDL	BDL	2.50±070
Manganese, (mg/L)	0.10±0.02	0.01±0.01	0.10±0.02	0.15±0.02	BDL	BDL	0.15±0.02
Cadmium, (mg/L)	0.0002±0.02	BDL	BDL	0.0025±0.01	BDL	BDL	0.0025±0.0001
Lead, (mg/L)	0.01±0.001	BDL	BDL	0.02±0.001	BDL	BDL	0.015±0.003
Nickel, (mg/L)	0.007±0.001	BDL	BDL	0.01±0.001	BDL	BDL	0.008±0.002
TCF, (MPN/100ml)	≥2400	210	460	≥2400	93	23	≥2400
E.coli	Absent	Absent	Absent	Present	Present	Absent	Present

BDL-Below Detection Limit, COD- Chemical Oxygen Demand, BOD- Biochemical Oxygen Demand, TCF-Total Coliforms

Table 4.4: Physico-chemical and bacteriological characteristics of the groundwater samples at Njeliamparamba

Sample ID	**NP-22**	**NP-23**	**NP-24**	**NP-25**	**NP-26**	**NP-27**	**NP-28**	**NP-29**
pH	6.37±0.01	6.54±0.04	6.06±0.01	6.70±0.03	5.13±0.02	7.25±0.02	7.04±0.01	6.84±0.02
EC, (µS/cm)	336.0±5.5	199.60±1.5	195.80±2.3	1280.0±7.0	402.0±1.1	279.0±3.6	285.0±4.3	352.0±4.60
TDS, (mg/L)	238.56±3.3	141.72±3.0	139.0±1.20	909.0±8.2	285.42±4.0	198.09±2.0	202.35±3.5	249.92±2.0
Sulphate, (mg/L)	18.96±0.6	15.80±0.8	3.76±0.50	49.80±1.09	12.80±0.50	10.12±0.10	14.16±0.12	24.80±1.0
Chloride, (mg/L)	61.35±1.0	49.81±1.0	56.93±1.50	164.64±4.0	81.16±2.0	54.72±2.30	71.10±3.10	64.04±2.20
Total Alkalinity, (mg/L)	51.04±2.0	28.56±1.0	20.40±1.0	137.20±3.30	70.16±2.50	51.03±1.50	16.32±0.60	48.96±1.10
Total Hardness, (mg/L)	65.5±3.50	35.40±0.90	30.0±1.30	124.50±2.80	45.60±1.0	40.7±1.30	38.9±1.20	66.8±2.30
Calcium, (mg/L)	27.20±0.90	11.20±0.20	4.80±0.50	64.0±3.0	64.60±1.80	12.80±0.30	17.60±0.50	24.40±1.0
Magnesium, (mg/L)	10.69±0.22	0.97±0.001	3.89±0.35	40.50±1.60	34.40±1.60	6.77±0.20	6.80±0.35	10.69±0.80
Sodium, (mg/L)	26.80±1.0	10.20±0.02	10.20±2.10	85.60±2.50	36.80±1.25	26.80±1.10	36.80±1.50	21.50±1.50
Potassium, (mg/L)	13.60±0.25	4.50±0.5	4.50±0.50	35.0±0.80	13.60±0.80	13.60±0.50	13.60±0.60	22.60±1.0
COD, (mg/L)	15.70±0.20	15.50±2.0	18.50±1.10	55.0±3.10	15.70±1.50	15.70±0.85	15.70±0.50	15.60±0.45
BOD, (mg/L)	1.60±0.15	1.50±0.20	0.98±0.60	8.0±2.50	1.0±0.10	1.20±0.12	1.05±0.10	1.0±0.10
Phosphate-P,(mg/L)	0.15±0.01	0.10±0.01	0.10±0.40	0.10±0.20	0.15±0.25	0.15±0.22	0.15±0.10	0.10±0.08
Nitrate, (mg/L)	6.55±0.05	BDL	BDL	0.75±0.10	4.55±2.0	3.55±1.8	6.55±1.5	1.0±0.08
Iron, (mg/L)	BDL	0.10±0.02	0.10±0.01	0.10±0.01	BDL	BDL	BDL	BDL
Copper, (mg/L)	BDL	BDL	BDL	0.02±0.003	BDL	BDL	BDL	BDL
Zinc, (mg/L)	BDL	BDL	BDL	1.65±0.12	BDL	BDL	BDL	0.10±
Manganese, (mg/L)	BDL	0.09±0.001	BDL	0.08±0.002	BDL	BDL	BDL	BDL
Cadmium, (mg/L)	BDL	BDL	BDL	0.002±0.0002	BDL	BDL	BDL	BDL
Lead, (mg/L)	BDL	BDL	BDL	0.016±0.002	BDL	BDL	BDL	BDL
Nickel, (mg/L)	BDL	BDL	BDL	0.006±0.004	BDL	BDL	BDL	BDL
TCF, (MPN/100ml)	460	210	150	≥2400	93	23	210	23
E.coli	Absent	Absent	Absent	Present	Absent	Absent	Absent	Absent

BDL-Below Detection Limit, COD- Chemical Oxygen Demand, BOD- Biochemical Oxygen Demand, TCF-Total Coliforms

Table 4.5: Descriptive statistics of the groundwater quality characteristics of Njeliamparamba and well No's exceeding the BIS limit

Water quality parameters	Minimum	Maximum	Mean± SD	BIS	Well No's exceeding the BIS limit
pH	5.02	7.25	6.06±0.06	6.5-8.5	1-11, 15, 18, 21, 22, 24, 25
EC, (µS/cm)	181.30	1626.0	785.73±471	-	-
TDS, (mg/L)	128.72	1154.0	557.88±334	500	1-9, 11, 15, 18, 21, 25
SO_4^{2-}, (mg/L)	1.05	90.0	39.86±27.73	200	Nil
Cl^-, (mg/L)	49.81	260.50	141.11±76.5	250	5,6,8,9, 18, 21, 25
TA, (mg/L)	11.80	251.0	103.05±75.0	200	1, 2, 8, 9, 25
TH, (mg/L)	30.0	371.0	161.92±12.4	200	1-6, 8, 9, 11, 15, 18, 21, 25
Ca^{2+}, (mg/L)	4.80	101.50	52.08±32.20	75	1-6, 8, 15, 18, 21, 25
Mg^{2+}, (mg/L)	0.97	55.60	25.22±17.30	30	1-5, 8, 9,15, 18, 21, 25, 26
Na^+, (mg/L)	10.20	171.0	70.39±43.5	-	-
K^+, (mg/L)	3.60	142.0	30.83±26.7	-	-
COD, (mg/L)	15.50	252.60	67.4±69.0	250	5, 6, 8, 18
BOD, (mg/L)	0.98	10.0	4.08±3.50		-
PO_4^{2-}, (mg/L)	0.01	0.35	0.14±0.08	-	-
NO_3^-, (mg/L)	BDL	90.60	16.91±22.1	45	5, 6, 8, 18
Fe, (mg/L)	BDL	0.52	0.16±0.15	0.3	
Cu, (mg/L)	BDL	0.06	0.01±0.02	0.05	
Zn, (mg/L)	BDL	0.10	0.02±0.03	5.0	
Mn, (mg/L)	BDL	0.15	0.05±0.05	0.1	
Cd, (mg/L)	BDL	0.02	0.002±0.005	0.003	
Pb, (mg/L)	BDL	0.03	0.005±0.009	0.01	
Ni, (mg/L)	BDL	0.04	0.008±0.012	0.02	

BDL-Below Detection Limit, COD- Chemical Oxygen Demand, BOD- Biochemical Oxygen Demand, TH –Total hardness, TA-Total Alkalinity

Among the 29 groundwater samples collected from the vicinity of Njeliamparamba, pH and electrical conductivity values ranged from 5.02±0.02 to 7.25±0.02 and 181.0±3.1µS/cm to1626.0±10.4µS/cm, respectively. 69% of the samples were found to be acidic in nature; and the rest of the samples were within the permissible limits prescribed by Bureau of Indian Standards (BIS, 2012). Total dissolved solid values in the groundwater samples ranged from 128.72±2.0mg/L in NP-20 to 1154.0±9.0mg/L in NP-8. The TDS value exceeded the acceptable limit proposed by the Bureau of Indian Standards for drinking water (500mg/L) in 48% of the analysed samples. High concentration of TDS in the groundwater samples indicates the leaching of salts from MSW leachate. The water along with leachate may percolate into the groundwater which may lead to increase in TDS values. The classification of groundwater samples based on TDS values is presented in Table 4.6 (Davis & De Wiest, 1966).

Table 4.6: Classification of groundwater based on TDS
(Davis & De Wiest, 1966)

TDS (mg/L)	Water type	Percentage of samples
<500	Desirable for drinking	48
500-1,000	Permissible for drinking	38
<3,000	Useful for irrigation	14
>3,000	Unfit for drinking and irrigation	Nil

Alkalinity values in the collected groundwater samples ranged from 11.80±3.27mg/L to 251.0±5.78mg/L with average value of 103.05±75.0mg/L. Alkalinity concentration in five groundwater samples of Njeliamparamba was found to be exceeded the BIS limit (200mg/L). Chloride and sulphate concentrations in the groundwater samples varied from 49.81±1.0mg/L to 260.50±4.04mg/L and 1.05±0.79mg/L to 90.0±3.06mg/L, respectively. The BIS acceptable limit for chloride (250mg/L) exceeded in seven groundwater samples. Chloride was signified as the inorganic contaminants in the leachate because it is not easily adsorbed by soil, difficult to decompose and easy to measure. Sulphate concentrations of all the groundwater was found to be within the BIS acceptable limit (200mg/L).

Nitrate concentration up to 45.0mg/L is considered as normal. The nitrate concentration in the groundwater samples varied from BDL to 90.60±1.06mg/L with mean value of 16.91±22.1mg/L. The high concentrations of nitrate could be due to the seepage of wastewater dumped in the dumping site and other sources such as rainfall, depth of aquifers, and distance of the wells from the pollution source. Concentration of phosphate in the groundwater samples varied from 0.01±0.01mg/L to 0.35±0.02mg/L with an average value of 0.14±0.08mg/L.

Total hardness value of the collected groundwater samples ranged from 30.0±1.30 to 371.0±5.51mg/L with an average value of 161.92±12.40mg/L. The BIS acceptable limit for total hardness (200mg/L) exceeded in twelve groundwater samples. Based on Sawyer & McCarthy (1967) classification for total hardness, 38% of the samples in the study area fall under ‘‘soft class’’, 21% under ‘‘moderate class’’, 17% under ‘‘hard class’’ and the remaining 24 % falls under ‘‘very hard’’ class (Table 4.7).

Table 4.7: Classification of groundwater samples based on total hardness (Sawyer & McCarthy, 1967)

Total Hardness as $CaCO_3$ (mg/L)	Classification	Percentage of samples
<75	Soft	38
75-150	Moderately Hard	21
150-300	Hard	17
>300	Very Hard	24

Calcium and magnesium content of the groundwater samples varied from 4.80±0.66mg/L to 101.50±1.50mg/L and 0.97±0.001mg/L to 55.60±0.95mg/L, respectively. The BIS limit for calcium and magnesium in the groundwater sample is 75.0mg/L and 30.0mg/L, respectively. Calcium and magnesium content exceeded the BIS acceptable limit in 11 groundwater samples. Magnesium salts are cathartic and diuretic, and high concentration can cause laxative effect, while deficiency causes structural and functional changes (Selvam et al., 2013). Sodium concentration in the groundwater samples of Njeliamparamba ranged from 10.20±0.10mg/L to 171.0±5.50mg/L with a mean value of 70.39±43.50mg/L. Concentration of potassium ranged from 3.60±0.44 to 142.0±2.35mg/L with 30.83±26.70mg/L as the average. The presence of high concentrations of potassium in the groundwater samples is an indication of the leachate percolation. Figure 4.5 and 4.6 shows the mean concentrations of cations and anions in the groundwater samples of Njeliamparamba.

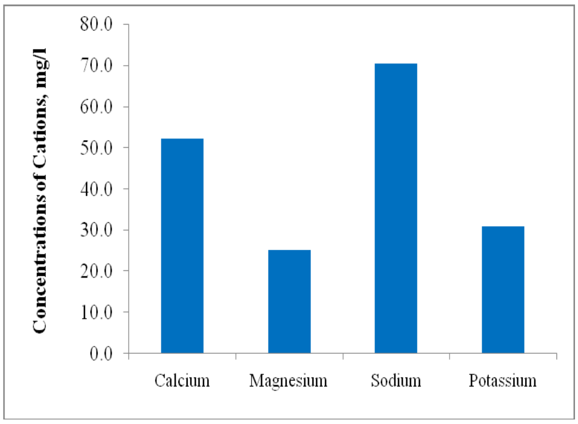


Figure 4.5: Major cationic concentrations in the groundwater samples of Njeliamparamba

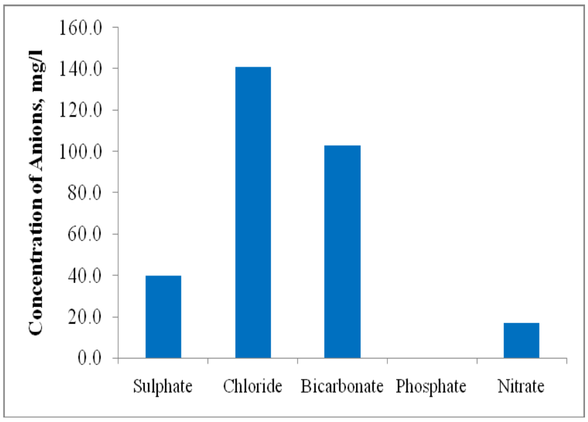


Figure 4.6: Major anionic concentrations in the groundwater samples of Njeliamparamba

The predominant cation trend was in the order of $Na^+ > Ca^{2+} > K^+ > Mg^{2+}$ with sodium being dominant cation and the predominant anion trend was in the order of $Cl^- > HCO_3^{2-} > SO_4^{2-} > NO_3^- > PO_4^{3-}$ with chloride being the dominant anion.

The COD level in the groundwater samples varied from 15.50±2.0mg/L to 252.6±2.52 mg/L, indicating the presence of organic contaminants in the water. High conductivity and COD might be due to the percolation of leachate in wells located near the site and organic strength produced by it. Xiaoli et al. (2007)

reported that the majority of the organic chemical substances are either degraded during biochemical reactions in the landfill, or leached out from the landfill site with water movement. Biochemical Oxygen Demand is used to determine the amount of oxygen demanding waste in water. BOD values were remarkably high at eight sampling sites (NP-1, NP-2, NP-5, NP-6, NP-15, NP-18, NP-21, and NP-25) (Table 4.1 to 4.4). Presence of high concentration of organic matter in the samples might be the reason for high BOD levels in this area. Kim (2005) has reported that the BOD value of 1mg/L is indicating the presence of oxidizable organic contaminants (water of high quality). While, high BOD values (5-10mg/L) indicate the presence of high amount of organic contaminants (water of low quality). The organochlorine pesticide such as lindane, aldrine, dieldrine, endosulphan, DDD and DDE analysis of the twenty nine groundwater samples was performed. The concentration of all the analysed pesticides was found to be within the acceptable limit prescribed by BIS.

4.3.1.1 Heavy metal analysis

The groundwater samples were analysed for heavy metals such as iron, copper, manganese, lead, nickel, cadmium and zinc and the results are presented in Table 4.2 to Table 4.5. The analysed heavy metals were detected in most of the groundwater samples. Heavy metal concentrations of all the groundwater samples were found to be within the BIS acceptable limit except, lead in 31% of the samples (NP-1, NP-2, NP-5, NP-6, NP-8, NP-9, NP-18, NP-21 and NP-25). The concentration of lead in most of the groundwater samples decreased with an increase in sampling distance from the dumpsite. This indicates the dumping of MSW in landfill for longer period can results in the subsequent leaching of metals in to water bodies lying in close vicinity of dumping site.

4.3.1.2 Bacteriological status of the groundwater samples

The presents of coliform bacteria in drinking water indicates the disease-causing organisms (pathogens) could be in the water system. Most coliforms that can contaminate water bodies come from the feces of human and other warm-blooded animals (Karak et al., 2012). Their present is an indicator that a potential health risk exists for an individual exposed to that water. *E.coli* is a subgroup of the fecal coliform group and their presence usually indicates recent fecal contamination. Bacteriological analysis of the 29 groundwater samples collected from the vicinity of Njeliamparamba clearly indicated that microbial contamination is in the groundwater samples. Most of the groundwater samples were found to be contaminated with total coliform. Very high count of total coliform (≥2400) contamination was reported in 38% of the total groundwater samples analyzed (Table 4.2 to Table 4.5). 69% of the groundwater samples were contaminated with *E.coli*. The results indicated that the bacterial contamination of groundwater possibly due to leachate percolation. The coliforms can multiply when leachate enters in to oxygenated system (Karak et al., 2012). Neill (2004) reported that when leachate was diluted with the bacteria-free water then there was an increase in the number of thermotolerant coliforms.

4.3.1.4 Hydrogeochemical facies of groundwater

Piper diagram (Piper, 1944) is a graphical representation of the chemistry of a water sample to understand problems concerning the hydrogeochemical evolution of groundwater. It is the most commonly used method to classify the water into different water category based on the anion and cation concentrations in the form of major ion percentage. The relative abundance of cations (Ca^{2+} and Mg^{2+}) is plotted on the cation triangle; whereas the relative abundance of anions (Cl^-, SO_4^{2-} and HCO_3+CO_3^{2-}) is plotted on the anion triangle. The overall chemical property of the water is represented in the centrally placed quadrilateral field (diamond shaped) by projecting the position of the plots in the triangular field. Back & Hanshaw (1965) suggested subdivisions of the tri-linear diagram to describe composition class (Figure 4.9). Water types are frequently used in the characterization of waters as a diagnostic tool. The piper plot of groundwater samples collected from Njeliamparamba is shown in Figure 4.8.

The result of the piper plot showed that 14% of the samples lie within (Na^++K^+) axis, 86% of samples come under in ‘‘No dominant’’ axis and while none of the sample lies Ca^{2+} and Mg^{2+} axis. In anions region of the plot, 90 % of the water samples lie within (Cl^-) axis while only 10 % lie in ‘‘No dominant’’ axis. From the plot, it is observed that the alkalies (Na^+ and K^+) exceed the alkaline earths (Ca^{2+} and Mg^{2+}) and strong acids (SO_4^{2-}+Cl^-) exceed weak acids (HCO_3^-). Out of the 29 groundwater samples studied 17% of the samples comes under sodium-chloride type, 7% are of calcium-chloride type, while the remaining 76% are of mixed type (No cation-anion exceed 50%). Hydrochemical water types obtained based on the dominance of cations and anions in the groundwater samples of Njeliamparamba is given Table 4.8.

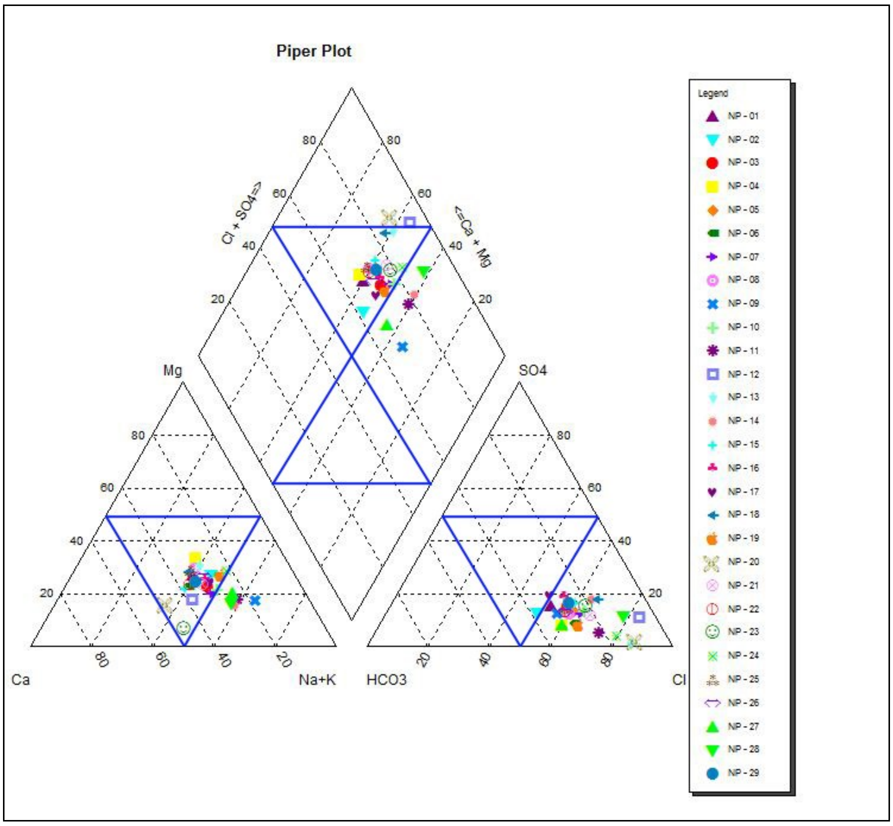
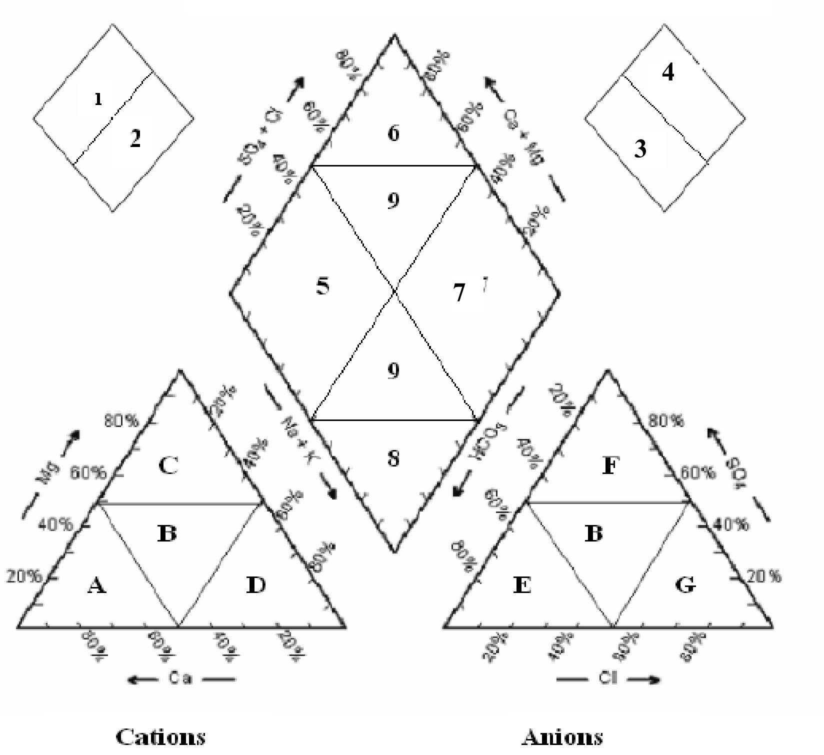


Figure 4.8: Piper diagram showing major groundwater facies of Njeliamparamba



A-Calcium type,
B- No dominant type,
C- Magnesium type,
D- Sodium and potassium type,
E- Bicarbonate type,
F- Sulphate type,
G- Chloride type.
1-Alkaline earth (Ca+Mg) exceed alkalies (Na+K),
2 -Alaklies exceeds alkaline earths,
3- Weak acids ($C0_3$+HCO_3) exceed strong acids (SO_4+Cl),
4- Strong acids exceeds weak acids,
5-Magnesium bicarbonate type,
6- Calcium-chloride type,
7-Sodium-chloride type,
8- Sodium-bicarbonate type,
9- Mixed type (No cation-anion exceed 50%)

Figure 4.9: Classification diagram for anion and cation facies in the form of major ion percentages (Adapted from Back & Hanshaw, 1965)

Table 4.8: Major water types of groundwater samples of Njeliamparamba

Station ID	Water Type
NP-1	Ca-Na-Mg-Cl-HCO_3
NP-2	Na -Ca-Mg-Cl-HCO_3
NP-3	Na-Ca-Mg-Cl-HCO_3
NP-4	Mg-Na-Ca-Cl
NP-5	Ca-Na-Mg-Cl-HCO_3
NP-6	Ca-Na-Mg-Cl-HCO_3
NP-7	Na-Ca-Mg-Cl
NP-8	Ca-Mg-Na-Cl-HCO_3
NP-9	Na-K-Cl-HCO_3
NP10	Na-Ca-Mg-Cl
NP11	Na-Ca-Cl
NP12	Ca-Na-Mg-Cl
NP13	Na-Mg-Ca-Cl
NP14	Na-Ca-Cl
NP15	Ca-Na-Mg-Cl
NP16	Ca-Na-Mg-Cl-HCO_3
NP17	Na-Ca-Mg-Cl-HCO_3
NP18	Ca-Na-Mg-Cl
NP19	Na- Mg-Ca-Cl-HCO_3
NP20	Ca-Na-Cl
NP-21	Na-Ca-Mg-Cl
NP-22	Ca- Na-Mg-Cl-HCO_3
NP-23	Ca-Na-Cl-HCO_3
NP-24	Na- Mg-Cl-HCO_3
NP-25	Ca-Na-Mg-Cl-HCO_3
NP-26	Na-Ca-Mg-Cl-HCO_3
NP-27	Na-Ca-Mg-Cl-HCO_3
NP-28	Na-Ca-Cl
NP-29	Ca- Na-Mg-Cl-HCO_3

4.3.2. Physico-chemical and bacteriological characteristics of groundwater samples at Laloor

The results of the physico-chemical and bacteriological characteristics of twenty groundwater samples collected in the vicinity of Laloor municipal solid waste dumping sites are shown in Table 4.9 to Table 4.11.

Table 4.9: Physico-chemical and bacteriological characteristics of groundwater samples of Laloor dumping site

Sample ID	**LLR-1**	**LLR-2**	**LLR-3**	**LLR-4**	**LLR- 5**	**LLR-6**	**LLR-7**
pH	5.76±0.03	6.83±0.18	6.28±0.2	6.62±0.22	5.93±0.24	5.33±0.27	5.68±0.24
EC, (µS/cm)	147.30±9.18	230.0±10	550.0±20.20	996.0±8.72	480.0±10.02	503.0±16.92	131.60±5.35
TDS, (mg/L)	104.50±6.51	163±4.58	390.5±8.19	707.16±7.09	340.8±6.24	375.13±8.08	93.43±4.42
Chloride, (mg/L)	38.35±2.68	24.91±3.16	85.16±3.08	220.0±3.21	86.93±3.75	101.83±2.55	22.02±2.53
TA, (mg/L)	10.40±2.20	41.6±3.30	83.44±2.75	106.48±2.24	48.96±3.98	42.64±1.88	20.40±1.55
Sulphate, mg/L	1.36±0.42	2.68±0.19	41.80±1.9	43.0±2.08	27.88±3.46	11.72±0.37	0.40±0.10
TH, (mg/L)	34.0±2.08	80.0±2.52	130.0±3.60	82.0±2.08	64.0±2.08	80.0±4.01	28.0±2.08
Sodium, (mg/L)	14.34±1.17	16.7±1.91	33.14±2.60	79.05±2.11	44.65±2.45	55.0±2.65	10.94±1.35
Potassium, (mg/L)	1.56±0.08	5.07±0.14	17.67±2.34	55.75±4.02	48.85±3.43	10.59±1.05	2.36±0.26
Calcium, (mg/L)	11.50±0.47	24±1.53	58.9±2.51	47.2±2.61	30.80±2.90	45.6±2.99	3.20±0.36
Magnesium, (mg/L)	2.50±0.05	4.86±0.02	19.77±0.77	22.97±0.08	12.92±0.56	13.88±0.70	4.86±0.96
Nitrate, (mg/L)	19.39±0.51	4.81±0.06	49.05±1.04	50.40±1.35	35.95±0.77	49.95±1.10	BDL
Phosphate-P, (mg/L)	BDL	BDL	BDL	BDL	BDL	BDL	BDL
COD, (mg/L)	15.60±1.0	21.50±1.30	21.2±1.0	58.90±1.50	13.50±1.0	38.0±1.20	23.0±1.30
BOD, (mg/L)	0.01±0.002	0.05±0.01	1.50±0.15	4.50±0.20	0.50±0.11	2.0±0.05	0.20±0.10
Fe, (mg/L)	BDL	BDL	0.18±0.01	0.23±0.02	0.12±0.02	0.10±0.01	BDL
Cu, (mg/L)	BDL	BDL	0.02±0.01	0.03±0.01	0.01±0.01	0.01±0.01	BDL
Mn, (mg/L)	BDL	BDL	0.05±0.02	0.04±0.01	BDL	BDL	BDL
Zn, (mg/L)	1.30±0.12	1.02±0.10	2.05±0.20	3.1±0.40	1.03±0.30	1.40±0.20	0.05±0.15
Cd, (mg/L)	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Pb, (mg/L)	BDL	BDL	0.003±0.0001	0.008±0.0002	0.002±0.0001	0.001±0.0001	BDL
Ni, (mg/L)	BDL	BDL	0.003±0.0002	0.005±0.0001	0.002±0.0001	BDL	BDL
TCF, (MPN/100ml)	1100	≥2400	≥2400	≥2400	≥2400	≥2400	460
E.coli	Absent	Present	Present	Present	Present	Present	Absent

BDL-Below Detection Limit, COD- Chemical Oxygen Demand, BOD- Biochemical Oxygen Demand, TH –Total hardness, TH –Total hardness, *TCF-Total Coliforms*

Table 4.10: Physico-chemical and bacteriological characteristics of groundwater samples of Laloor dumping site

Sample ID	**LLR-8**	**LLR-9**	**LLR-10**	**LLR-11**	**LLR-12**	**LLR-13**	**LLR-14**
pH	5.71±0.11	5.24±0.12	5.37±0.06	5.90±0.15	5.42±0.06	6.63±0.04	6.50±0.15
EC, (µS/cm)	709±18.03	229±4.51	675±3.61	411.0±10.50	411.0±9.54	146.0±4.16	141.10±3.05
TDS, (mg/L)	503.4±19.14	162.59±5.51	479.25±2.52	362.81±5.13	291.81±3.61	103.66±4.24	100.0±2.52
Chloride, (mg/L)	207.6±3.56	49.14±5.94	142.7±1.91	99.04±2.02	92.7±2.36	36.46±1.74	30.46±3.23
TA, (mg/L)	54.08±0.12	16.32±2.16	56.32±1.16	58.16±0.33	42.24±1.53	25.16±0.51	12.24±1.46
SulpHate, (mg/L)	29.68±0.86	4.16±0.03	35.24±0.02	34.10±0.03	10.20±0.03	3.04±0.01	2.76±0.63
TH, (mg/L)	98.50±3.51	460.0±1.53	80.80±1.53	98.90±1.53	52.0±2.0	21.8±1.53	24.0±1.53
Sodium, (mg/L)	40.98±3.04	24.04±2.10	62.46±1.60	48.13±1.07	48.27±1.15	10.91±6.91	25.18±1.61
Potassium, (mg/L)	11.40±1.14	2.24±0.12	28.31±0.26	24.23±0.22	23.08±0.31	1.79±0.20	14.50±0.15
Calcium, (mg/L)	32.20±2.62	16.40±0.15	49.60±0.15	49.60±0.20	38.90±0.25	14.80±0.15	4.80±0.15
Magnesium, (mg/L)	18.83±0.87	4.86±0.33	23.88±0.34	25.83±0.55	12.92±0.60	3.88±0.20	2.91±0.27
Nitrate, (mg/L)	50.85±0.61	29.16±0.19	46.66±0.44	49.50±0.76	43.60±0.66	30.0±0.26	16.56±0.14
PHospHate-P, (mg/L)	BDL	BDL	BDL	BDL	BDL	BDL	BDL
COD, (mg/L)	60.0±1.5	30.80±1.0	45.70±1.20	8.50±0.05	5.60±0.03	2.0±0.01	1.0±0.01
BOD, (mg/L)	4.0±0.06	0.30±0.005	3.50±0.05	3.0±0.04	2.60±0.02	0.25±0.003	0.30±0.001
Iron, (mg/L)	0.20±0.01	BDL	BDL	0.18±0.01	BDL	BDL	BDL
Copper, (mg/L)	0.01±0.01	BDL	BDL	0.02±0.01	BDL	BDL	BDL
Manganese, (mg/L)	BDL	BDL	BDL	0.02±0.01	BDL	BDL	BDL
Zinc, (mg/L)	1.52±0.10	0.08±0.01	0.05±0.003	1.30±0.02	BDL	BDL	BDL
Cadmium, (mg/L)	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Lead, (mg/L)	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Nickel, (mg/L)	BDL	BDL	BDL	BDL	BDL	BDL	BDL
TCF(MPN/100ml)	≥2400	460	≥2400	≥2400	≥2400	≥2400	240
E.coli	Present	Absent	Present	Present	Absent	Present	Absent

BDL-Below Detection Limit, COD- Chemical Oxygen Demand, BOD- Biochemical Oxygen Demand, TH –Total hardness, TH –Total hardness, TCF-Total Coliforms

Table 4.11: Physico-chemical and bacteriological characteristics of groundwater samples of Laloor dumping site

Sample ID	**LLR-15**	**LLR-16**	**LLR-17**	**LLR-18**	**LLR-19**	**LLR-20**
pH	7.0±0.20	6.48±0.11	7.80±0.03	7.06±0.08	7.41±0.02	7.12±0.1
EC, µS/cm	105.30±3.77	209.0±7.09	572.0±6.42	164.0±3.06	353.0±2.52	118.30±2.67
TDS, (mg/L)	74.76±1.64	148.39±3.79	406.0±3.61	116.40±3.06	250.63±3.06	84.0±2.08
Chloride, (mg/L)	17.79±1.40	56.93±3.02	99.60±1.86	20.58±1.85	89.81±1.42	21.35±1.18
TA,(mg/L)	16.32±1.41	5.60±0.31	121.76±1.40	36.32±0.66	56.72±1.16	30.40±1.21
Sulphate, (mg/L)	4.04±0.12	2.48±0.10	1.88±0.23	11.56±0.55	12.52±0.65	0.32±0.02
TH, (mg/L)	30.50±1.53	36.0±2.52	68.60±2.52	40.0±1.53	56.0±1.53	24.0±1.52
Sodium, (mg/L)	8.34±0.54	25.87±0.69	75.05±1.59	10.95±1.01	34.44±1.77	13.32±0.94
Potassium, (mg/L)	4.14±0.17	5.65±0.58	35.45±1.78	3.70±0.38	12.8±0.53	2.62±0.56
Calcium, (mg/L)	10.80±0.25	12.80±0.68	34.40±1.21	6.40±0.31	26.0±1.53	4.80±0.66
Magnesium, (mg/L)	3.88±0.19	2.97±0.08	15.83±0.70	5.83±0.54	6.88±0.34	2.92±0.71
Nitrate, (mg/L)	26.10±0.40	43.96±0.64	18.13±0.132	31.86±0.14	34.51±0.35	21.24±0.64
Phosphate-P, (mg/L)	BDL	BDL	BDL	BDL	BDL	BDL
COD, mg/L	1.0±0.05	2.50±0.08	6.70±1.0	2.0±0.06	2.10±0.05	0.50±0.01
BOD, (mg/L)	0.50±0.02	1.50±0.05	0.10±0.06	0.20±0.03	0.15±0.01	0.10±0.01
Iron, (mg/L)	BDL	BDL	0.12±0.02	BDL	0.01±0.01	BDL
Copper, (mg/L)	BDL	BDL	0.04±0.01	BDL	0.02±0.01	BDL
Manganese, (mg/L)	BDL	BDL	0.06±0.01	BDL	BDL	BDL
Zinc, (mg/L)	BDL	BDL	0.05±0.02	BDL	BDL	BDL
Cadmium, (mg/L)	BDL	BDL	BDL	BDL	BDL	BDL
Lead, (mg/L)	BDL	BDL	0.01±0.01	BDL	BDL	BDL
Nickel, (mg/L)	BDL	BDL	0.01±0.01	BDL	BDL	BDL
TCF, MPN/100Ml	≥2400	≥2400	460	≥2400	≥2400	460
E.coli	Absent	Present	Absent	Present	Present	Present

BDL-Below Detection Limit, COD- Chemical Oxygen Demand, BOD- Biochemical Oxygen Demand, TH –Total hardness, TH –Total hardness, TC-Total Coliforms

The pH values of groundwater samples ranged from 5.24±0.12 to 7.80±0.03 with a mean pH of 6.30. 50.0% of the samples were found to be acidic in nature; and the rest of the samples are within the permissible limits prescribed by Bureau of Indian Standards (BIS, 2012). The maximum electrical conductivity was found at the station (LLR 04) near to the dumping site (996.0±8.72micro Siemens/cm). Same trend was also found for total dissolved solids; TDS concentrations in the groundwater samples ranged from 74.76±1.64mg/L to 707.16±7.09mg/L with a mean value of 262.08±3.06mg/L. The TDS value exceeded the acceptable limit proposed by the Bureau of Indian Standards for drinking water (500mg/L) in two sampling sites (LLR-4 and LLR-8). Chloride concentration in the groundwater samples varied from 17.79±1.40mg/L to 220.0±3.21mg/L with 77.17±1.50mg/L as the average. Chloride concentration in the two groundwater samples (LLR-4 and LLR-8) of Laloor was above the BIS limit (200mg/L). Alkalinity and sulphate concentrations in the collected groundwater samples, ranged from 5.60±0.31mg/L to 121.76±1.40mg/L and 0.32±0.02mg/L to 43.0±2.08mg/L, respectively. The concentrations of alkalinity and sulphate in the groundwater samples of Laloor were found to be within the BIS limit.

The concentration of total hardness varied from 21.80±1.53 to 130.0±3.60mg/L. It is observed that hardness of all the analysed samples was found to be within BIS acceptable limit (200mg/L). The concentration of calcium and magnesium in the groundwater samples varied from 3.20±0.36mg/L to 58.90±2.51mg/L and 2.50±0.05mg/L to 25.83±0.55 mg/L. The calcium and magnesium content of the groundwater samples of Laloor was found to be within the BIS limit. Concentrations of sodium and potassium ranged from 8.34±0.54mg/L to 79.15±2.11 mg/L and 1.56±0.08 mg/L to 55.75±4.02 mg/L, respectively. Highest concentration of sodium and potassium were detected in the groundwater sample of LLR-4.

Nitrate-N concentration of the groundwater samples ranged from BDL to 11.30mg/L. The Nitrate-N concentration up to 10.0mg/L is considered as normal value. Nitrate-N exceeded the BIS acceptable limit in five samples. Concentration of COD of the groundwater samples varied from 0.50mg/L to 60.0mg/L with an average of 18.01mg/L. The concentration of organochlorine pesticides like lindane, aldrine, dieldrine, endosulphan, DDD and DDE were below detection limit in all the analysed samples.

The mean value of the major ions (cations and anions) in groundwater samples of Laloor followed the order: $Na^+ > Ca^{2+} > K^+ > Mg^{2+}$ and $Cl^- > HCO_3^- > NO_3^- > SO_4^{2-}$(Figure 4.10 and 4.11).

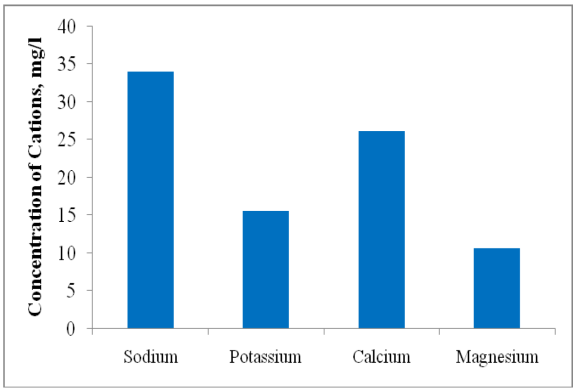


Figure 4.10: Major cationic concentrations in the groundwater samples of Laloor

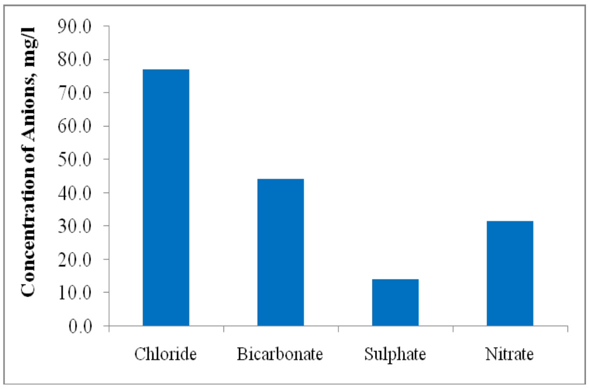


Figure 4.11: Major anionic concentrations in the groundwater samples of Laloor

4.3.2.1 Heavy metal analysis

The groundwater samples were analyzed for heavy metal such as Fe, Cu, Mn, Pb, Ni, Cd and Zn, and the results are presented in Table 4.10 to Table 4.12. The concentration of heavy metals in all the analysed samples was found to be within the guideline value for drinking water specified by BIS. Heavy metal concentrations of all the analysed groundwater samples were found to be within the BIS acceptable limit

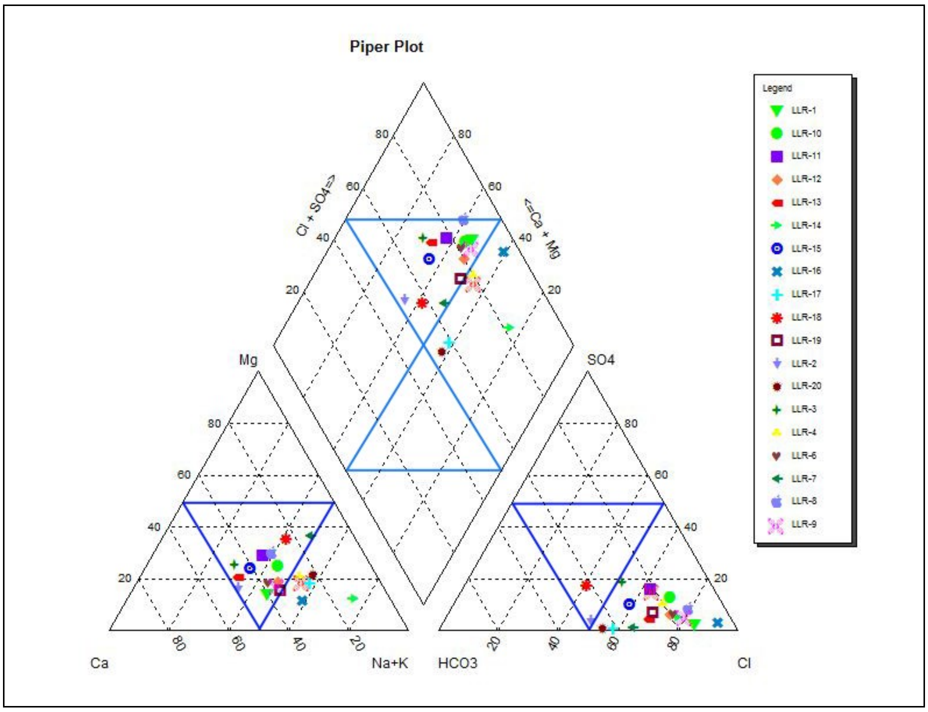
4.3.2.2 Bacteriological status of the groundwater samples

The bacteriological analysis of the groundwater samples of Laloor revealed that majority of the samples were bacteriologically contaminated with coliforms. Very high count of total coliform (≥ 2400) contamination was reported in 48.0% of the total samples (Table 4.10 and Table 4.11). *E.coli* was detected in 45% of the groundwater samples analysed.

4.3.2.4 Hydrochemical facies

In order to understand the chemical character of the groundwater samples and relationship between the dissolved ionic constituents, the analytical data obtained from the groundwater samples of Laloor are plotted on a Piper plot to understand the hydrogeochemical facies in the area. The piper plot of groundwater samples collected from different sampling stations of Laloor is shown in Figure 4.12.

The cation region of the plot showed that only 30% lies within (Na^++K^+) axis; none of the samples lies in Ca^{2+} and Mg^{2+} axis, and 70% of the samples fall in ‘‘No dominant type’’ region. In anions region of the plot, 90% of the groundwater samples lie within (Cl^-) axis and the remaining 10% lie within the ‘‘No dominant type’’ region. In terms of weak acids/ strong acids, all the groundwater samples in Laloor are of strong acids exceeds weak acids. Further analysis of the piper plot shows that 30% of the samples are of Na-Cl type. Water types obtained based on the dominance of cations and anions in the groundwater samples of Laloor is given Table 4.12.



4.12: Piper diagram showing major groundwater facies of Laloor

Table 4.12: Major water types of groundwater samples of Laloor

Station ID	Water Type
LLR1	Na-Ca-Cl
LLR2	Ca-Na-Mg-Cl-HCO_3
LLR3	Ca-Mg-Na-Cl-HCO_3
LLR4	Na-Ca-Mg-Cl
LLR5	Na-Ca-K-Mg-Cl
LLR6	Na-Ca-Mg-Cl
LLR7	Na-Mg-Cl-HCO_3
LLR8	Na-Ca-Mg-Cl
LLR9	Na-Ca-Cl
LLR10	Na-Ca-Mg-Cl
LLR11	Ca -Mg -Na-Cl
LLR12	Na-Ca-Mg-Cl
LLR13	Ca-Na-Cl- HCO_3
LLR14	Na-K-Cl
LLR15	Ca- Na-Mg-Cl-NO_3^--HCO_3
LLR16	Na-Ca-Cl-NO_3^-
LLR17	Na-Ca-Mg-Cl-HCO_3
LLR18	Mg-Na-HCO_3- Cl-NO_3^-
LLR19	Na-Ca-Cl-HCO_3
LLR20	Na-Cl^- -HCO_3-NO_3^-

4.3.3 Physico-chemical and bacteriological analysis of groundwater samples at Pettipalam MSW dumping site

A total of four groundwater samples and one pond samples were collected in the vicinity of the dumping site and analysed for physico-chemical and bacteriological parameters (Table 4.13).

Table 4.13: Physico-chemical and bacteriological characteristics of groundwater samples of Pettipalam dumping site

Sample ID	**PPM-1**	**PPM -2**	**PPM -3**	**PPM -4**	**PPM -5**
pH	6.17±0.20	6.50±0.15	8.63±0.45	6.8±0.20	5.72±0.30
EC, (µS/cm)	227.0±6.50	327.0±7.3	22677.0±504	320.0±4.0	153.0±3.80
TDS, (mg/L)	161.0±44.6	232.0±105.4	16100.0±310	227.20±2	108.20±1.9
Chloride, (mg/L)	50.84±3.30	82.58±2.50	6167.0±402	82.58±3.0	30.32±1.50
TA, (mg/L)	42.50±5.60	40.60±4.2	1035.0±203	39.0±1.60	24.60±1.10
Sulphate, (mg/L)	12.88±0.20	16.92±0.35	1072.0±101	17.24±0.5	16.20±0.25
TH, (mg/L)	62.0±2.80	8.0±5.60	2100.0±115	80.0±6.50	24.0±1.0
Calcium, (mg/L)	25.80±2.40	32.0±3.0	1013.0±22.50	28.80±3.30	9.60±1.50
Magnesium, (mg/L)	14.86±1.50	11.94±1.20	253.0±90.0	1.94±0.56	1.97±0.24
Sodium, (mg/L)	8.50±0.60	35.50±4.50	3200.0±150.0	27.50±2.8	15.60±1.20
Potassium, (mg/L)	3.60±1.50	4.60±2.40	1085.0±110	13.50±1.5	1.30±0.50
Nitrate, (mg/L)	BDL	BDL	250±0.10	BDL	BDL
Phosphate, (mg/L)	BDL	BDL	2.50±0.35	BDL	BDL
COD, (mg/L)	BDL	BDL	960.0±150.0	BDL	BDL
BOD, (mg/L)	BDL	BDL	4.30±0.10	BDL	BDL
Iron, (mg/L)	0.10±0.02	0.08±0.01	2.0±0.02	0.03±0.01	0.04±0.01
Copper, (mg/L)	BDL	BDL	0.50	BDL	BDL
Manganese, (mg/L)	0.01±0.002	0.02±0.01	0.07±0.02	0.01±0.01	0.03±0.01
Zinc, (mg/L)	BDL	BDL	BDL	BDL	BDL
Cadmium, (mg/L)	BDL	BDL	BDL	BDL	BDL
Lead, (mg/L)	BDL	BDL	BDL	BDL	BDL
Nickel, (mg/L)	BDL	BDL	BDL	BDL	BDL
TCF, (MPN/100ml)	100	300	≥2400	151	75
E.coli	Absent	Absent	Present	Present	Absent

BDL-Below Detection Limit, COD- Chemical Oxygen Demand, BOD- Biochemical Oxygen Demand, TH –Total hardness, TA-Total Alkalinity TCF-Total Coliforms

pH values of all the groundwater samples collected near the Pettipalam dumping site were found to be within the BIS limit of 6.50 and 8.50. The higher pH value of 8.63 was obtained in the sampling stations of PPM-3, which is collected from a pond near to the dumping site. The electrical conductivity values were detected as remarkably high at the pond sample. Electrical conductivity and TDS ranged from 153.0±3.80 to 22677.0±504 µS/cm and 108.30±1.9mg/L to 16100.0±310mg/L, respectively. The concentrations of chloride, total alkalinity, sulphate, nitrate and phosphate varied from 30.32±1.50 to 6167.0±402mg/L, 24.60±1.10 to 1035.0±203mg/L, 12.88±0.20 to 1072.0±101mg/L and BDL to 250.0±0.10mg/L, respectively.

Total hardness was found to be in the range from 24.0±1.0 to 2100.0±115.0mg/L. Calcium, magnesium, sodium and potassium concentrations in the collected water samples, ranged from 9.60±1.50 to 1013.0±22.50mg/L, 1.94±0.56 to 253.0±90.0mg/L, 8.50±0.60 to 3200.0±150.0mg/L and 1.30±0.50 to 1085.0±110.0mg/L, respectively. The major cations and anions in the groundwater samples of Pettipalam were in the following order: $Na^+ > Ca^{2+} > K^+ > Mg^{2+}$ with sodium being dominant cation and $Cl^- > HCO_3^- > SO_4^{2-} > NO_3^-$ with chloride being the dominant anion.

The level of COD and BOD in the groundwater samples were found to be within the BIS limit, but in pond sample exceeded the limit (960.0±150.0mg/L and 4.30±0.10, respectively). Groundwater samples were subjected to organo-chlorine pesticide and the results showed that all the chlorinated pesticides were found to be Below Detection Limit. The samples were subjected to heavy metals such as Fe, Mn, Cu, Ni, Pb, Cd and Zn using standard methodology. Analytical results showed that iron and manganese was detected in all the five groundwater samples of Pettipalam, but found to be within the acceptable limit prescribed by BIS (2012).

The maximum concentration of all the parameters was found in pond sample (PPM-3) when compared to the groundwater samples. The pond is situated 20 meter from the dumping site, is probably an indication of the effect of leachate on its quality. The results from the study revealed that all the tested physico-chemical groundwater quality parameters were within the acceptable limit of BIS except the bacteriological parameters. Presence of *E.coli* and total coliform bacteria in the groundwater samples indicated the microbial pollution of the groundwater.

4.3.3.1 Hydrochemical facies

The piper plot of groundwater samples collected in the vicinity of Pettipalam dumping site is shown in Figure 4.13. In anions region of the plot, all the water samples lie within (Cl^-) axis while none fall within the ‘‘No dominant type’’ region. The cation region of the plot showed that only one samples lies within (Na^++K^+) axis; none of the samples fall in $Ca^{2+}$and Mg^{2+} axis, while remaining three samples fall in ‘‘No dominant type’’ region. The groundwater samples of Pettipalam are of strong acids exceeds weak acids, dominance of alkalies (Na^++K^+) over alkaline earth (Ca^{2+}+Mg^{2+}) and mainly $CaCl_2$ type. Hydrochemical water types obtained based on the dominance of cations and anions in the groundwater samples of Pettipalam is given Table 4.14.

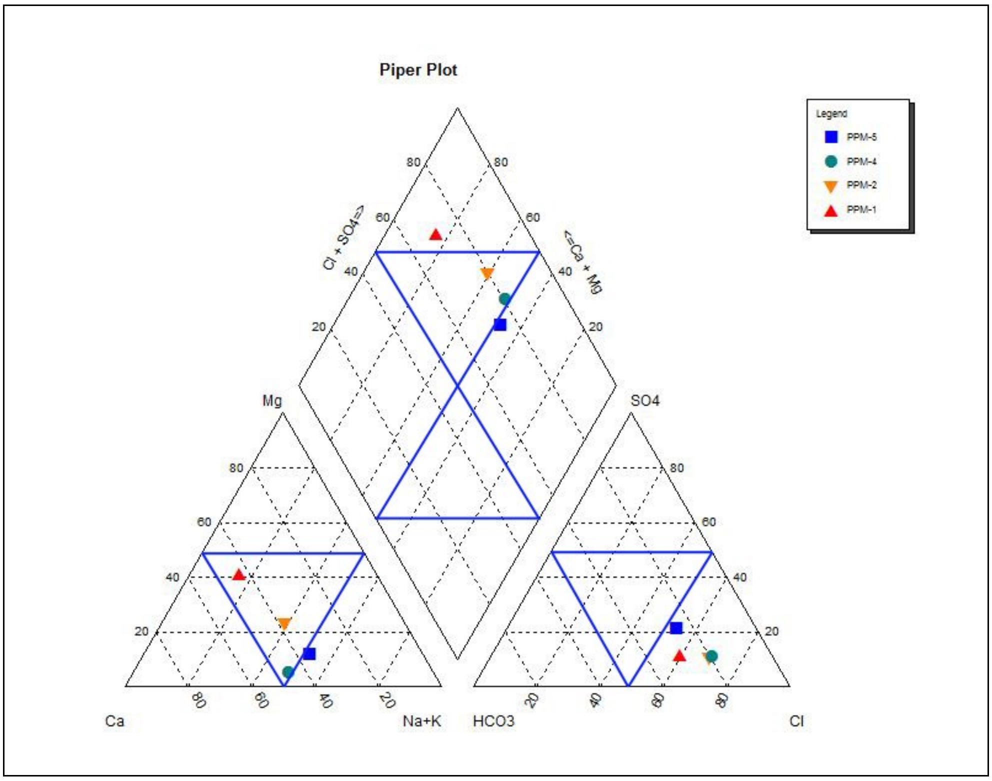


Figure 4.13: Piper diagram showing major groundwater facies of Pettipalam

Table 4.14: Major water types of groundwater samples of Pettipalam

Sample ID	Water types
PPM-1	$Ca-Mg-Cl^{-}-HCO_3^{-}$
PPM-2	$Ca-Na-Mg-Cl^{-}$
PPM-3	$Na-Ca-Cl^{-}$
PPM-4	$Ca-Na-Cl^{-}$
PPM-5	$Na-Ca-Cl^{-}-HCO_3^{-}SO_4^{-}$

4.3.4 Physico-chemical and bacteriological analysis of groundwater samples at Vellaramkunnu MSW dumping site

A total of five groundwater samples were collected from the vicinity of Vellaramkunnu dumping site and analysed for various physico-chemical and bacteriological parameters and the results are shown in Table 4.15.

Table 4.15: Physico-chemical and bacteriological characteristics of groundwater samples of Vellaramkunnu dumping site

Sample ID	**VLK-1**	**VLK -2**	**VLK -3**	**VLK -4**	**VLK -5**
pH	7.05±0.24	7.33±0.10	6.98±0.20	7.45±0.32	7.32±0.10
EC, (µS/cm)	131.70±4.0	102.80±6.50	81.80±4.50	227.0±5.0	130.80±4.0
TDS, (mg/L)	93.50±7.0	72.98±6.50	58.10±3.80	161.0±7.5	92.80±4.50
Chloride, (mg/L)	32.36±1.0	21.49±0.10	18.49±0.12	37.23±0.20	32.48±0.20
Total Alkalinity, (mg/L)	23.13±3.0	18.50±3.20	15.21±2.80	23.13±3.0	22.74±4.60
Sulphate, (mg/L)	2.80±0.12	2.20±0.20	2.19±0.09	8.88±0.20	2.68±0.30
Total Hardness, (mg/L)	40.0±1.2	26.0±1.50	28.0±1.0	54.0±2.60	40.0±1.60
Calcium, (mg/L)	14.40±1.0	9.60±0.95	8.40±0.35	22.20±1.50	14.40±1.20
Magnesium , (mg/L)	0.97±0.05	3.89±1.0	2.92±1.80	13.89±2.0	0.97±0.08
Sodium, (mg/L)	10.50±0.14	8.50±0.23	6.60±0.12	28.60±0.15	9.50±0.13
Potassium, (mg/L)	4.0±0.12	3.40±0.12	1.52±0.10	15.68±0.13	4.20±0.12
Phosphate, (mg/L)	0.04±0.01	0.03±0.01	0.02±0.01	0.09±0.02	0.02±0.01
Nitrate, (mg/L)	2.50±0.10	3.85±0.15	1.80±0.10	3.50±0.14	2.60±0.17
Phosphate, (mg/L)	BDL	BDL	BDL	BDL	BDL
COD, (mg/L)	BDL	BDL	BDL	BDL	BDL
BOD, (mg/L)	BDL	BDL	BDL	BDL	BDL
Iron, (mg/L)	0.12±0.02	0.09±0.01	0.04±0.01	0.10±0.01	0.08±0.01
Copper, mg/L	BDL	BDL	BDL	BDL	BDL
Manganese, (mg/L)	0.02±0.004	0.03±0.001	0.01±0.002	0.06±0.001	0.02±0.003
Zinc, (mg/L)	BDL	BDL	BDL	BDL	BDL
Cadmium, (mg/L)	BDL	BDL	BDL	BDL	BDL
Lead, (mg/L)	BDL	BDL	BDL	BDL	BDL
Nickel, (mg/L)	BDL	BDL	BDL	BDL	BDL
TCF, (MPN/100ml)	400	100	156	1300	85
E.coli	Absent	Present	Absent	Present	Absent

BDL-Below Detection Limit, COD- Chemical Oxygen Demand, BOD- Biochemical Oxygen Demand, TCF-Total Coliforms

The pH of the groundwater samples ranged from 6.98±0.20 to 7.45±0.24, which is within the acceptable limit as per BIS standard. Electrical conductivity and TDS ranged from 81.80±4.50 to 227.0±5.0µS/cm and 58.07±3.80mg/L to 161.17±7.50mg/L, respectively. The concentrations of chloride, total alkalinity, total hardness, sulphate, nitrate and phosphate varied from 18.49±0.12 to 37.23±0.20mg/L, 15.21±2.80 to 23.13±3.0mg/L, 26.0±1.50 to 54.0±2.60mg/L, 2.20±0.20 to 8.88±0.20mg/L and 1.80±0.10 to 3.85±0.15mg/L, 0.02±0.01 to 0.09±0.02mg/L, respectively. Calcium, magnesium, sodium and potassium, concentrations in the collected water samples, ranged from 8.40±0.35 to 22.20±1.50mg/L, 0.97±0.05 to 13.89±2.0mg/L, 6.60±0.12 to 28.60±0.15mg/L and 1.52±0.10 to 15.68±0.13mg/L, respectively.

The major cations and anions in the groundwater samples of Vellaramkunnu are in the following order: $Ca^{2+} > Na^{+} > K^{+} > Mg^{2+}$ with calcium being dominant cation and $Cl^{-} > HCO_3^{-} > SO_4^{2-} > NO_3^{-}$ with chloride being the dominant anion.

The samples were subjected to chlorinated pesticide and the results showed that all the pesticides were found to be Below Detection Limit. The concentrations of COD and BOD in the groundwater samples were found to be within the BIS limit. The samples were also subjected to heavy metals analysis and the results showed that iron and manganese was detected in all the five groundwater samples of Vellaramkunnu, but found to be within the acceptable limit prescribed by BIS. The heavy metals such as Cu, Ni, Pb, Cd and Zn were not detected in the analysed samples. The result of physio-chemical parameters of groundwater samples lie within BIS (2012) limits for drinking purpose (Table 4.15). Though, the presence of total coliform and *E.coli* bacteria revealed the presence of microbial pollution of the groundwater, which is an indication of the water quality unsuitable for domestic purposes.

4.3.4.1 Hydrochemical facies

Chemical data of the groundwater samples collected in the vicinity of Vellaramkunnu dumping site is presented by plotting them on a Piper diagram (Figure 4.14). In cation region of the plot, all the groundwater samples lie within Cl^{-} axis, while none lie within the ‘‘No dominant type’’ region axis. In anions region of the plot, 40 % of the samples lie in the (Ca^{2+}) axis while remaining 60 % fall in ‘‘No dominant type’’ region and none of the samples fall in Mg^{2+} and (Na^{+}+ K^{+}) axis. The groundwater samples of Vellaramkunnu are dominance of strong acids over weak acids, and alkaline earth (Ca^{2+}+Mg^{2+}) over alkalies (Na^{+}+K^{+}). All the groundwater samples of the study area is mixed type, indicating no cation-anion exceed 50%. The water types obtained based on the dominance of cations and anions in the groundwater samples of Vellaramkunnu is given Table 4.16.

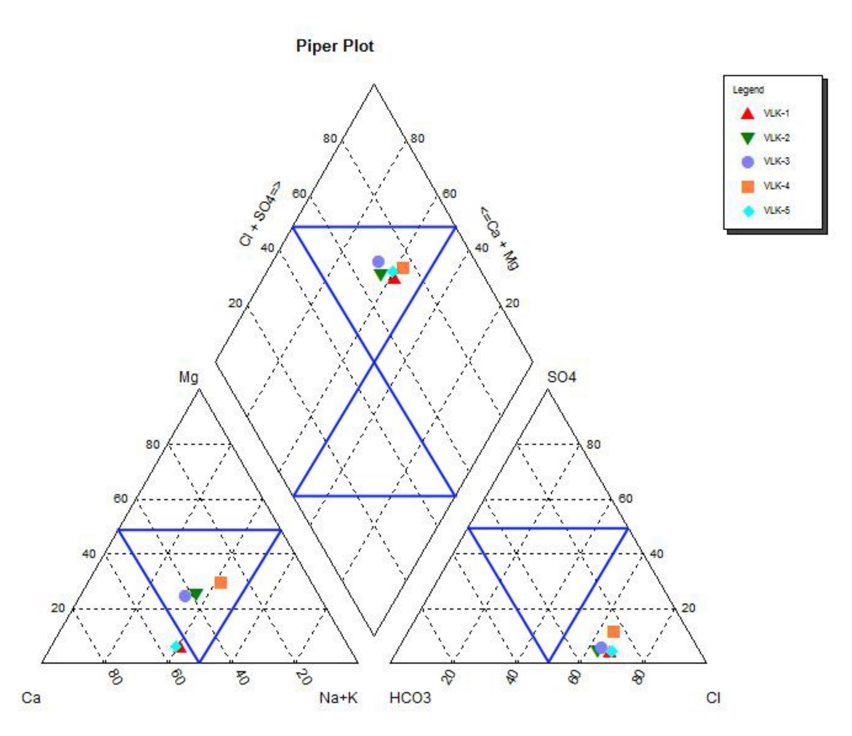


Figure 4.14: Piper diagram showing major groundwater facies of Vellaramkunnu

Table 4.16: Major water types of groundwater samples of Vellaramkunnu

Sample ID	Water types
VLK-1	Ca-Na-Cl-HCO_3
VLK -2	Ca-Na-Mg-Cl-HCO_3
VLK -3	Ca-Na- Mg-Cl-HCO_3
VLK -4	Na –Mg-Ca-Cl
VLK -5	Ca-Na-Cl-HCO_3

4.4 Summary

Assessment of groundwater quality in the vicinity of four selected municipal solid waste dumping sites in Kerala were investigated. A total of 59 groundwater samples were collected from the four selected MSW dumping sites (Njeliamparamba, Laloor, Pettipalam and Vellaramkunnu) in Kerala, and were subjected to various physico-chemical and bacteriological analysis. The results of analysis indicated that Njeliamparamba was found to be the area of most contaminated. Results obtained in Njeliamparamba revealed that, the quality of the groundwater samples within 300 meter from the dumping site were found to be highly polluted. High amounts TDS, Cl^-, HCO_3^-, Ca^{2+}, Mg^{2+}, NO_3^-, COD, BOD, lead, total coliform and *E.coli* were reported in groundwater samples. 48% of the samples were found to be unsuitable for drinking purpose. The effect of leachate migration from the Laloor dumping site might have caused higher concentrations of nitrate and coliform bacteria. In Pettipalam dumping site, a pond sample was found to be highly contaminated which is 20 meter from the dumping site. Presence of coliforms bacteria in the Pettipalam and Vellaramkunnu dumping site indicated the presence of microbial pollution of the groundwater. With the help of Piper diagram, the interpretation of hydrochemical facies of groundwater samples in Njeliamparamba, Laloor and Pettipalam indicated that, dominant ions comprised of (Na^++K^+) Cl^- type, and the type of water that predominates in Vellaramkunnu is calcium chloride type.

JASEELA C.”A STUDY ON THE SOIL AND WATER QUALITY OF SELECTED SITES AROUND SOLID WASTE DUMPING AREAS IN KERALA STATE”. THESIS. CWRDM (CENTRE FOR WATER RESOURCES DEVELOPMENT AND MANAGEMENT), UNIVERSITY OF CALICUT, 2018.

Chapter 5

DETERIORATION OF GROUNDWATER QUALITY IN THE VICINITY OF NJELIAMPARAMBA DUMPING SITE DUE TO LEACHATE MIGRATION

5.1 Introduction

The main environmental problem of waste dumping sites is the potential risk of leachate migration and subsequent influence on groundwater quality (Rahim et al., 2010). The health hazards and environmental degradation due to the leachate migration from uncontrolled dumping sites and its impact on groundwater and other water resources are well known facts (Akinbile & Yusoff, 2011; Manimekalai & Vijayalakshmi, 2012). In India, more than 90% of the generated municipal solid waste is directly dumped on land in an unsatisfactory way (Chatterjee, 2010). Waste placed in landfills undergoes a number of physical, chemical and microbiological changes that leads to the discharge of a toxic liquid known as leachate, which contains innumerable organic and inorganic compounds. The leachate will continuously migrate through the soil strata, ultimately contaminating the groundwater resources if no action is taken (Kanmani & Gandhimathi, 2013). The rate and characteristics of leachate produced depends on many factors such as type of solid waste deposited in the landfill and its composition, particle size, degree of compaction, hydrology of the site, landfill age, moisture content, climate and other site specific conditions (Jhamnani & Singh, 2009). Areas near landfills have a greater possibility of groundwater contamination because of the potential pollution source of leachate originating from the nearby dumping site.

The pollution potential of a particular landfill site can be assessed through various indices. Environmental indices such as the Water Quality Index (WQI) and Leachate Pollution Index (LPI) have been developed to determine the extent of pollution. The potential of leachate from different landfills to contaminate local systems can be evaluated using an index known as LPI (Kumar & Alappat, 2003). This index values can also be used to determine if a landfill requires immediate remediation. Additionally, the CCME WQI is a very useful and efficient tool for summarisation and monitoring data to understand the groundwater quality (Selvam et al., 2013).

The main objectives of this study are to assess groundwater using WQI and leachate quality using LPI and spatial interpretation of different water quality parameters using Geographic Information System at Njeliamparamba municipal solid waste disposal site.

5.2Materials and methods

5.2.3 Sampling and analysis

The sampling and analysis of a leachate sample and 18 groundwater samples were conducted during November 2014 (post-monsoon) and May 2015 (pre-monsoon). A random sampling method was used to collect groundwater samples within a 0.5 km radius of the landfill site and examine its impact on the groundwater quality. Pre-cleaned polyethylene bottle (1 L) were used to collect the leachate samples from the drains of the dumping site and groundwater samples from wells around the landfill site. The details of study area are discussed in chapter 4. Figure 5.1 shows the map of Njeliamparamba showing the sampling locations.

The pH, electrical conductivity and dissolved solids were recorded on site at the time of sampling with a multi-parameter PCSTestr35. To analyse biological oxygen demand (BOD), samples were collected in 300 ml BOD bottles and dissolved oxygen was fixed onsite (Modified Winkler's method). The total hardness, $Ca^{2+,}$ Mg^{2+}, Cl^{-} and total alkalinity were analysed by titrimetric methods (APHA, 2012). The Na^{+} and K^{+} concentrations were determined by the Flame Photometric Method while SO_4^{2-}, PO_4^{2-} and NO_3^{2-} were analysed by UV-VIS Spectrophotometer (Thermo Evolution 201, USA). The chemical oxygen demand (COD) was measured by open reflux digestion method and BOD was estimated by Azide modification of the Winkler method. For heavy metal analyses(Fe, Zn, Ni, Cu, Pb and Cd), samples were separately collected in to a pre-washed polyethylene containers (100 ml) and acidified onsite to avoid precipitation of metals, after which they were analyzed using Thermo M5 Series Atomic Absorption Spectrophotometer. The bacteriological analysis (total coliform, faecal coliform and *E.coli*) was conducted by the Multiple Tube Dilution technique. All chemicals used in this study were of analytical reagent grade and glassware used for analysis was washed with acid solution followed by distilled water. To ensure standard quality control/quality assurance procedures, replicates were analyzed for each sample. Sampling and analysis were conducted according to the Standard Methods for Examination of Water and Wastewater (APHA, 2012).

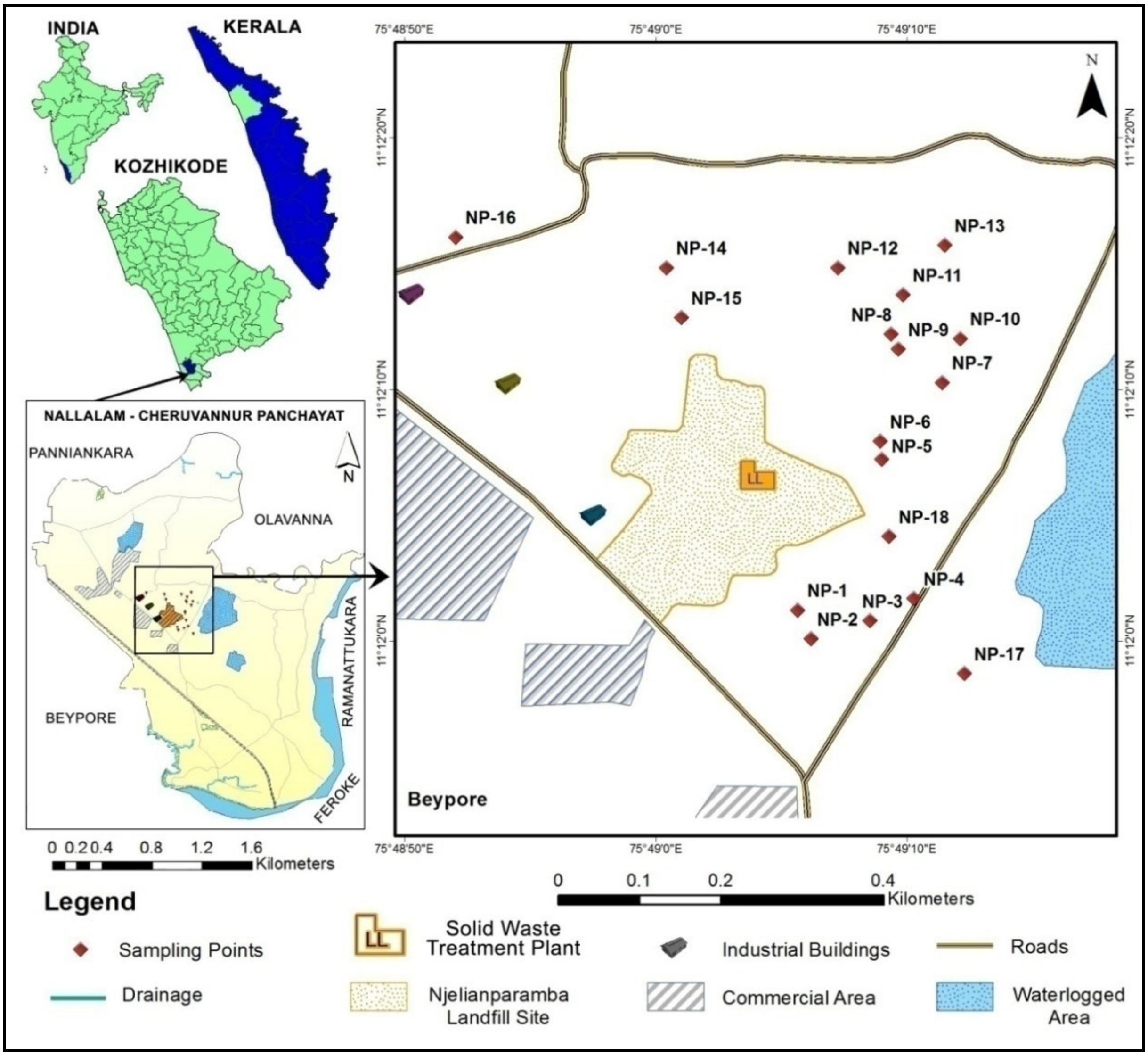


Figure 5.1: Map of Njeliamparamba showing the sampling locations

5.2.4 Spatial Interpretation using Geographic Information System

The base maps for generating the study maps were collected from the Soil Survey Department of the Kozhikode district. The map of Njeliamparamba was digitized and various findings were spatially represented using the ArcMap 10.1 software. A GARMIN GPS was used to record the latitude and longitude of sampling points which were imported into the GIS platform. The interpolation technique, Inverse Distance Weighting (IDW) was used for the spatial modelling of the study results. IDW is an algorithm used to interpolate data spatially or estimate values between measurements. The distribution of total coliform, fecal coliform, *E.coli* and variations in the dissolved solids with distance from landfill site in groundwater samples of the study area are represented through interpolated GIS maps that were processed by the IDW method.

5.2.5 CCME Water Quality Index (WQI)

CCME Water Quality Index was calculated to understand the overall quality of groundwater samples in the study area. This index gives detailed information concerning index calculation, and its application in summarizing complex water quality data that can be simply understood by the public (Hurley et al., 2012). CCME WQI includes three elements- Scope (F1): the number of water quality parameters (variables) not meeting water quality objectives; Frequency (F2): the number of times the objectives are not met; Amplitude (F3): the extent to which the objectives are not met. The CCME WQI is calculated using the equation below.

$$CCMEWQI = 100 - \frac{\sqrt{F_1^2 + F_2^2 + F_3^2}}{1.732}$$

The factor of 1.732 normalizes the resultant values to a range between 0 and 100, where zero signifies very poor water quality and values close to 100 signify excellent water quality. CCME Index value and their specifications are given in the Table 5.1.

Table 5.1: CCME WQI classification and their specifications (CCME, 2001)

CCME WQI	Specifications
Excellent (CCME WQI values 95-100)	Conditions are very close to natural levels
Good (CCME WQI values 0-94)	Minor degree of threat or impairment
Fair (CCME WQI values 65-79)	Occasionally threatened or impaired
Marginal (CCME WQI values 45-64)	Frequently threatened or impaired
Poor (CCME WQI values 0-44)	Almost always threatened or impaired

5.3 Results and Discussion

5.3.1 Leachate characterisation

The results of physico- chemical analyses of the leachate samples are compared with the National Standards set by Ministry of Environment and Forests, Government of India (MoEF, 2000) in Table 5.2.

Table 5.2: Physico-chemical characteristics of leachate

Parameters	pre-monsoon	post-monsoon	Leachate disposal Standard (MoEF, 2000)
pH	5.02±0.05	4.54±0.08	5.50 - 9.0
TDS, (mg/L)	16300.0±5.60	14300.0±4.56	2100
Chloride , (mg/L)	8483.0±4.0	4954.0±3.24	1000
COD, (mg/L)	36000.0±5.4	34012.0±5.20	250
BOD_5, (mg/L)	11022.0±5.0	10230.0±6.70	30
SO_4^{2-}, (mg/L)	792.0±3.1	532.0±2.30	-
NO_3^-, (mg/L)	111.0±1.0	101.0±1.56	-
F^-, (mg/L)	0.60±0.40	0.52±0.60	2
Na^+, (mg/L)	2872.0±3.5	2042.0±2.20	-
K^+, (mg/L)	3536.0±2.5	3399.0±2.45	-
Fe, (mg/L)	30.0±0.20	29.0±0.10	-
Cu, (mg/L)	0.35±0.08	0.29±0.05	3
Zn, (mg/L)	1.60±0.20	1.40±0.27	5
Cd, (mg/L)	0.10±0.01	0.12±0.01	2
Ni, (mg/L)	1.12±0.06	1.0±0.04	3
Pb, (mg/L)	0.23±0.70	0.22±0.50	0.1

The pH of leachate was 5.02±0.50 to 4.54±0.08 in the pre- and post-monsoon seasons respectively, indicating the leachate is acidic in nature. The pre- and post-monsoon dissolved solids were 16300.0±5.60mg/L and 14300.0±4.56mg/L respectively which were considerably high than the concentration set by the Ministry of Environment and Forests, discharge standard for leachate disposal. The high values can be attributed due to large concentration of cations and anions which indicated the presence of inorganic materials in the samples. The leachate was characterized with high COD (36000.0±5.4004mg/L in pre-monsoon and 34012.0±5.20mg/L in post-monsoon) and BOD_5 (11022.0±5.004mg/L in pre-monsoon and 10230.0±6.70mg/L in post-monsoon). The COD and BOD value is much higher than that of the leachate disposal standard, thus discharge into the sewer is not allowed. It is generally recognized that organics in leachate are characterized by different biodegradability. A measure of biodegradability is BOD5/COD ratio (Zayen, et al., 2010) of the leachate sample (BOD_5/COD=0.31 in pre-monsoon and 0.30 in post-monsoon) indicated an intermediate age landfill (leachate characteristics in between young and mature landfill).The high BOD and COD indicate the high organic pollution. Leachate contained high levels of chloride that exceed the recommended standards for leachate disposal. Because chloride is inert and non-biodegradable, it can be used as an indicator of contamination (D'Souza & Somashekar, 2012).

High levels of chloride (4954.0±3.24mg/L) that exceeded the recommended standards for leachate disposal was detected in the leachate. The presence of chloride ion is an indication of the leaching process from the dumping yard (D'Souza, & Somashekar, 2013). The high concentrations of sodium, potassium, nitrate and sulphate in the leachate sample also indicated impact of landfill leachate. The concentrations of Cu (0.29±0.05mg/L), Zn (1.40±0.27mg/L), Ni (1.0±0.04mg/L), Cd (0.12±0.0104mg/L) and Mn (0.11±0.67mg/L) were present in the leachate sample; but found to be below the standards for discharge in public sewer. The concentration of Pb (0.23±0.50mg/L) exceeded the permissible limits of MoEF regulations. The source of Pb can be attributed due to the leachate from lead batteries, chemicals for photograph processing and lead based paints at the landfill site (Mor et al., 2006). The high level of Fe indicates the dumping of steel scrap in the landfill. The dark brown color of the leachate likely originated from the oxidation of ferrous to ferric form and the formation of ferric hydroxide colloids and complexes with fulvic and humic substances (Kale et al., 2010).

5.3.1.1 Leachate Pollution Index

The LPI (Leachate Pollution Index) provides a proficient method for evaluating extent of leachate pollution from landfill sites. This index is a comparative and quantitative measure of leachate pollution potential that can be efficiently applied to areas prone to leachate migration and subsequent groundwater pollution. To determine the LPI, the sub-index values must be calculated based on the concentration of the leachate pollutants obtained from the sub-index curves for the pollutant variables. The weights for these parameters were calculated based on the significance levels of the individual pollutants. The p values obtained were multiplied by the respective weights assigned to each parameter to determine the LPI using the equation (Kumar & Alappat, 2005).

$$LPI = \sum_{i=1}^{n} WiPi \qquad \text{- (5.1)}$$

where LPI = the weighted additive leachate pollution index, Wi = the weight for the ith pollutant variable, Pi = the sub index value of the ith leachate pollutant variable, n = number of leachate pollutant variables used in calculating LPI

$$\sum_{i=1}^{n} Wi = 1$$

However, when the data for all the leachate pollutant variables included in LPI is not available, the LPI can be calculated using the dataset of the available leachate pollutants. In such case, the LPI can be calculated by the equation:

$$LPI = \frac{\sum_{i=1}^{m} WiPi}{\sum Wi} \qquad \text{- (5.2)}$$

Where m is the number of leachate pollutant variables for which data is available, but in that case, $m < 18$ and $\Sigma w_i < 1$. The weights calculated for each pollutant variable based on the significance values are shown in Table 5.3.

Table 5.3: Weights of the pollutant parameters included in LPI (Kumar & Alappat, 2005)

Pollutant	Significance	Pollutant weight
pH	3.509	0.055
Total dissolved solids	3.196	0.050
BOD5	3.902	0.061
COD	3.963	0.062
TKN	3.367	0.053
Ammonia nitrogen	3.250	0.051
Total iron	2.830	0.045
Copper	3.170	0.050
Nickel	3.321	0.052
Zinc	3.585	0.056
Lead	4.019	0.063
Total chromium	4.057	0.064
Mercury	3.923	0.062
Arsenic	3.885	0.061
Phenolic compounds	3.627	0.057
Chlorides	3.078	0.048
Cyanide	3.694	0.058
Total coliform bacteria	3.289	0.052
Total	63.165	1.000

The contamination potential of leachate can be calculated in terms of LPI. The calculated LPI of Njeliamparamba dumping sites were 28.81 and 25.09 in the pre-and post-monsoon seasons respectively and are discussed in Table 5.4. The LPI value at Njeliamparamba was higher than its standard value of 7.4 which is the permissible limit for the leachate disposal set by the Municipal Solid Waste Management and Handling Rules, Government of India (2000).

Table 5.4: LPI in the pre-monsoon and post-monsoon seasons

Leachate Constituents	Mean value		Individual pollution rating Pi		Weight Wi		Overall pollution rating PiWi	
	Pre-monsoon	post-monsoon	pre-monsoon	post-monsoon	pre-monsoon	post-monsoon	pre-monsoon	post-monsoon
pH	5.02	4.54	8	8	0.055	0.055	0.44	0.44
TDS, (mg/L)	16300	14300	38	35	0.050	0.050	1.9	1.75
Chloride,(mg/)	8483	4954	79	40	0.048	0.048	3.79	1.92
COD, (mg/L)	36000	34012	82	81	0.062	0.062	5.08	5.02
BOD, (mg/L)	11022	10230	66	64	0.061	0.061	4.03	3.90
Ammonia-N, (mg/L)	111	101	10	10	0.051	0.051	0.51	0.51
Fe, (mg/L)	30	29	5	5	0.045	0.045	0.23	0.23
Cu, (mg/L)	0.35	0.29	5	5	0.050	0.050	0.25	0.25
Zn, (mg/L)	1.6	1.4	5	5	0.056	0.056	0.28	0.28
Ni, (mg/L)	1.12	1.0	5	5	0.052	0.052	0.26	0.26
Pb, (mg/L)	0.23	0.22	5	5	0.063	0.063	0.32	0.32
Total					0.593	0.593	17.08	14.88
LPI							**28.81**	**25.09**

The LPI for the two seasons was calculated to determine the seasonal variation in the pollution. Pollution potential values reported during pre-monsoon season indicate that the leachate had more polluting potential during pre-monsoon season than the post-monsoon season. Groundwater quality status was lower during the pre-monsoon season, confirming that the pre-monsoon season is more susceptible for pollution potential. The LPI values computed in this study were significantly higher than those reported for other metropolitan cities in India. The LPI value of Pune metropolitan landfill site was 24.67 in pre-monsoon and 19.04 in post-monsoon season (Kale et al., 2010) and unscientific landfill site in Banglore was 17.1 (D'souza & Somashekar, 2013). These studies concluded that LPI serves as a crucial tool for policy makers and public to identify the pollution threat from landfill. LPI of the leachate shall be treated prior to discharge to meet the leachate disposal standard.

5.3.2 Water quality assessment of groundwater samples

Descriptive statistics of water quality characteristics of groundwater samples of Njeliamparamba during pre- and post-monsoon seasons is discussed in Table 5.5.

Table 5.5: Descriptive statistics of water quality characteristics of groundwater samples of Njeliamparamba during pre- and post-monsoon seasons

	Pre-monsoon			**Post-monsoon**			**Acceptable Limit (BIS,2012)**
Parameters	**Maximum**	**Minimum**	**Mean ± SD**	**Maximum**	**Minimum**	**Mean ± SD**	
pH	7.68	4.76	6.60±0.99	7.13	4.36	6.13±0.90	6.50-8.50
EC, (µS/cm)	1644.0	292.0	939.39±418.51	1487.0	181.00	810.11±386.35	-
TDS, (mg/L)	1170.0	202.0	665.39±297.94	1055.0	130.0	564.66±265.48	500
SO_4^{2-}, (mg/L)	440.0	44.0	78.26±112.28	272.0	19.00	89.31±82.96	200
Cl^-, (mg/L)	620.0	44.0	210.44±148.64	310.0	3.92	156.50±80.32	250
TA(mg/L)	357.0	3.40	160.18±127.02	503.23	42.58	139.56±129.03	200
TH, (mg/L)	524.0	34.90	251.87±154.35	440.0	44.0	200.99±129.67	200
Ca^{2+}, (mg/L)	116.0	9.31	55.71±34.48	164.16	6.80	50.21±38.39	75
Mg^{2+}, (mg/L)	84.85	0.94	27.34±22.64	38.88	BDL	20.55±13.85	30
Na^+, (mg/L)	294.0	26.00	128.56±71.74	112.0	11.20	86.74±44.94	-
K^+, (mg/L)	364.0	3.63	68.92±91.62	38.88	3.30	18.69±13.53	-
COD, (mg/L)	264.0	48.0	124.0±59.06	220.0	24.0	89.36±48.05	-
BOD, (mg/L)	10.0	0.90	6.0±1.50	10.50	1.50	5.50±1.0	-
NO_3^-, (mg/L)	95.63	1.35	27.42±23.06	83.00	BDL	98.13±279.46	45
Fe, (mg/L)	0.67	BDL	0.16±0.42	0.52	BDL	0.08±0.12	0.30
Cu, (mg/L)	0.04	BDL	0.01±0.02	0.04	BDL	0.01±0.2	0.05
Zn, (mg/L)	0.22	BDL	0.07±0.04	0.03	BDL	0.00±0.01	5.0
Mn, (mg/L)	0.23	0.03	0.09±0.06	0.18	BDL	0.05±0.05	0.10
Cd, (mg/L)	0.02	BDL	0.01±0.001	0.004	BDL	0.0001±0.001	0.003
Ni, (mg/L)	BDL	0.04	0.008±0.0012	BDL	0.035	0.006±0.00015	0.02
Pb, (mg/L)	BDL	0.0.3	0.005±0.0009	BDL	0.02	0.003±0.001	0.01

BDL-Below Detection Limit

40% of the samples were acidic in nature; and the pH of the water samples varied from 4.76 to 7.68 and 4.36 to 7.13 in the pre- and post-monsoon seasons respectively. The relatively high value of EC and dissolved solids in both the seasons indicates the presence of inorganic material in the samples. The highest dissolved solids were reported in sample collected within 200m from the dumping site, indicating that of free ions leached from the waste into the groundwater (Dharmarathne & Gunatilake, 2013). Of the samples collected, 70% samples had high dissolved solid levels than the limit prescribed by the Bureau of Indian Standards for drinking water (BIS, 2012). The higher concentration of dissolved solids during the pre-monsoon suggests that the leachate have more pollution potential during pre-monsoon season. COD is a measure of oxygen equivalent to the organic matter content of water susceptible to oxidation by a strong chemical oxidant and thus an index of organic pollution. The concentration of COD ranged from 48.0 to 264.0mg/L and 24.0 to 220.0mg/L during the pre-and post-monsoon seasons respectively.

5.3.2.1 Major anions in groundwater samples

Groundwater contamination can be traced by considering excess chloride ions as an index of pollution (Kale et al., 2010). Higher concentrations of chlorides were observed in wells close to the dumping site (NP-1, NP-5, NP-6, NP-8, NP-9 and NP-18). The highest value was recorded in well NP-8 which is 106 meter away from the site. Pollution sources such as domestic effluents, fertilizers, and septic tanks, as well as natural source such as rainfall can lead to high Cl^- content in groundwater. Sulphate concentrations in the samples were found to range from 40.0 to 440.0mg/L and 19.0 to 272.0mg/L in the pre- and post-monsoon seasons respectively. The major sources of nitrate in groundwater include domestic sewage, runoff from agricultural fields and leachate from landfill sites. Drinking water containing more than 45mg/L NO_3^- can cause methamoglobinemia in infants and gastric carcinomas (Hopps, 1986; Jalali, 2005). The nitrate concentrations exceeded the desirable limit at three locations. Nitrate concentration in groundwater samples is attributed to dumping of organic waste at landfill site (Kathale, 2012).

5.3.2.2 Major cations in groundwater samples

Almost all samples contained concentration of major cations which exceeded their limits. The hardness of samples was found to range from 35.0 to 524.0mg/L and 44.0 to 440.0mg/L in the pre- and post-monsoons, respectively. 70% of the sample stations reported hardness values exceeded the maximum desirable limit of 200mg/L prescribed by BIS. High levels of hardness may affect water supply system resulting in excessive soap consumption, calcification of arteries and cause urinary concretions, diseases of kidney bladder and stomach disorder (CPCB, 2008). Ca^{2+} and Mg^{2+} are important ions influencing total hardness. Calcium ranged from 9.0 to 164.0mg/L with an average value of 55.71mg/L for pre-monsoon samples and 6.80 to 164.0mg/L with an average value of 47.91mg/L for post-monsoon samples was reported in the samples. The acceptable limit of calcium ion concentration in groundwater is 75mg/L (BIS, 2012). The concentration of Mg^{2+} ions ranged from 0.94 to 84.0mg/L and BDL to 38.88mg/L in the pre- and post-monsoon seasons, respectively. As per BIS, the permissible limit of magnesium ion in groundwater is 30.0mg/L. Concentration of sodium ranged from 26.0 to 249.0mg/L and 11.20 to 112.0mg/L in the pre- and post-monsoon seasons, respectively. The occurrence of sodium above acceptance levels in wells, which is 200 meter from the dumping site, indicates possible leachate migration into groundwater (Adeolu et al., 2011). Potassium concentrations in well samples were also high during pre-monsoon than post-monsoon season.

5.3.2.3 Heavy metals in groundwater samples

The groundwater samples were analysed for Cu, Fe, Mn, Cd and Zn and the results are given in Table 5.5. Iron levels in the groundwater ranged from BDL to 0.67mg/L and BDL to 0.52mg/L in the pre- and post-monsoon seasons, respectively. The concentrations of Cu, Zn and Ni were found to be within the acceptable limit in both the seasons prescribed by the BIS. The concentration of Mn exceeded the limit in three sampling sites in both the seasons. The Cd concentrations of the sample ranged from BDL to 0.02mg/L and BDL to 0.004mg/L in the pre- and post-monsoon seasons, respectively. The concentration of lead in the collected groundwater samples ranged from BDL to 0.03mg/L and BDL to 0.02mg/L in the pre- and post-monsoon seasons, respectively. The concentration of lead exceeded in 50% of the samples collected in the study area. The dumping of MSW in a landfill for longer period can cause subsequent leaching of metals that deteriorate groundwater sources in the vicinity of dumping site. Also, the presence of favourable moisture content in the waste effect the degradation rate generating organic acid, it can enhance the concentration of heavy metals in the leachate runoff (Karak et al., 2013).

5.3.2.4 Spatial distribution of bacteria in the groundwater sources

The bacteriological analysis of the groundwater quality was spatially represented and analysed in the form of GIS maps. The distribution of bacteria and the distance between the well and landfill site were the two major criteria used to prepare the maps. The distribution of total coliform, fecal coliform and *E.coli* bacteria was represented through interpolated GIS maps that were processed by the Inverse Distance Weighting (IDW) method. As shown in Figure 5.2, 39% of the total samples analyzed were contaminated with a very high count of total coliform (>=2400). Similarly, 33% of the total samples analyzed were contaminated with fecal coliform (>=2400), (Figure 5.3). As shown in Figure 5.4, 44% of the samples were contaminated with *E.coli*. All well samples were grossly contaminated with bacteria with the highest concentration being observed in wells close to the dumping site. The results also demonstrate that large amounts of organic matter were present in groundwater samples caused by leachate percolation which provided nutrients for microbial growth.

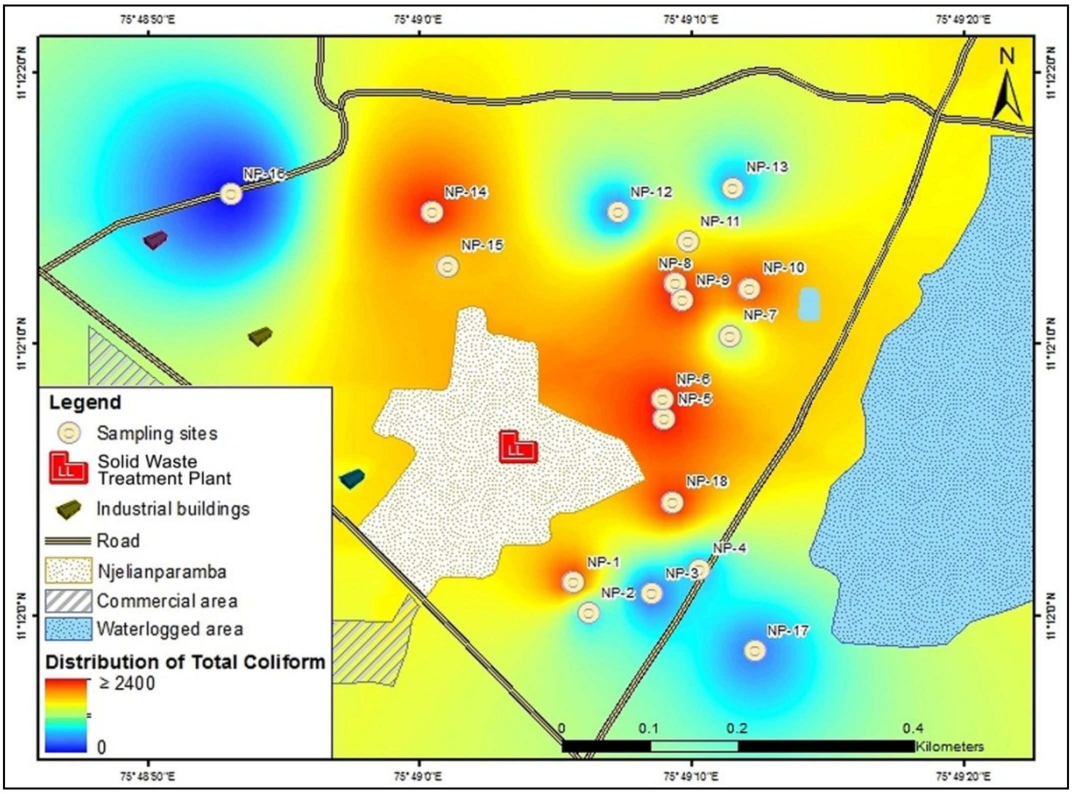


Figure 5.2: Distribution of total coliforms in groundwater samples

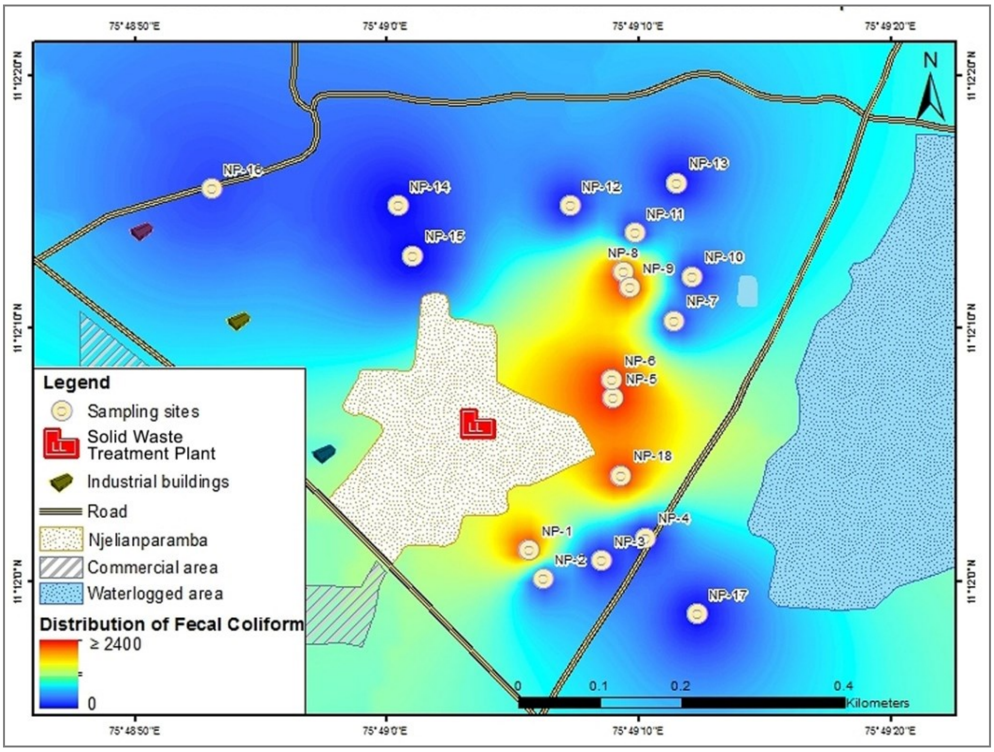


Figure 5.3: Distribution of fecal coliforms in groundwater samples

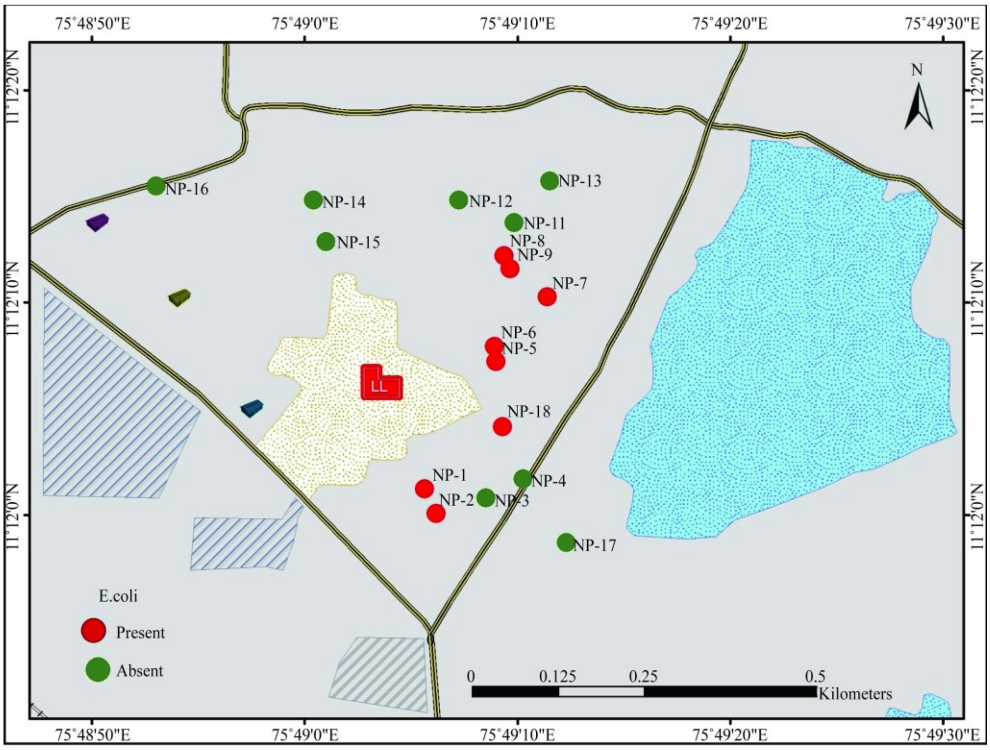


Figure 5.4: Distribution of *E.coli* in groundwater samples

5.3.2.5 Spatial distribution of CCME WQI in the groundwater sources

The CCME WQI has been used to rate overall water quality in spatial comparisons of sites. Figure 5.5 represents the spatial distribution of CCME WQI in groundwater and it explains the three classes of water quality in the study area.

CCME WQI of the study area was calculated in the pre- and post-monsoon seasons. According to CCME WQI, six sampling sites (NP-1, NP-5, NP-6, NP-8, NP-9 and NP-18) showed poor WQI values. All the six sites were located 200m from the dumpsite. Additionally, eight sites showed marginal water quality and four stations showed fair water quality. A CCME WQI map was created using the CCME WQI (2001) classification to understand the groundwater quality in the study area. GIS-based spatial analysis techniques have been shown to be a powerful tool to represent water quality evaluated by

CCME WQI values. Analysis using this method suggests that the majority of the sites in this study area falls had poor and marginal category. The spatial distribution map clearly showed that portions of the study area close to the landfill had poor groundwater quality.

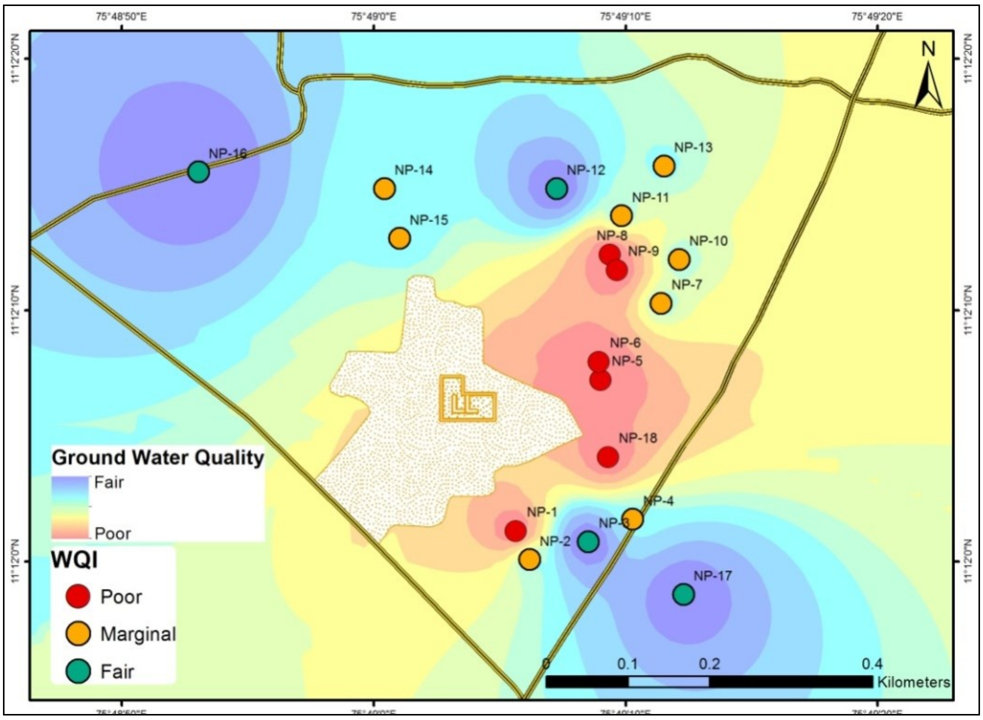


Figure 5.5: Spatial distribution of CCME WQI in Njeliamparamba

5.3.2.6 Impact of distance from landfill on solid waste leachate

The spatial variation of the dissolved solids in groundwater samples and distances from the landfill to the study area were represented using Geographic Information System. Samples were collected spatially at different distances from the landfill site. These two criteria were used to determine the groundwater quality at the sampling sites with proximity to the landfill. Figure 5.6 represents the variation of total dissolved solids with distance from the landfill site.

The total sampling sites were grouped into three buffer zones based on the TDS concentration. Buffer zone I, which contained most of the sampling sites, corresponds to the distance of 0 to 200m from the landfill. Sites in zone I included; NP-1 to NP-9, NP-12, NP-14, NP-15 and NP-18. The TDS values of those sites were high, indicating that the water is unfit for any use. Zone II was 200 to 300m from the landfill site. Although it is not as hazardous as Zone I, use of water from those sites is not recommended. Zone III consisted of 300-500m from the landfill. Groundwater samples from this zone had low TDS. The zonation map showed that the sampling sites within zone I and II contain more soluble salts in groundwater and cannot be used for any purpose.

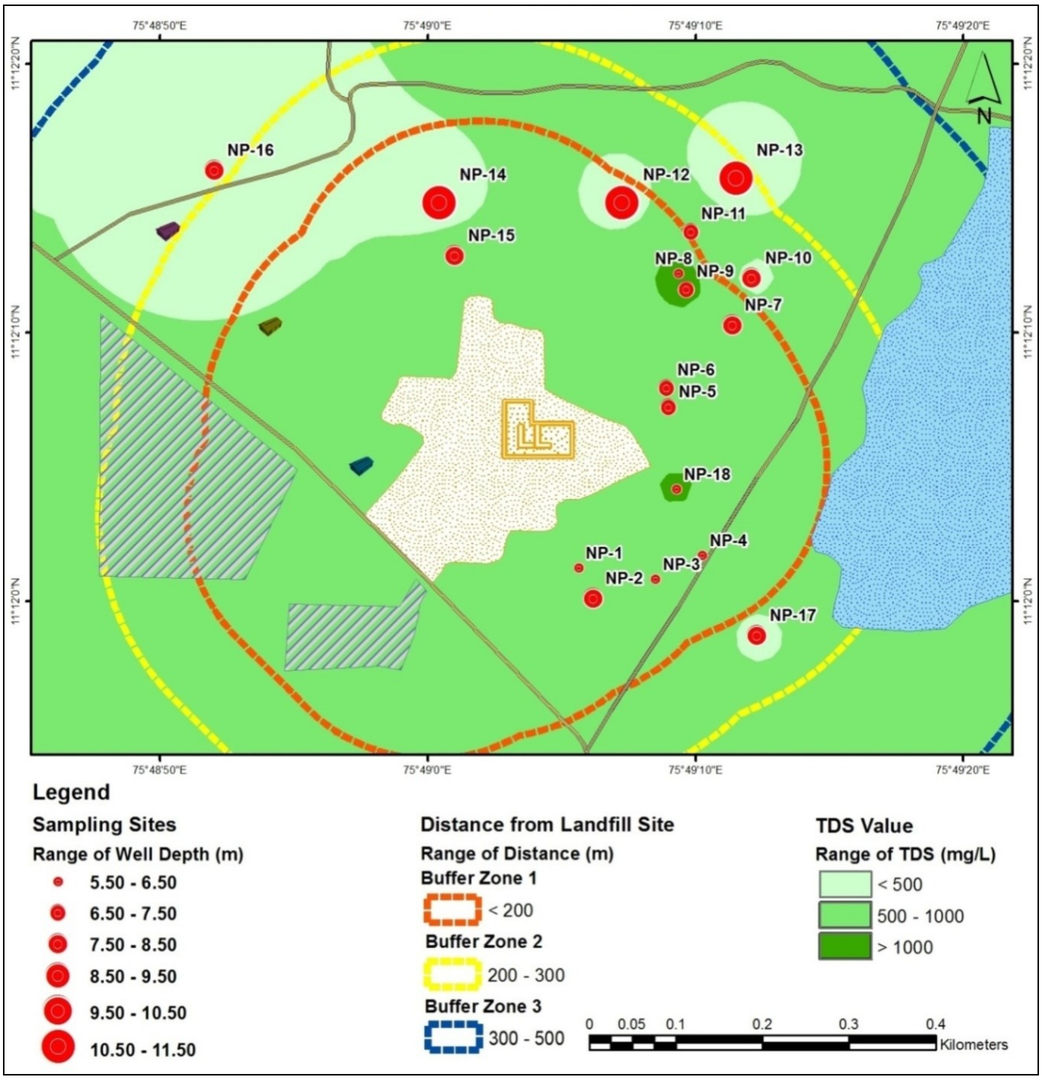


Figure 5.6: Variation of TDS with distance from landfill site

As shown in Figure 5.6, generally speaking, the contamination of groundwater mainly appears within 500m from the dumping site and most of the severe groundwater contamination occurs within 200 m. This result revealed that the samples from wells situated close to the landfill site were found to be more heavily contaminated than those located far away. These findings indicate that the gravitational movement of the leachate is hindered by the mass of the soil matter. Over increasing time, the viscous fluid may penetrate deeper and spread all over a longer distance.

5.3.2.7 Correlation analysis of TDS and chloride with their well depth and distance from the landfill site

Correlation analysis is a descriptive technique to assess the degree of association among variables. Statistical package for Social Sciences (SPSS version 19.0) was used for correlation analysis. In this study, Pearson correlation coefficients were determined for various water quality parameters.

Table 5.6: Correlation coefficient for different parameters

Parameters	Distance	Depth	TDS
Distance	1	0.416	-0.863
Depth	0.416	1	-0.510
TDS	-0.863	-0.510	1
Chloride	-0.733	-0.516	0.977

Table 5.6 shows the Pearson's correlation matrix between the two parameters (TDS and chloride) and their well depth and distance from the landfill site. Chloride is a useful tracer of groundwater contamination (Mor et al., 2006) and TDS is a valuable index of total ions in samples. Strong negative correlations (-0.863 and -0.733) were obtained for the concentrations of TDS and chloride respectively with their distance from the landfill site. The significant negative correlation for TDS with distance from the dumpsite shows

that the concentration of contaminants in groundwater normally decreases with increasing distance from pollution. A moderately high negative correlation was obtained for TDS and chloride with well depth, which also indicated that the concentration of contaminants in groundwater samples decreased with increasing depth. Correlation analysis confirmed that groundwater quality improved with increases in well depth and the distance of the well from the pollution source.

5.3.2.8 Correlation analysis of different physico-chemical parameters

Pearson correlation matrix of different physico-chemical parameters of the groundwater samples of Njeliamparamba are presented in Table 5.7. It shows the strength of the linear relationships between each pair of water quality variables. There is a very strong association between EC and TDS; demonstrated the fact that EC depends largely on the dissolved solids present in the samples. TDS and EC shows very strong positive correlation with sulphate (r =0.895) and chloride (r=0.977), total alkalinity (r=0.907), total hardness (r=0.897), calcium(r=0.911), magnesium (r=0.888), sodium (r=0.874) and significant positive correlation with potassium (r=0.724), COD (r=0.739) and nitrate (r=0.613). These positive correlations indicate that the contaminants in the groundwater samples collected in the vicinity of Njeliamparamba probably originated from the same pollutant sources. The negative correlation between total hardness and NO_3^- and were probably due to the effect of nitrogen fixing bacteria decreases with increasing hardness of water (Ganiyu et al., 2016; Fabiyi, 2008). Phosphate shows negative correlation with all other water quality parameters except sulphate.

Table 5.7: Pearson correlation matrix of different physico-chemical parameters of Njeliamparamba

Water quality parameters	**EC**	**TDS**	**SO_4^{2-}**	**Cl^-**	**TA**	**TH**	**Ca^{2+}**	**Mg^{2+}**	**Na^+**	**K^+**	**COD**	**PO_4^{2-}**	**NO_3^-**
EC	1												
TDS	1.000[b]	1											
SO_4^{2-}	0.895[b]	0.895[b]	1										
Cl^-	0.977[b]	0.977[b]	0.868[b]	1									
TA	0.907[b]	0.907[b]	0.850[b]	0.860[b]	1								
TH	0.897[b]	0.897[b]	0.821[b]	0.846[b]	0.826[b]	1							
Ca^{2+}	0.911[b]	0.911[b]	0.873[b]	0.880[b]	0.831[b]	0.921[b]	1						
Mg^{2+}	0.888[b]	0.888[b]	0.825[b]	0.828[b]	0.862[b]	0.915[b]	0.940[b]	1					
Na^+	0.874[b]	0.874[b]	0.787[a]	0.836[b]	0.857[b]	0.844[b]	0.808[b]	0.810[b]	1				
K^+	0.727[a]	0.727[a]	0.652	0.698	0.729[a]	0.596	0.551	0.596	0.737[a]	1			
COD	0.739[a]	0.739[a]	0.575	0.727[a]	0.494	0.595	0.646	0.576	0.403	0.337	1		
BOD	0.941[b]	0.941[b]	0.852[b]	0.924[b]	0.844[b]	0.856[b]	0.814[b]	0.796[a]	0.723[a]	0.698	0.774[a]	1	
NO_3^-	0.613	0.613	0.441	0.596	0.396	-0.341	0.477	0.394	0.393	0.338	0.886	-0.035	1

[a] Correlation is significant at the .05 level (2-tailed)

[b] Correlation is significant at the .01 level (2-tailed)

5.3.2.9 Suitability for irrigation purposes

5.3.2.9.1 Sodium adsorption ratio

Sodium adsorption ratio (SAR) is a measure of sodium hazard of irrigation water. Groundwater with high sodium content can displace the calcium and magnesium in the soil and will reduce the infiltration, permeability and ability to form stable aggregates, thus water with high SAR values cannot be used for irrigation purpose. Values obtained for Na, Ca and Mg in the samples were converted into meq/l units in order to calculate the SAR, based on the following formula (Rahim et al., 2010).

$$\text{Sodium Adsorption Ratio (SAR)} = \frac{Na^{+}}{\sqrt{\left(Ca^{2+} + Mg^{2+}\right)/2}} \times 100$$

The waters having SAR values <10 are considered as excellent category, 10–18 are good category, 18–26 are fair category, and >26 poor or unsuitable for irrigation use (USSL, 1954). In the present study, all the groundwater sample collected from Njeliamparamba falls under excellent category (<10) for irrigation.

5.3.2.9.2 Soluble Sodium Percentage (SSP)

Soluble Sodium Percentage (SSP) is also used to evaluate sodium hazard**.** Wilcox (1955) has put forwarded a classification scheme for rating irrigation waters on the basis of Soluble Sodium Percentage. The SSP was calculated by using the following equation:

$$\text{Soluble Sodium Percentage (SSP)} = \frac{\left(Na^{+} + K^{+}\right)}{\left[Ca^{2+} + Mg^{2+} + Na^{+} + K^{+}\right]} \times 100$$

Where all the ions are expressed in meq/l

The waters having SSP values <20 are considered as excellent category, 20–40 are good category, 40-60 are permissible category, 60-80 are doubtful, and >80 poor or unsuitable for irrigation use (Wicox, 1955). The calculated values of SSP varied from 31.83 to 55.67 (mean value = 62.70) indicating moderate degree of restriction on the use of this water for irrigation. When the concentration of sodium ion is high in irrigation water, Na^+ ion tends to be absorbed by clay particles, displacing Mg^{2+} and Ca^{2+} ions. This exchange process in soil reduces the permeability and ultimately results in soil with poor internal drainage (Ayers & Westcot, 1985)

5.3.2.9.3 Magnesium Hazard Ratio (MHR)

Generally, Ca^{2+} and Mg^{2+} maintain a state of equilibrium in groundwater. More Mg^{2+} ions present in waters adversely influence the soil quality and thereby the crop yield. Magnesium hazard value is proposed by reference (Szabolcs & Darab, 1964) for irrigation water was evaluated by the formula:

$$\text{Magnesium Hazard Ratio (MHR)} = \frac{Mg^{2+}}{\left[Ca^{2+} + Mg^{2+}\right]} \times 100$$

Where, Ca^{2+} and Mg^{2+} ions are in meq/l. If the value of magnesium hazard ratio is less than 50, then the water is safe and suitable for irrigation (Khodapanah et al., 2009). From the calculated value (Table 3), the MHR values ranged from 31.68 to 53.17 (mean =) and the Majority of the groundwater samples of Njeliamparamba have MH<50 and suitable for irrigation. About 11.11% of the groundwater can be classified as unsuitable for irrigation use (MHR>50).

5.3.2.9.4 Kelly's ratio (KR)

Kelly (1940) determined the hazardous effect of sodium on irrigational water quality in terms of Kelly's Ratio and can be calculated by the formula

$$\text{Kelly's ratio (KR)} = \frac{Na^{+}}{Ca^{2+} + Mg^{2+}}$$

The Kelly's ratio of unity or <1 is indicative of good quality of water for irrigation whereas above one is indicative of unsuitability for agricultural purpose due to alkali hazards (Kumar et al., 2014).The obtained values for Kelly's Ratio of groundwater samples of Njeliamparamba varied from 0.47 to 1.26 with an average value of 0.71 indicating good quality for the use of this water in irrigation, except three samples. The calculated values of the different irrigational water quality parameters of groundwater samples collected from Njeliamparamba are presented in Table 5.8.

Table 5.8: Calculated values of different irrigational water quality Parameters of groundwater samples collected from Njeliamparamba

Sample ID	SSP	SAR	MHR	KR
NP-1	34.37	2.25	45.06	0.52
NP-2	42.73	2.90	49.94	0.75
NP-3	44.76	3.20	42.29	0.81
NP-4	31.99	1.89	53.17	0.47
NP-5	35.25	2.19	40.54	0.54
NP-6	34.76	1.87	38.05	0.53
NP-7	43.84	2.55	39.37	0.78
NP-8	31.83	2.04	48.15	0.47
NP-9	55.67	4.32	49.03	1.26
NP-10	45.47	1.91	42.79	0.83
NP-11	54.81	3.41	42.57	1.21
NP-12	38.51	1.56	31.68	0.63
NP-13	38.07	1.20	50.25	0.61
NP-14	54.83	2.82	38.01	1.21
NP-15	34.78	1.99	35.94	0.53
NP-16	33.04	0.96	46.02	0.49
NP-17	41.89	1.87	45.65	0.72
NP-18	32.48	1.84	44.76	0.48

5.4 Summary

The impact of landfills leachate on the surrounding groundwater quality in Njeliamparamba, India is a major environmental concern of the area.

In this study, physico-chemical and bacteriological parameters of leachate and groundwater samples collected in and around the landfill site were analysed. The results showed that, the wells within 200 meter from the dumping site (NP-5, NP-6, NP-8, NP-9 and NP-18) were most by affected by leachate percolation. Spatial distribution of groundwater quality parameters was measured by GIS. LPI and WQI in the study were applied to assess the overall quality of the leachate and groundwater. Those methods appear to be more systematic and provide a comparative evaluation of the quality of sampling sites. The LPI value at Njeliamparamba for both the seasons exceeded the standard LPI of 7.4 proposed for leachate disposal. A CCME WQI map was also generated using the same technique to understand the water potability spatially. The CCME WQI indicted that majority of the study area had poor and marginal water quality. The contamination of groundwater mainly appears within 500 meter from the dumping site and most of the severe groundwater contamination occurs within 200 meter. The quality improved with increase in distance of the well from the pollution source. The majority of the parameters showed an inverse relationship between concentration and distance. The results of the present study indicated that the Njeliamparamba municipal dumping site was prone to groundwater contamination through leaching. There is no natural or other possible reason for high concentration of the pollutants; it can be concluded that leachate has significant impact on groundwater quality in the area. Because dumping is a continuous process, without proper treatment facilities, groundwater in the surrounding area will gradually become more adversely affected by that activity. Quality assessments for irrigation suitability showed that majority of the groundwater samples of Njeliamparamba were found to be suitable for agriculture purposes.

JASEELA C.”A STUDY ON THE SOIL AND WATER QUALITY OF SELECTED SITES AROUND SOLID WASTE DUMPING AREAS IN KERALA STATE”. THESIS. CWRDM (CENTRE FOR WATER RESOURCES DEVELOPMENT AND MANAGEMENT), UNIVERSITY OF CALICUT, 2018.

Chapter 6

SOIL QUALITY CHARACTERISTICS AND ASSESSMENT OF SOIL CONTAMINATION AT NJELIAMPARAMBA MSW DUMPING SITE

6.1 Introduction

Soil is ‘‘a dynamic natural body on the surface of the earth in which plants grow, composed of mineral and organic materials and living forms’’ (Srivastava et al., 2014). In addition, it acts as protective filtering layer laid over the groundwater that mitigates the impact of several harmful pollutants (Venkatesan & Swaminathan, 2009). The rapid urbanization, population explosion and industrialization have greatly accelerated the generation of municipal solid waste on land and thus pollution loads on the urban environment to unmanageable quantity, which is adversely affecting soil properties (both biotic and abiotic). The soil is an important component of landfill site which is a media where polluted materials are deposited. This component is a natural source which needs careful monitoring because of continuous transportation to other media such as air, ground and surface water from soil media by evaporation, erosion and infiltration (Mandal & Sengupta, 2006; Kanmani &

Gandhimathi, 2013). Precipitation that infiltrates through the MSW, leach the constituents from the decomposed waste mass (generation of leachate) while moving downward causes the surface and subsurface soil to contaminate with organic and inorganic solutes (Jeyapriya & Saseetharan, 2010). Many factors which control the mobility of contaminants in soils profile such as soil pH, soil texture, percentage of organic matter, cation exchange capacity and amount of rainfall (Ali et al., 2014).

Soil contamination by heavy metals in the environment is of major concern because of their toxicity, wide source, non biodegradable properties, and their ability to accumulate for long period of time and threat to human life and the environment (Dong et al., 2011; Aydi, 2015). Solid waste disposal methods (open dumps, landfills, sanitary landfills or incinerators) represent a major source of metals released into the environment (Iwegbue et al., 2010; Waheed et al., 2010; Bretzel & Calderisi, 2011; Rizo et al., 2012; Kanmani & Gandhimathi, 2013;). Soils are regarded as the ultimate sink for heavy metals discharged into the environment, as many heavy metals are bound to soils and the main difficulty lies in complex nature of soil (Obiajunwa et al., 2002, Dang et al., 2002; Machender et al., 2010). The major sources of heavy metals in landfills are the co-disposed industrial wastes, electronic goods, electro plating waste, painting waste, used batteries, etc., when dumped with municipal solid wastes increase the heavy metals in dumpsites (Erses & Onay, 2003; Kanmani & Gandhimathi, 2013). Slow leaching of these metals under acidic environment during the degradation process leads to the generation of leachate with high metal concentration causes soil and groundwater contamination (Hong et al., 2002).

The main objective of the study was to assess the soil quality characteristics at Njeliamparamba dumping site and to determine the status of heavy metal contamination in the region using various indices such as Enrichment Factor, Contamination Factor, Degree of Contamination, Pollution Load Index, Principal Component Analysis and Correlation Analysis.

6.2 Materials and Methods

6.2.1 Soil sampling and methods

Soil samples were collected in the vicinity of Njeliyamparamba MSW dumping site. The area is located between latitude of 11^0 13′ 30″ N to 11^0 11′ N and longitude of 75^0 48′ E to 75^0 50′30″ E. A total number of fifty soil samples were collected at the depth of 0-30cm and 30-60cm layer of the soil using auger boring during September 2015. Out of 25 sites, 19 samples (NP-01 to NP-19) were collected within the buffer zone (within 1km distance from the dumping yard) and 6 samples (NP-20 to NP-25) were outside the zone were collected, properly labeled and brought to the laboratory for analysis. The details of soil sampling stations of the study area are given in Figure 6.1. All soil samples were air dried to a constant weight, sieved to 2 mm through a stainless steel sieve and homogenized preserved in clean plastic containers for subsequent use.

The collected samples were subjected to various physico-chemical analyses such as pH, electrical conductivity, chloride, sulphate, alkalinity, exchangeable sodium, potassium, calcium and magnesium, inorganic phosphorous, organic carbon, total heavy metals like zinc, cadmium, copper, manganese, iron, lead, nickel and soil texture. pH and electrical conductivity was measured electrometrically with glass electrode pH meter in water using soil/water ratio of 1:10. The concentration of sulphate was determined by Turbidimetric method using Systronics Digital Nephelo-Turbidity meter 132. The total alkalinity was measured by acid base titration and Argentometric method was used for the estimation of chloride (soil/water ratio of 1:10).

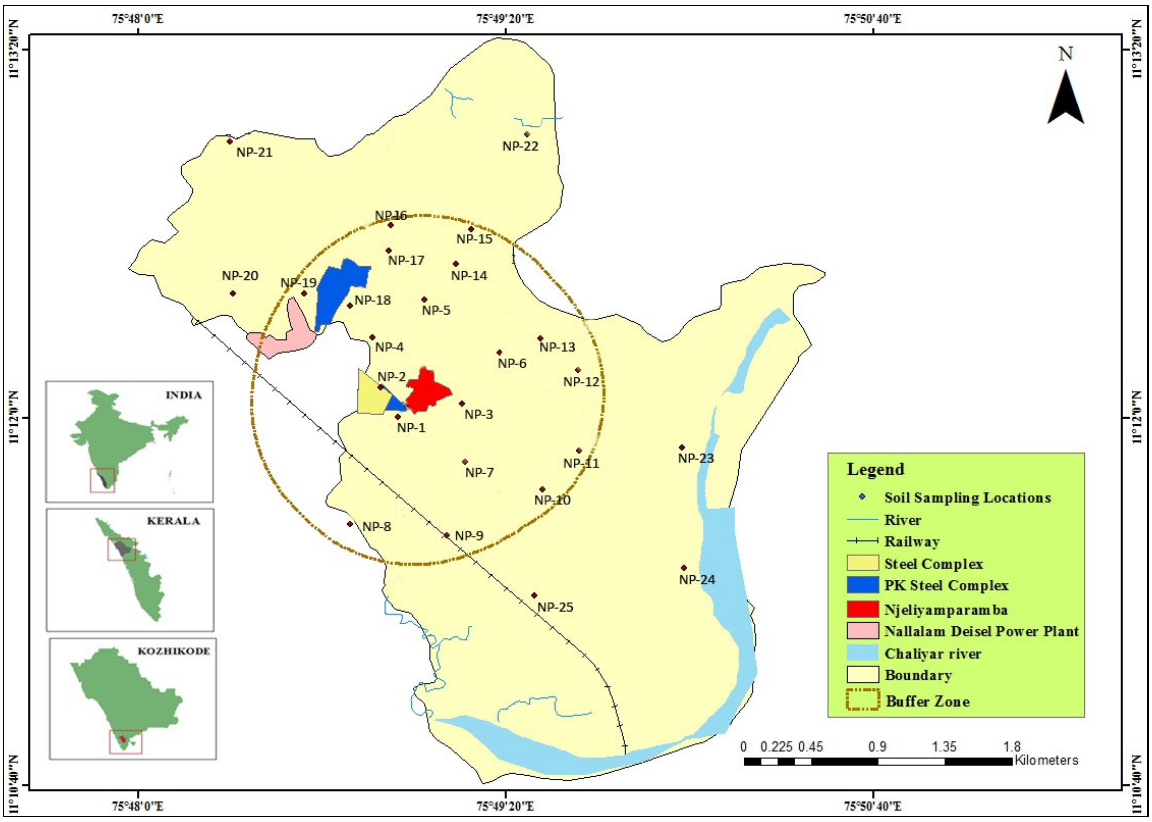


Figure 6.1: Sampling stations for the collection of soils in the study area

Plate 6.1: Collection of soil sample **Plate 6.2:** Survey from the study area

The organic carbon content in the soil samples was determined using Walkley and Black wet oxidation method and soil organic matter content was determined from organic carbon. Exchangeable Na, K, Ca and Mg were extracted using ammonium acetate, Na and K concentrations were determined using Systronics Flame Photometer 128, exchangeable Ca and Mg by Complexometric titration method. The soil texture was determined by hydrometer method. Extraction of the soil samples with 1M HCl was used for the analysis of inorganic phosphorous and was determined by using the UV Visible spectrophotometer (Thermo Scientific -Evolution 201). For the heavy metal analysis, the digestion of soil samples was performed with a mixture of HNO_3 and $HClO_4$ acid (USEPA, 1999).The digested samples were analyzed for heavy metals by Thermo M5 series Atomic Absorption Spectrophotometer. Ammonium saturation displacement method was used for the determination of cation exchange capacity of soil. Diethylene Triamine Penta Acetic acid (DTPA) extracting solution was used for the estimation of available metals (micronutrients) of soil. All the chemicals and reagents used for the study were of analytical grade and instruments were of limit of precise accuracy.

6.2.2 Contamination assessment and data analysis

6.2.2.1 Enrichment Factor

The enrichment factor was calculated by comparing the concentration of test element with that of a reference element (Buat-Menard & Chesselet, 1979). In this study, Iron was chosen as the element of normalization and the world average shale provided as background metal levels. Enrichment factor was determined using the formula:

$$EF = (M/Fe)_{Sample} / (M/Fe)_{Background}$$

Where, $(M/Fe)_{Sample}$ is the ratio of metal and Fe concentrations in the sample, and $(M/Fe)_{Background}$ is the ratio of metal and Fe concentrations of the background. Five contamination categories are generally recognized on the basis of the enrichment factor which are EF<2, deficiency to mineral enrichment; EF = 2-5, moderate enrichment; EF = 5-20, significant enrichment; EF = 20-40, very high enrichment; EF>40, extremely high enrichment (Sutherland, 2000).

6.2.2.2 Contamination factor and Degree of Contamination

Contamination factor ($C_f{}^i$) and the degree of contamination (C_d) were used (Hakanson et al., 1980) to assess the soil contamination of given toxic substance and is given by

$$C^i{}_f = C^i{}_{0-1} / C_n{}^i \text{ and } \quad C_d = \Sigma^n{}_{i=1} C_f^i$$

Where, $C^i{}_{0-1}$ is the mean content of the substance; $C^i n$ is the reference value for the substance. The degree of contamination (C_f) is defined as the sum of all contamination factors. The following criteria are used to describe the values of the contamination factor and degree of contamination and are given in the Table 6.1.

Table 6.1: Contamination factor and degree of contamination

C_f	C_d	Description
$C_F < 1$	$C_d < 7$	Low degree of contamination
$1 < C_f < 3$	$7 < C_d < 14$	Moderate degree of contamination
$3 < C_f < 6$	$14 < C_d < 28$	Considerable degree of contamination
$C_f > 6$	$C_d > 28$	Very high degree of contamination

6.2.2.3 Pollution Load Index

The pollution load index (PLI) was propsed by Tomlinson et al. (1980) for detecting pollution which permits a comparison of pollution levels between sites and at different times. The PLI was obtained as a concentration factor of each heavy metal with respect to the background value. The PLI was calculated based on the following equation.

$$PLI = (C_{f1} x C_{f2} x \ C_{f3} \ldots . Cf_{n)} \ {}^{1/n}$$

Where, C_f is the contamination factor; n, number of metals. The pollution load index can be classified as no pollution (PLI<1), moderate pollution (1<PLI<2), heavy pollution (2<PLI<3), and extremely heavy pollution (3<PLI) (Zarei et al. 2014; Aydi, 2015).

6.2.3 Statistical analysis

Statistical methods are strong tools for monitoring current environmental quality of soils in terms of heavy metal accumulation and predicting future soil contamination (Shakery et al., 2010). Correlation matrix (Pearson's correlation coefficient) and multivariate statistical analysis including principal component analysis (PCA) were performed using the SYSTAT 12 software statistical software package. The correlation coefficient measures the strength of inter-relationship between two parameters while PCA identify possible sources. Pearson correlation coefficient was calculated in order to determine correlation relationships between heavy metal contents in both depths.

6.3 Results and discussion

6.3.1 Physico-chemical characteristics of soil

The results of physicochemical characteristics of the soil samples collected from surface (0-30 cm depth) and sub-surface (30-60cm depth) soil samples are discussed in Table 6.2 and Table 6.3.

Table 6.2: Physico-chemical characteristics of surface and sub-surface soils of Njeliamparamba

Sample ID	Depth	pH	EC (µS/cm)	Chloride (mg/kg)	Alkalinity (mg/kg)	Sulphate (mg/kg)	Exchangeable Na (mg/kg)	Exchangeable K (mg/kg)	Exchangeable Ca (mg/kg)	Exchangeable Mg (mg/kg)	TOC (%)	OM (%)	Inorganic P (mg/kg)
NP-1	0-30	8.72	196.30	867.0	519.90	546.65	760.0	447.0	1044.0	81.46	0.16	0.28	150.0
	30-60	8.0	62.10	717.0	424.85	501.50	595.0	345.0	1008.0	61.46	0.08	0.14	85.0
NP-2	0-30	7.89	133.0	833.0	572.0	762.65	599.0	354.0	2660.0	408.90	2.48	4.21	64.6
	30-60	7.89	67.0	653.0	477.0	717.60	534.0	252.50	1099.0	388.90	1.05	1.79	29.6
NP-3	0-30	7.50	258.0	983.0	819.0	2980.0	718.20	552.0	1540.0	355.10	0.32	0.55	75.0
	30-60	7.50	101.0	883.0	724.0	2035.0	653.0	450.0	1019.0	335.10	0.20	0.34	40.0
NP-4	0-30	5.07	14.03	691.0	662.0	1068.0	529.0	366.0	661.0	236.0	1.52	2.62	140.0
	30-60	5.07	11.60	593.35	567.0	1023.0	114.0	264.0	310.0	216.0	0.52	0.89	85.0
NP-5	0-30	7.82	73.0	799.50	600.0	1239.0	656.0	412.0	1143.0	237.54	2.92	4.96	160.0
	30-60	7.82	37.50	701.50	550.0	994.0	441.0	310.0	792.0	217.54	1.22	2.07	95.0
NP-6	0-30	6.81	190.0	683.0	454.70	888.0	664.0	446.0	1460.0	355.10	0.60	1.04	58.10
	30-60	6.81	93.50	593.0	359.70	843.50	599.0	344.0	1109.0	335.10	0.40	0.69	23.10
NP-7	0-30	4.73	192.0	269.50	139.0	590.65	529.70	329.0	1460.0	1174.50	2.60	4.48	160.0
	30-60	4.73	107.60	229.50	44.91	545.65	364.0	227.0	909.6	754.50	0.97	1.72	125.0
NP-8	0-30	5.30	93.90	485.75	419.0	519.0	846.0	569.0	1539.0	243.50	1.52	2.62	740.0
	30-60	5.30	222.0	445.50	324.85	474.50	681.20	467.0	1188.0	223.50	0.62	1.07	565.0
NP-9	0-30	6.20	128.0	269.50	339.80	448.0	444.50	329.0	1539.0	123.80	1.04	1.79	180.0
	30-60	6.20	328.0	229.50	244.76	403.50	279.20	227.0	1088.6	103.80	0.54	0.93	125.0
NP-10	0-30	7.10	23.10	312.75	799.00	203.0	625.70	354.0	819.0	846.30	0.60	1.03	200.0
	30-60	7.10	28.30	272.75	704.79	158.45	460.0	252.0	468.7	826.30	0.10	0.17	165.0
NP-11	0-30	5.26	34.70	237.30	179.90	402.65	297.0	189.0	148.0	114.34	2.63	4.56	175.0
	30-60	5.26	31.60	187.30	84.88	357.65	132.0	87.50	112.6	94.34	1.14	1.96	140.0
NP-12	0-30	6.11	46.20	177.0	254.70	56.65	206.0	104.0	820.0	360.30	2.36	4.02	51.0
	30-60	6.11	39.70	127.0	159.72	11.0	141.0	94.50	469.6	340.30	1.46	2.48	16.0
NP-13	0-30	5.70	37.50	690.85	690.20	1395.0	1018.0	850.0	1141.0	183.40	1.56	2.69	130.0
	30-60	5.70	20.60	540.85	595.20	1350.0	603.0	748.0	790.0	163.40	0.56	0.96	95.0

Table 6.3: Physico-chemical characteristics of surface and sub-surface soils of Njeliamparamba

Sample ID	Depth	pH	EC (µS/cm)	Chloride (mg/kg)	Alkalinity (mg/kg)	Sulphate (mg/kg)	Exchangeable Na (mg/kg)	Exchangeable K (mg/kg)	Exchangeable Ca (mg/kg)	Exchangeable Mg (mg/kg)	TOC (%)	O M (%)	Inorganic P (mg/kg)
NP-14	0-30	6.04	176.90	982.0	620.0	2310.0	936.0	578.0	1223.0	682.54	1.72	2.97	140.0
	30-60	6.04	67.50	802.50	525.0	1710.0	521.0	476.0	872.0	562.50	0.82	1.41	95.0
NP-15	0-30	7.25	221.0	880.0	517.0	178.65	407.0	201.50	1783.0	132.34	1.12	1.93	800.0
	30-60	7.25	72.60	700.0	422.0	133.65	292.0	99.0	1032.0	112.0	0.62	1.07	445.0
NP-16	0-30	8.91	109.60	480.0	380.0	189.05	930.7	578.0	823.0	79.74	1.80	3.10	100.0
	30-60	8.91	72.10	300.0	285.0	159.05	515.0	476.0	472.0	59.74	0.90	1.55	55.0
NP-17	0-30	5.73	156.30	862.0	937.0	1830.0	1125.0	769.0	2823.0	210.54	0.20	0.34	150.0
	30-60	5.73	56.90	682.50	737.0	1280.0	710.0	667.0	1072.0	190.50	0.10	0.17	85.0
NP-18	0-30	5.63	816.0	1290.0	857.0	1150.0	1316.0	901.0	2023.0	763.50	4.80	8.28	980.0
	30-60	5.63	148.30	1110.0	762.0	805.65	901.0	799.0	1072.0	643.0	2.30	3.96	460.0
NP-19	0-30	4.94	93.60	802.0	680.0	1950.0	846. 0	467.0	1223.0	210.54	1.68	2.90	150.0
	30-60	4.94	47.0	622.50	585.0	1410.0	431.0	365.0	872.0	190.50	0.78	1.34	101.0
NP-20	0-30	7.07	44.0	140.0	185.10	403.0	265.0	46.50	240.0	219.0	0.60	1.04	175.0
	30-60	7.07	33.0	115.0	90.10	358.50	100.0	21.50	185.0	199.0	0.10	0.17	120.0
NP-21	0-30	7.01	66.0	89.0	298.90	191.0	222.0	28.50	320.0	164.0	0.44	0.76	100.0
	30-60	7.01	56.0	64.50	203.86	146.50	165.0	13.0	265.0	144.0	0.35	0.60	65.0
NP-22	0-30	6.32	30.50	312.0	564.30	245.0	210.0	71.0	340.0	274.0	0.64	1.11	375.0
	30-60	6.32	36.0	287.0	469.30	200.55	165.0	46.0	285.0	254.0	0.14	0.24	320.0
NP-23	0-30	6.58	22.0	122.0	72.80	147.0	196.0	38.50	240.0	876.0	0.68	1.18	300.0
	30-60	6.58	21.0	97.0	52.84	102.50	105.0	13.50	185.0	656.0	0.18	0.31	245.0
NP-24	0-30	6.00	31.50	170.50	110.0	255.0	141.0	37.0	240.0	193.20	0.96	2.01	150.0
	30-60	6.00	15.0	145.50	70.76	210.65	96.0	12.0	185.0	113.20	0.36	0.62	95.0
NP-25	0-30	4.82	150.0	185.0	110.80	274.0	221.0	33.0	360.0	45.0	1.84	3.18	150.0
	30-60	4.82	98.0	160.0	15.76	229.50	165.0	8.0	305.0	25.0	0.84	1.44	90.0

The pH value of the soil samples showed acidic to neutral pH. This may be attributed to the decomposition of organic matter leading to the formation of organic acids which indicated slightly acidic soils. Organic matter varied within the range of 0.14% to 8.28% in surface soil and 0.14% to 3.96% in sub-surface soil. The range of parameters such as chlorides, total alkalinity and sulphate for surface soil varied in the ranges of 89.0–1290.0, 72.80–937.0 and 56.65–2980.0mg/kg respectively and in the sub-surface soil varied in the ranges of 11.60-328.0, 64.50-1110.0, and 15.76-762.0mg/kg. Concentration of inorganic phosphorous varied from 51.0 mg/kg to 980.0 mg/kg for surface soil and 16.10mg/kg to 565.0mg/kg for sub-surface soil.

Exchangeable sodium concentration in surface soil varied from 141.0mg/kg to 1316.0mg/kg and sub-surface soil varied from 3.50 mg/kg to 799.0mg/kg, respectively. Exchangeable potassium concentration ranged from 28.50mg/kg to 901.50 mg/kg for surface soil and 3.50mg/kg to 799.0mg/kg for sub-surface soil. Concentration of the exchangeable calcium and magnesium ranged from 48.0mg/kg to 2823.0mg/kg and 45.0mg/kg to 1174.0mg/kg respectively for surface soil and 112.56 mg/kg to 1188.0 mg/kg and 25.0 mg/kg to 826.0 mg/kg for sub-surface soil. Furthermore, the concentrations of all the parameters in the surface samples were found to be more than in sub-surface samples.

6.3.2 Soil texture

Soil texture is one of the important physical properties of soil and it affects soil properties includes water-holding capacity, organic matter content, cation exchange capacity, nutritional status, pH buffering capacity, drainage, aeration, susceptibility to erosion, and soil tilth (Berry et al., 2007). The texture triangle explains the 12 different soil textural classes which include various proportions of sand, silt, and clay. Although, soils can be generally categorized as one of the four major textural classes, which are sand, silt, loam, and clay (Berry et al., 2007). The diameters of the particle size ranges from 0.05 to 2.0 mm for sand, 0.002 to 0.05 mm for silt, and less than 0.002 mm for clay. The loam refers to a soil with a combination of sand, silt and clay sized particles and it usually holds water well and drains easily. The composition of loams on the textural triangle (USDA-NRCS, 1999) is about 40% sand, 40% silt and 20% clay.

Clay soils hold nutrients and water much better than sandy soils. As water drains from sandy soils, it often carries nutrients along with it. When nutrients leach into the soil, they are not available for plants to use. Silt has the best ability to hold large amounts of water in a form, plant can use. The higher the clay content, the higher is the organic matter and higher the sand content, lower is the organic matter (Edward, 1997). Clay minerals are able to bound nutrients chemically in their surfaces, holding plant nutrients in the soil. The soil textural triangle showing the twelve classes is shown in Figure 6.2 and results of texture analysis of soil samples are given in Table 6.4 and Table 6.5.

The variations in the soil textural composition were observed at the sampling sites. The soils samples from the study area for both the horizon (0-30 and 30-60 cm depth) were predominantly sandy loam, loam and clay loam in texture. The results of the study revealed that the sand fraction of the soil decreased slightly with increasing soil depth. 74.07% of the samples in the study area recorded sandy loam texture, 20% of the samples recorded clay loam texture, 8% of the samples recorded loam texture and only 2% of the samples recorded sandy clay loam texture. The results of the texture analysis indicated that the majority of the soil samples of the study area showed sandy loam texture. Sandy texture is unsuitable for waste disposal because they are highly permeable and allow large quantities of leachate. Similarly, soils with clay and silt concentrations greater than 31% are unsuitable for waste disposal because they encourage surface flooding and potential pollution from surface runoff (Anikwe, 2002). The percentage of sand, clay and silt in the analysed samples varied from 44%, 10%, 1.25% to 82%, 37% and 29%, respectively. The percentage of sand was higher at the sampling sites NP-16, NP-17 and NP-22 at 0-30 depth (82.0%) and minimum in NP-11 and NP-18 at 30-60cm depth.

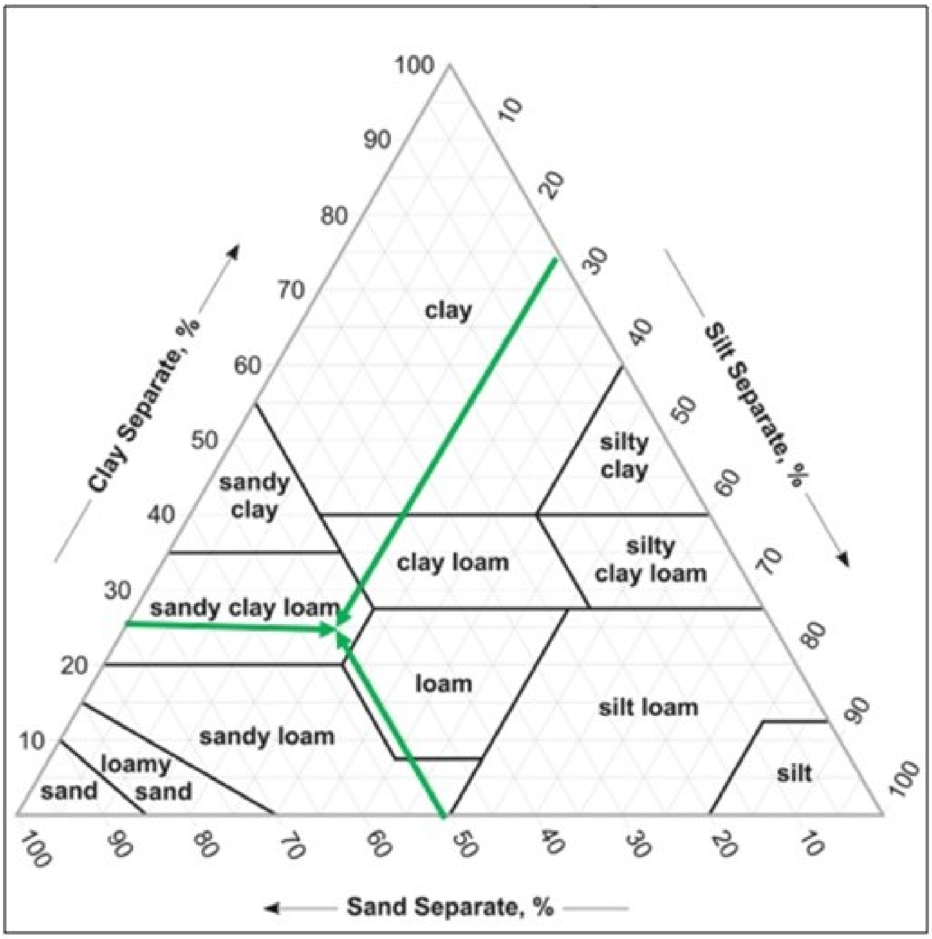


Figure 6.2: Textural triangle showing the percentages of sand, silt and clay in 12 textural classes

[The intersection of the green colour arrows shows that a soil with 50% sand, 25% clay and 25% silt separate, has a sandy clay loam texture (Adapted from USDA-NRCS, 1999)]

Table 6.4: Texture analysis of surface and sub-surface soils in Njeliamparamba

Sl. No	Sample code	Depth (cm)	Sand (%)	Clay (%)	Silt (%)	Soil type
1	NP- 1	(0-30)	81.0	13.25	7.75	Sandy Loam
2		(30-60)	80.75	18.0	1.25	Sandy Loam
3	NP- 2	(0-30)	46.50	34.50	19.0	Clay Loam
4		(30-60)	45.0	35.50	19.50	Clay Loam
5	NP- 3	(0-30)	81.25	10.0	8.75	Sandy Loam
6		(30-60)	80.0	11.0	9.0	Sandy Loam
7	NP- 4	(0-30)	47.0	25.0	28.0	Loam
8		(30-60)	45.0	26.0	29.0	Loam
9	NP- 5	(0-30)	46.50	34.50	19.0	Clay Loam
10		(30-60)	45.0	35.50	19.50	Clay Loam
11	NP- 6	(0-30)	81.0	13.25	7.75	Sandy Loam
12		(30-60)	80.75	18.0	1.25	Sandy Loam
13	NP- 7	(0-30)	46.50	34.0	19.50	Clay Loam
14		(30-60)	45.50	35.0	19.50	Clay Loam
15	NP- 8	(0-30)	81.0	10.0	9.0	Sandy loam
16		(30-60)	80.25	11.50	8.25	Sandy loam
17	NP- 9	(0-30)	80.25	14.0	5.75	Sandy Loam
18		(30-60)	80. 0	15.50	4.50	Sandy Loam
19	NP- 10	(0-30)	81.25	10.0	8.75	Sandy loam
20		(30-60)	80.0	11.25	8.75	Sandy loam
21	NP-11	(0-30)	45.0	35.0	20.0	Clay Loam
22		(30-60)	44.0	37.0	19.0	Clay Loam
23	NP- 12	(0-30)	81.25	10.0	8.75	Sandy Loam
24		(30-60)	80.0	11.0	9.0	Sandy Loam
25	NP- 13	(0-30)	80.75	15.25	4.0	Sandy Loam
26		(30-60)	79.50	19.0	1.50	Sandy Loam
27	NP- 14	(0-30)	80.0	12.0	8.0	Sandy Loam
28		(30-60)	66.50	26.0	7.50	Sandy clay loam
29	NP- 15	(0-30)	80.0	12.25	7.75	Sandy Loam
30		(30-60)	79.0	16.0	5.00	Sandy Loam
31	NP- 16	(0-30)	82.0	13.50	4.50	Sandy Loam
32		(30-60)	79.0	17.0	4.0	Sandy Loam

Table 6.5: Texture analysis of surface and sub-surface soils in Njeliamparamba

Sl.No	Sample code	Depth (cm)	Sand (%)	Clay (%)	Silt (%)	Soil type
33	NP- 17	(0-30)	82.0	13. 0	5.0	Sandy Loam
34		(30-60)	81.50	12.75	5.75	Sandy Loam
35	NP- 18	(0-30)	45.0	35.0	20.0	Clay Loam
36		(30-60)	44.0	37.0	19.0	Clay Loam
37	NP- 19	(0-30)	80.25	15.50	4.25	Sandy Loam
38		(30-60)	79.50	16.0	4.50	Sandy Loam
39	NP- 20	(0-30)	80.75	16.50	4.75	Sandy Loam
40		(30-60)	79.0	18.75	2.30	Sandy Loam
41	NP- 21	(0-30)	81.25	10.0	8.75	Sandy Loam
42		(30-60)	80.0	11.0	9.0	Sandy Loam
43	NP- 22	(0-30)	82.0	13.5	4.50	Sandy Loam
44		(30-60)	79.0	17.0	4.0	Sandy Loam
45	NP- 23	(0-30)	81.0	13.25	7.75	Sandy Loam
46		(30-60)	80.75	18.0	1.25	Sandy Loam
47	NP- 24	(0-30)	81.25	10.0	8.75	Sandy Loam
48		(30-60)	80.0	11.25	8.75	Sandy Loam
49	NP- 25	(0-30)	46.50	25.50	28.0	Loam
50		(30-60)	45.0	26.50	28.50	Loam

6.3.3 Pesticide analysis of soil

Soil samples collected from the two depths was subjected to pesticide analysis. The pesticide lindane was detected in two samples and aldrin was detected in three samples collected from 0-30 cm depth. The concentration of aldrin ranged from below detection limit to 14.73µg/Kg. Highest concentration of aldrine was observed at the sampling site NP-5. Lindane was found only in one sample (NP-18) and the concentration ranged from below detection limit to 9.31µg /Kg. The results revealed that the pesticides were only detected in the surface soil samples. Endosulphan, dieldrin, DDE and DDE were not detected in any of the samples. The pesticides lindane and aldrin might have been detected due to the dumping of containers of lindane or aldrin used for household control of pests in the area.

6.3.4 Heavy metal analysis of soil

The concentrations of heavy metal present in the surface and sub-surface soil samples are discussed in Table 6.6 and Table 6.7.

Table 6.6: Concentration of heavy metals in soil samples collected from Njeliamparamba

Sample ID	Depth	Fe (g/kg)	Cu (mg/kg)	Cd (mg/kg)	Ni (mg/kg)	Pb (mg/kg)	Zn (mg/kg)	Mn (mg/kg)
NP-1	0-30	48.96	43.95	BDL	42.25	155.08	104.3	241.60
	30-60	28.23	18.95	BDL	27.43	52.08	53.75	103.45
NP-2	0-30	104.81	51.33	BDL	49.13	154.03	78.93	374.30
	30-60	100.49	43.10	BDL	33.90	87.0	79.30	274.30
NP-3	0-30	45.52	38.05	BDL	47.60	143.0	0.57	69.50
	30-60	24.70	30.85	BDL	29.50	65.0	0.29	63.05
NP-4	0-30	40.85	22.60	BDL	28.25	153.60	143.05	175.75
	30-60	32.66	2.45	BDL	8.25	85.0	57.0	100.75
NP-5	0-30	50.11	50.40	BDL	48.25	140.05	140.80	184.0
	30-60	40.85	39.75	BDL	45.75	87.63	131.80	173.75
NP-6	0-30	37.16	32.65	BDL	44.25	160.0	16.65	70.70
	30-60	22.60	33.38	BDL	1.45	55.0	14.80	34.25
NP-7	0-30	77.16	59.30	BDL	47.87	90.22	83.03	51.65
	30-60	47.42	40.42	BDL	28.52	48.75	70.42	31.70
NP-8	0-30	91.33	24.62	BDL	8.95	96.02	65.25	150.27
	30-60	50.17	14.27	BDL	6.95	44.0	48.88	125.12
NP-9	0-30	57.41	17.25	BDL	42.10	59.20	61.40	83.45
	30-60	40.58	33.55	BDL	19.15	48.40	41.12	44.80
NP-10	0-30	94.33	53.20	BDL	39.65	104.67	122.22	189.27
	30-60	40.97	40.50	BDL	25.42	56.02	65.25	140.27
NP-11	0-30	77.85	46.70	BDL	44.25	333.25	63.48	276.53
	30-60	43.37	36.83	BDL	44.30	131.10	58.60	200.68
NP-12	0-30	37.87	42.48	BDL	27.15	167.0	47.05	46.25
	30-60	30.07	33.98	BDL	18.40	78.0	33.80	33.75
NP-13	0-30	23.02	18.95	BDL	33.25	178.0	4.60	25.0
	30-60	11.96	BDL	BDL	5.75	98.0	BDL	13.50
NP-14	0-30	20.16	31.83	BDL	42.58	162.70	94.78	31.83
	30-60	14.13	18.88	BDL	20.75	99.68	60.10	18.88
NP-15	0-30	30.53	18.65	5.50	28.78	105.68	37.68	250.23
	30-60	21.37	12.73	3.0	7.88	65.40	31.53	176.53
NP-16	0-30	36.56	17.95	5.0	34.25	172.35	48.65	64.50
	30-60	28.63	12.08	4.10	28.48	98.93	32.45	37.35
NP-17	0-30	18.02	35.88	BDL	40.13	153.88	81.48	35.88
	30-60	17.08	12.40	BDL	0.40	102.43	35.0	12.40
NP-18	0-30	24.31	60.75	9.55	49.40	520.45	168.0	168.05
	30-60	22.14	53.20	4.25	32.88	275.15	80.38	43.63
NP-19	0-30	45.01	21.08	BDL	19.70	170.0	95.38	21.08
	30-60	42.96	5.98	BDL	5.48	95.0	72.58	15.98

BDL- Below Detection Limit

Table 6.7: Concentration of heavy metals in soil samples collected from Njeliamparamba

Sample ID	Depth	Fe (g/kg)	Cu (mg/kg)	Cd (mg/kg)	Ni (mg/kg)	Pb (mg/kg)	Zn (mg/kg)	Mn (mg/kg)
NP-20	0-30	15.70	7.50	BDL	BDL	66.0	26.50	17.40
	30-60	3.54	6.35	BDL	BDL	BDL	1.20	7.10
NP-21	0-30	95.95	29.15	BDL	30.90	45.0	50.90	61.25
	30-60	47.79	26.65	BDL	33.30	BDL	39.20	51.50
NP-22	0-30	53.28	26.25	1.50	44.30	44.53	60.15	189.05
	30-60	43.89	24.60	BDL	39.38	10.10	52.85	111.92
NP-23	0-30	67.74	22.95	BDL	33.25	56.0	57.15	394.70
	30-60	44.20	27.85	BDL	24.0	34.0	50.25	236.30
NP-24	0-30	17.65	0.70	BDL	20.0	67.0	12.60	48.50
	30-60	15.04	0.20	BDL	18.0	22.0	48.60	32.67
NP-25	0-30	66.66	43.58	2.13	14.35	28.33	93.95	88.50
	30-60	53.47	24.66	BDL	BDL	23.08	47.72	73.33

The concentration of heavy metals varied among different sampling stations. The heavy metals such as Fe, Cu, Ni, Pb and Zn were detected in all the analysed soil samples. The concentrations of Fe, Cu, Cd, Ni, Pb, Zn and Mn ranged from 3.54 to 104.81g/kg, 0.20 to 60.75mg/kg, BDL to 9.55mg/kg, 0.40 to 49.40, 10.10 to 520.45mg/kg, 0.29 to 168.0mg/kg and 7.10 to 394.70mg/kg with the mean values of 42.93g/kg, 28.80mg/kg, 4.38mg/kg, 29.06mg/kg, 108.50mg/kg, 60.52mg/kg and 109.32mg/kg, respectively. Based on the average concentration, the heavy metal concentration in the collected soil sample was found to vary in the order of Fe >Mn > Pb >Zn>Ni >Cu> Cd. The highest concentrations of Cu, Cd, Ni, Zn and Pb were detected at the surface sampling station of NP-18. Lead was present in all the analysed soil samples, in which fourteen samples had the Pb concentration above the desirable limit of 140.0mg/kg. Cadmium was present in eight soil samples and the Cd concentration was found to be below the CCME limit of 10.0mg/kg.

6.3.5 Comparison with different world soils

The average metal concentrations found in this study were compared with values reported from other similar studies. This method is generally used as quick and practical method for tracing heavy metal enrichment (Harikumar et al., 2009). The maximum and minimum concentration of heavy metals in the soils of Njeliamparamba were compared with other world soil collected in the vicinity of landfill site and relevant standards proposed by the Canadian Council of Ministers of the Environment soil quality guidelines (CCME, 2007) are given in Table 6.8. The results indicated that the concentrations of heavy metals like Cu, Cd, Ni, Pb and Zn are close to, or even higher than those measured values in the Tunisia, Morocco, Greek and the Ethiopian soils near landfills. The comparison study with different soils revealed that the higher concentrations of all the analysed heavy metals except Pb were obtained in the soils of Greek than all other compared soils. As per the references, soils from Ethiopia reported maximum concentration of lead. Also, the maximum concentration of heavy metals in the soils of Njeliamparamba is close to, or even higher than the soil quality guidelines proposed by the Canadian Council of Ministers of the Environment.

Table 6.8: Comparison of heavy metal concentrations in soils of Njeliamparamba with similar studies reported from soils of other parts of the world soil (collected in the vicinity of landfill site) and CCME soil quality standards

Heavy metals	**Range of heavy metals (Present study)**	**Range of heavy metals (Tunisia[a])**	**Range of heavy metals (Morocc[b])**	**Range of heavy metals (Greek[c])**	**Range of heavy metals (Ethiopia[d])**	**CCME (2007)**
Fe (g/kg)	3.54-104.81	-	-	-	-	-
Cu (mg/kg)	BDL-60.75	0.10–1.70	1.0–11.50	8.13–356.25	-	63.0
Cd (mg/kg)	BDL-9.55	0.30–1.20	-	0.50-18.75	0.56-5.9 0	10.0
Ni (mg/kg)	BDL-49.40	4.60–390	47.0–62.0	5.63–63.75	3.0-46.0	50.0
Pb (mg/kg)	BDL-520.45	1.80–13.20	62.0–656.0	2.50–92.50	17.0-852.0	140.0
Zn (mg/kg)	BDL-168.0	7.60–76.80	63.0–68.0	6.38–343.75	1.94-131.80	200.0
Mn (mg/kg)	7.10-394.70	-	-	-	-	-

[a]Aydi, 2015; [b] Nhari et al. (2014); [c]Kasassi et al. (2008);[d] Beyene & Banerjee, (2011)

CCME- Canadian Council of Ministers of the Environment, BDL- Below Detection Limit

6.3.6 Assessment of heavy metal contamination in Njeliamparamba soil

6.3.6.1 Contamination Factors, Degree of Contamination, Pollution Load Index

The Contamination Factors (C_f), Degree of Contamination (C_d), Pollution Load Index (PLI) are widely used to evaluate the degree of heavy metal pollution in the soils (Bhuiyan et al. 2010; Aydi, 2015). The summary of calculated C_f, C_d and PLI for the studied metals in the surface and sub-surface soils of Njeliamparamba are listed in Table 6.9 and Table 6.10 and its descriptive statistics are presented in Table 6.11.

Table 6.9: Contamination factor, degree of contamination and PLI of surface soil

Sample ID	C_f					C_d	PLI
	Cu	Cd	Ni	Pb	Zn		
NP-1	0.70	0.0	0.85	1.11	0.52	3.17	0.16
NP-2	0.81	0.0	0.98	1.10	0.39	3.29	0.16
NP-3	0.60	0.0	0.95	1.02	0.0	2.58	0.05
NP-4	0.36	0.0	0.57	1.10	0.72	2.74	0.14
NP-5	0.80	0.0	0.97	1.00	0.70	3.47	0.17
NP-6	0.52	0.0	0.89	1.14	0.08	2.63	0.10
NP-7	0.94	0.0	0.96	0.64	0.42	2.96	0.15
NP-8	0.39	0.0	0.18	0.69	0.33	1.58	0.09
NP-9	0.27	0.0	0.84	0.64	0.31	2.06	0.11
NP-10	0.84	0.0	0.79	0.75	0.61	3.0	0.15
NP-11	0.74	0.0	0.89	2.38	0.32	4.32	0.17
NP-12	0.67	0.0	0.54	1.19	0.24	2.65	0.12
NP-13	0.30	0.0	0.67	1.27	0.02	2.26	0.07
NP-14	0.51	0.0	0.85	1.16	0.47	2.99	0.15
NP-15	0.30	0.55	0.58	0.75	0.19	2.36	0.42
NP-16	0.28	0.50	0.69	1.23	0.24	2.94	0.49
NP-17	0.57	0.0	0.80	1.10	0.41	2.88	0.14
NP-18	0.96	0.96	0.99	3.72	0.84	7.46	1.23
NP-19	0.33	0.0	0.39	1.21	0.48	2.42	0.12

NP-20	0.12	0.0	0.0	0.47	0.13	0.72	0.01
NP-21	0.46	0.0	0.62	0.32	0.25	1.66	0.09
NP-22	0.42	0.15	0.89	0.32	0.30	2.07	0.35
NP-23	0.36	0.0	0.67	0.40	0.29	1.72	0.10
NP-24	0.01	0.0	0.40	0.48	0.06	0.95	0.03
NP-25	0.69	0.21	0.29	0.20	0.47	1.86	0.33

**Values calculated based on the normalizing element, Fe with natural background shale value of 46.70 g/kg* (Harikumar et al., 2009)

Table 6.10: Contamination factor, degree of contamination and PLI of sub-surface soil

	C_f						
Sample ID	**Cu**	**Cd**	**Ni**	**Pb**	**Zn**	C_d	**PLI**
NP-1	0.30	0.0	0.55	0.37	0.27	1.49	0.05
NP-2	0.68	0.0	0.68	0.62	0.40	2.38	0.08
NP-3	0.49	0.0	0.59	0.46	0.0	1.55	0.02
NP-4	0.04	0.0	0.17	0.61	0.29	1.10	0.03
NP-5	0.63	0.0	0.92	0.63	0.66	2.83	0.09
NP-6	0.53	0.0	0.03	0.39	0.07	1.03	0.03
NP-7	0.64	0.0	0.57	0.35	0.35	1.91	0.07
NP-8	0.23	0.0	0.14	0.31	0.24	0.92	0.04
NP-9	0.53	0.0	0.38	0.35	0.21	1.47	0.05
NP-10	0.64	0.0	0.51	0.40	0.33	1.88	0.07
NP-11	0.58	0.0	0.89	0.94	0.29	2.70	0.08
NP-12	0.54	0.0	0.37	0.56	0.17	1.63	0.06
NP-13	0.00	0.0	0.12	0.70	0.0	0.82	0.0
NP-14	0.30	0.0	0.42	0.71	0.30	1.73	0.06
NP-15	0.20	0.30	0.16	0.47	0.16	1.28	0.23
NP-16	0.19	0.41	0.57	0.71	0.16	2.04	0.35
NP-17	0.20	0.0	0.01	0.73	0.18	1.11	0.02
NP-18	0.84	0.43	0.66	1.97	0.40	4.29	0.71
NP-19	0.09	0.0	0.11	0.68	0.36	1.25	0.04
NP-20	0.10	0.0	0.0	0.0	0.01	0.11	0.0
NP-21	0.42	0.0	0.67	0.0	0.20	1.29	0.0
NP-22	0.39	0.0	0.79	0.07	0.26	1.51	0.04
NP-23	0.44	0.0	0.48	0.24	0.25	1.42	0.05
NP-24	0.0	0.0	0.36	0.16	0.24	0.76	0.02
NP-25	0.39	0.0	0.0	0.16	0.24	0.79	0.0

**Values calculated based on the normalizing element, Fe with natural background shale value of 46.70 g/kg* (Harikumar et al., 2009)

The mean C_f values for the metals in the surface soils followed the decreasing order of Pb(1.02)> Ni(0.69)> Cu(0.52)> Zn(0.35) >Cd (0.09) and demonstrated low contamination levels except Pb. The mean CF value for Pb (1.02) is relatively high in the samples studied, indicating that the surface soils are polluted by this metal. The degree of contamination was maximum at the sampling site NP 18(C_d=7.46), which showed moderate degree of contamination. On the basis of C_f value for each site, the sampling stations in Njeliamparamba were contaminated in moderate rate for Pb at14 sites, and considerable rate for Pb in one sample. The degree of contamination indicates moderate and Pb contributed mostly to the degree of contamination index of the study area and the remaining metals negligibly influenced the contamination in the study area. The mean C_f values for the metals in the sub-surface soils followed the decreasing order of Pb(0.50)> Ni(0.40)> Cu(0.38)> Zn(0.24) >Cd (0.05) and demonstrated low contamination.

The values of PLI were found to be low in all the studied samples except the sample NP-18 and varied between 0.01 and 1.23 for surface soils and 0.0 to 0.71 for sub-surface soils, indicating that the studied stations are in low pollution status (except one sample) considering the total of the studied metals. The maximum values of C_f, C_d and PLI were obtained for the surface soils compared to sub-surface soils.

Table 6.11: Descriptive statistics of contamination factor, degree of contamination and pollution load index for surface and sub-surface soils

	C^i_f for different metals					C_d	PLI
	Cu	Cd	Ni	Pb	Zn		
Maximum ^{a}	0.96	0.96	0.99	3.72	0.84	7.46	1.23
Minimum^a	0.01	0.0	0.0	0.20	0.0	0.72	0.01
Mean^a	0.52	0.09	0.69	1.02	0.35	2.67	0.20
Standard deviation^a	0.25	0.23	0.27	0.74	0.22	1.29	0.24
Maximum^b	0.84	0.43	0.92	1.97	0.66	4.29	0.71
Minimum ^{b}	0.0	0.0	0.0	0.0	0.0	0.11	0.0
Mean ^{b}	0.38	0.05	0.40	0.50	0.24	1.57	0.09
Standard deviation ^{b}	0.24	0.13	0.29	0.39	0.14	0.84	0.15

Letters “a” and “b” identify surface and subsurface soils

6.3.6.2 Enrichment Factor (EF)

The enrichment factor values for selected metals at surface and sub-surface soil sampling sites are listed in Table 6.12 and Table 6.13 and descriptive statistics of calculated enrichment factors are given in Table 6.14. Figure 6.3 and Figure 6.4 shows the variation of mean enrichment factors calculated for surface and sub-surface soils.

Table 6.12: Enrichment factors calculated for surface soils

	Enrichment factors				
Sample ID	**Cu**	**Cd**	**Ni**	**Pb**	**Zn**
NP-1	0.67	0.0	0.81	1.06	0.50
NP-2	0.36	0.0	0.44	0.49	0.18
NP-3	0.62	0.0	0.98	1.05	0.0
NP-4	0.41	0.0	0.65	1.25	0.82
NP-5	0.75	0.0	0.90	0.93	0.66
NP-6	0.65	0.0	1.11	1.44	0.10
NP-7	0.57	0.0	0.58	0.39	0.25
NP-8	0.20	0.0	0.09	0.20	0.17
NP-9	0.22	0.0	0.68	0.34	0.25
NP-10	0.42	0.0	0.39	0.23	0.30
NP-11	0.44	0.0	0.53	1.43	0.19
NP-12	0.83	0.0	0.67	1.47	0.29
NP-13	0.61	0.0	1.35	2.58	0.05
NP-14	1.17	0.0	1.97	2.69	1.10
NP-15	0.45	0.84	0.88	1.15	0.29
NP-16	0.36	0.64	0.87	1.57	0.31
NP-17	1.48	0.0	2.08	2.85	1.06
NP-18	1.85	1.83	1.90	7.14	1.61
NP-19	0.35	0.0	0.41	1.26	0.49
NP-20	0.35	0.0	0.0	1.40	0.39
NP-21	0.23	0.0	0.30	0.16	0.12
NP-22	0.37	0.13	0.78	0.28	0.26
NP-23	0.25	0.0	0.46	0.28	0.20
NP-24	0.03	0.0	1.06	1.27	0.17
NP-25	0.48	0.15	0.20	0.14	0.33

**Values calculated based on the normalizing element, Fe with natural background shale value of 46.70 g/kg* (Harikumar et al., 2009)

The EF values for Cu, Cd, Ni and Zn <2 showed deficiency to mineral enrichment while Pb also showed significant and moderate enrichment based on Sutherland (2000) classification. The EF values calculated for Pb indicated that the soils of Njeliamparamba can be considered as significant enrichment for surface sampling station of NP-18 (EF=7.14) and moderate enrichment for six sampling stations.

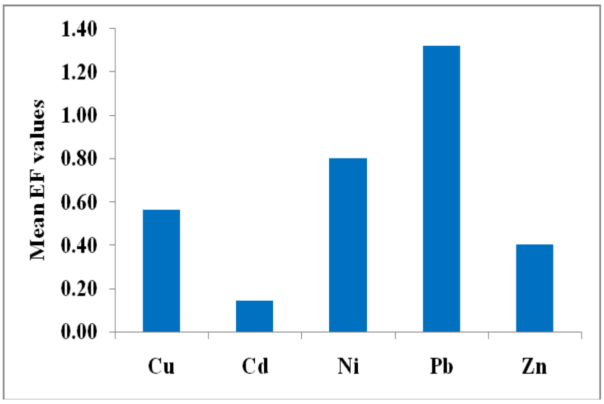


Figure 6.3: Variation of mean enrichment factor calculated for surface soils

Table 6.13: Enrichment factors calculated for sub-surface soils

	Enrichment factors				
Sample ID	**Cu, EF**	**Cd, EF**	**Ni, EF**	**Pb, EF**	**Zn, EF**
NP-1	0.50	0.0	0.91	0.62	0.44
NP-2	0.32	0.0	0.32	0.29	0.18
NP-3	0.93	0.0	1.12	0.88	0.0
NP-4	0.06	0.0	0.24	0.87	0.41
NP-5	0.72	0.0	1.05	0.72	0.75
NP-6	1.09	0.0	0.06	0.81	0.15
NP-7	0.63	0.0	0.56	0.34	0.35
NP-8	0.21	0.0	0.13	0.29	0.23
NP-9	0.61	0.0	0.44	0.40	0.24
NP-10	0.73	0.0	0.58	0.46	0.37
NP-11	0.63	0.0	0.95	1.01	0.32
NP-12	0.84	0.0	0.57	0.87	0.26
NP-13	0.0	0.0	0.45	2.73	0.0
NP-14	0.99	0.0	1.37	2.35	0.99
NP-15	0.44	0.66	0.34	1.02	0.34
NP-16	0.31	0.67	0.93	1.15	0.26
NP-17	0.54	0.0	0.02	2.00	0.48
NP-18	1.78	0.90	1.39	4.15	0.85
NP-19	0.10	0.0	0.12	0.74	0.39
NP-20	1.33	0.0	0.0	0.0	0.08
NP-21	0.41	0.0	0.65	0.0	0.19
NP-22	0.42	0.0	0.84	0.08	0.28
NP-23	0.47	0.0	0.51	0.26	0.27
NP-24	0.01	0.0	1.12	0.49	0.75
NP-25	0.34	0.0	0.0	0.14	0.21

**Values calculated based on the normalizing element, Fe with natural background shale value of 46.70 g/kg* (Harikumar et al., 2009)

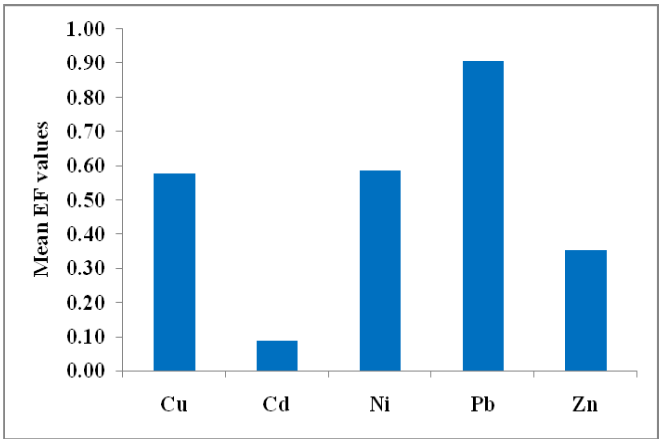


Figure 6.4: Variation of mean enrichment factor calculated sub-surface soils

Table 6.14: Descriptive statistics of enrichment factors calculated for the analysed metals

	Enrichment Factors				
Heavy metals	**Cu**	**Cd**	**Ni**	**Pb**	**Zn**
Maximum[a]	1.85	1.83	2.08	7.14	1.61
Minimum[a]	0.03	BDL	BDL	0.14	BDL
Mean[a]	0.56	0.14	0.80	1.32	0.40
Standard deviation[a]	0.41	0.41	0.55	1.44	0.38
Maximum[b]	1.78	0.90	1.39	4.15	0.99
Minimum[b]	0.0	0.0	0.0	0.0	0.0
Mean[b]	0.58	0.09	0.59	0.91	0.35
Standard deviation[b]	0.42	0.25	0.43	0.97	0.25

Letters "a" and "b" identify surface and subsurface soils

6.3.7 Correlation analysis of heavy metals with physico-chemical parameters of the soil samples of Njeliamparamba

The correlation coefficient matrix of soil heavy metals and physico-chemical properties such as p^H, OM, sand, clay, silt and CEC of the soil collected from the two depths are shown in Table 6.15. The pH of the surface and sub-surface soil samples showed positive correlation to all the analysed heavy metals except lead. The correlation analysis of heavy metals in the surface soil reveals that Fe shows marked positive correlation with Cu (r=0.357), Ni(r= 0.353), Zn(r= 0.314), Mn(r=0.350), Pb(r=0.125) and negative correlation to Cd(r=-0.088). Copper also shows marked positive correlation with Ni (r=0.460), Pb (r=0.317), Zn(r=0.450) and small positive correlation to Mn (r=0.173) &Cd(r=0.027). Similarly, marked positive correlation were also observed between Nickel with Fe(r=0.353), Cu(r=0.460); and Zn with Fe (r=0.314), Cu(r=0.450), Ni(r=0.262) and Mn with Fe(r=0.350), Ni(r=0.222), Zn (r=0.275) and Cu(r=0.172).

The correlation analysis of heavy metals in the sub-surface soil revealed that the marked positive correlation exist between Iron verses Cu (r=0.297), Cd (r=0.206), Ni (r=0.265), Pb (r=0.253), Zn (r=0.282), and Mn (r=0.233). Copper also showed marked positive correlation to metals such as Zn (r=0.546), Ni (r=0.417), Pb (r=0.353), Mn (r=0.354) and small positive correlation to Cd(r=0.009). Similarly, lead showed marked positive correlation to Fe (r=0.0.253), Cu (r=0.353), Cd (r=0.452) and Ni (r=0.042). Cadmium present in the sample was positively correlated with all the metals except Mn (r=-0.069). Zinc and manganese showed marked positive correlation was to all the analysed metals except Cd. These positive correlations indicate that the heavy metals in the soils possibly originated from the same pollutant sources. Close association of these metals confirm their identical source or common sink in the soils (Rafiei et al., 2010). Cadmium is negatively correlated to all the heavy metals except Pb, suggesting its independent variations in the soils.

Table 6.15: Pearson's correlation coefficients for analysed heavy metals with physico-chemical characteristics in the soil samples of Njeliamparamba landfill

	Fe^a	Cu^a	Cd^a	Ni^a	Pb^a	Zn^a	Mn^a	pH^a	OM^a	Sand^a	Clay^a	Silt^a	CEC^a
Fe^a	1.000												
Cu^a	0.357	1.000											
Cd^a	-0.088	0.027	1.000										
Ni^a	0.353	0.460	-0.067	1.000									
Pb^a	0.125	0.317	0.361	0.036	1.000								
Zn^a	0.314	0.450	-0.018	0.262	0.193	1.000							
Mn^a	0.350	0.173	-0.101	0.222	0.007	0.275	1.000						
pH^a	0.315	0.234	0.135	0.564	-0.154	0.094	0.273	1.000					
OM^a	-0.028	0.335	0.478	0.193	0.696	0.311	0.233	0.231	1.000				
Sand^a	-0.206	-0.417	-0.224	-0.361	-0.507	-0.073	-0.066	-0.250	-0.502	1.000			
Clay^a	0.260	0.429	0.249	0.419	0.518	0.048	0.100	0.254	0.527	-0.980	1.000		
Silt^a	-0.067	0.215	0.051	0.014	0.273	0.134	-0.082	0.141	0.222	-0.691	0.532	1.000	
CEC^a	0.050	0.366	0.508	0.216	0.703	0.337	0.140	0.229	0.915	-0.665	0.691	0.415	1.000
	Fe^b	Cu^b	Cd^b	Ni^b	Pb^b	Zn^b	Mn^b	pH^b	OM^b	Sand^b	Clay^b	Silt^b	CEC^b
Fe^b	1.000												
Cu^b	0.297	1.000											
Cd^b	0.206	0.009	1.000										
Ni^b	0.265	0.417	0.075	1.000									
Pb^b	0.253	0.353	0.452	0.042	1.000								
Zn^b	0.282	0.546	0.001	0.186	0.263	1.000							
Mn^b	0.233	0.354	-0.069	0.422	0.085	0.352	1.000						
pH^b	0.207	0.176	0.258	0.162	-0.019	0.294	0.019	1.000					
OM^b	-0.040	0.468	0.050	0.343	0.365	0.494	0.488	-0.006	1.000				
Sand^b	0.055	-0.347	0.109	-0.417	-0.178	0.059	-0.309	-0.001	-0.366	1.000			
Clay^b	-0.046	0.355	-0.190	0.417	0.195	-0.041	0.300	-0.040	0.363	-0.966	1.000		
Silt^b	-0.058	0.156	0.185	0.208	0.036	-0.085	0.186	0.126	0.197	-0.615	0.390	1.000	
CEC^b	-0.013	0.424	-0.049	0.367	0.208	0.236	0.453	0.091	0.784	-0.673	0.624	0.496	1.000

Letters "a" and "b" after the physic-chemical parameters identify surface (0-30 cm) and subsurface (30-60 cm) soil

Organic matter was positively correlated to all analysed metal content except Fe. Organic matter of the samples also showed significant positive correlation to CEC (for surface soil (r=0.915) (for sub-surface soil r=0.784). Humic materials have high adsorption influence on heavy metals (Sany et al., 2013). CEC of surface soil samples showed positive correlation with clay (r=0.691), organic matter (r=0.915) and silt (r= 0.415) and negatively correlated to sand (r=-0.621). The correlation analysis reveals that the formation of organic complexes with heavy metals as a ligand. Increase in soil organic content can lead to elevate the soil adsorption capacity. Negative correlations of sand with all the analysed heavy metals for samples collected from both the depths indicates that lack of these active sites needed for adsorbing these metals. The positive correlation occurred between clay content with heavy metals possibly reflecting the role of clay minerals in the adsorption of heavy metals. Some other positive correlations were also obtained for CEC with p^H and all the heavy metals.

6.3.8 Principle component analysis

The principal component analysis applied to all the heavy metal concentrations for the surface samples resulted mainly in to two principal components. Two factor components (eigen values>1) emerged accounting for 52.69% of cumulative variance. PC1 explained 33.35% of the variation in the data and represented strong contributions by the metals such as Fe, Cu, Ni, Zn and Mn Additionally, this component showed moderate positive contributions by Pb and negative contribution to Cd. Eigen values accounts that PC1 is the most significant components which represent 33.35% of the total variance in soil quality of Njeliamparamba. PC2 explained 21.34% of the variation in the data and represented strong contributions by the variables Cd and Pb, moderate contribution to Cu & Zn and negative contribution by Fe, Ni and Mn. The significant correlations of this metals indicated that these are discharged simultaneously and have a similar behaviour. Table 6.16 and Figure 6.17 represent the component loadings of different components and its percentages of variance. Figure 6.5 and Figure 6.6 shows the scree plot and factor loading plot for the sub-surface soils.

Table 6.16: Component loadings of heavy metals for sub-surface soils

	Component loadings	
Heavy metals	**PC 1**	**PC 2**
Fe	0.672	-0.334
Cu	0.771	0.256
Cd	-0.051	0.738
Ni	0.678	-0.096
Pb	0.228	0.825
Zn	0.696	0.119
Mn	0.537	-0.263

Table 6.17: Percentage of variance explained by different components

PC 1	**PC 2**
33.351	21.344

The Figure 6.5 and Figure 6.6 indicated all the heavy metals except Cd and Pb showed high positive contributions towards factor 1. The factor 2 showed high positive contributions towards Pb and Cd and small positive contributions towards Cu, Ni, Zn and Mn; negative contribution towards Fe, Ni and Mn.

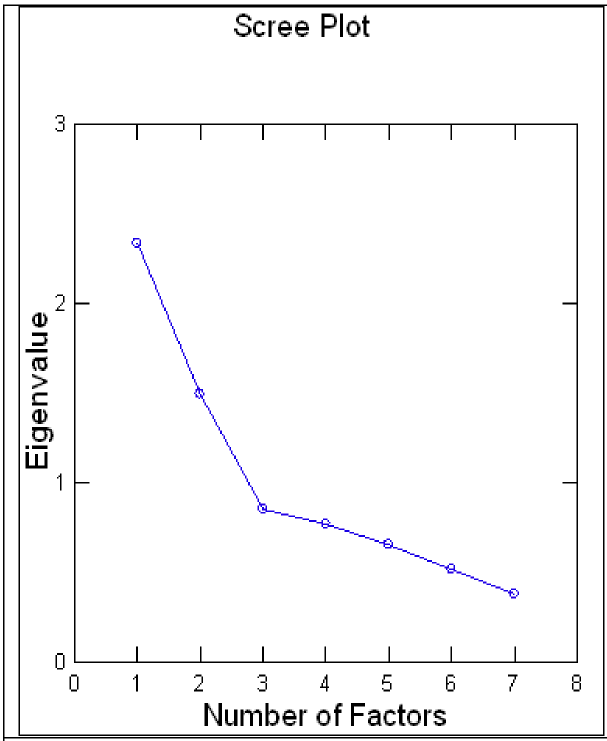


Figure 6.5: Scree polt for surface soil

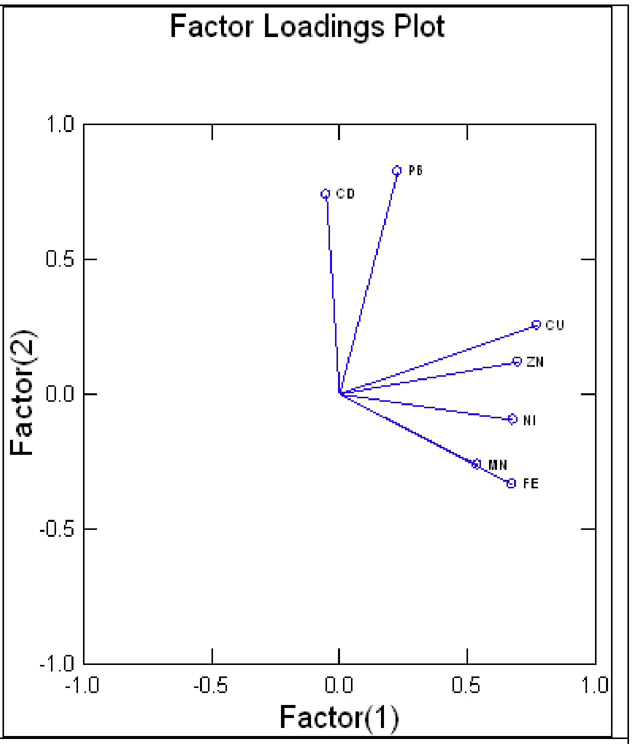


Figure 6.6: Factor polt for surface soil

6.3.9 Available micronutrients in soil

The bioavailability of metal compounds is influenced by the pH, temperature, redox potential, cation exchange capacity of the solid phase, competition with other metal ions, composition and quality of the soil solution (Mapanda et al., 2005). Only a small portion of each nutrients present in the soil is available to plants. Most of it is so firmly locked up in the mineral and organic matter that it is unavailable until decomposition takes place. Soils with low clay and organic matter content may be deficient in one or more micronutrients. Micronutrients are harmful when the available forms are present in the soil in larger amounts. Table 6.18 and Table 6.19 show the concentration of available metals in the soils collected from the two depths.

Table 6.18: Concentrations of available metals in soil samples of Njeliamparamba

Sl.No	**Sample ID**	**Depth (cm)**	**Fe (mg/kg)**	**Mn (mg/kg)**	**Cu (mg/kg)**	**Zn (mg/kg)**
1	NP- 01	0-30	10.25	1.88	1.82	3.42
2		30-60	10.05	1.79	1.14	2.44
3	NP-02	0-30	51.35	17.69	2.43	4.61
4		30-60	38.07	11.98	1.26	3.15
5	NP-03	0-30	97.77	22.24	3.44	8.55
6		30-60	78.08	18.06	2.69	4.13
7	NP-04	0-30	80.42	4.31	30.85	28.28
8		30-60	79.83	1.27	18.86	16.02
9	NP-05	0-30	84.51	6.13	1.57	24.54
10		30-60	68.96	1.24	1.32	4.58
11	NP- 06	0-30	75.19	19.87	6.24	13.45
12		30-60	65.69	1.57	4.32	2.01
13	NP-07	0-30	92.18	3.26	2.41	9.40
14		30-60	77.28	2.42	1.48	8.87
15	NP-08	0-30	68.02	25.75	10.67	21.80
16		30-60	34.43	1.89	8.27	9.46
17	NP-09	0-30	75.06	32.97	6.39	31.50
18		30-60	58.02	4.10	2.45	22.33
19	NP- 10	0-30	51.3	30.5	7.28	32.11
20		30-60	26.04	3.05	5.13	10.63
21	NP-11	0-30	57.55	24.57	33.56	31.48
22		30-60	53.69	22.96	1.65	24.47
23	NP-12	0-30	56.35	17.95	43.41	36.13
24		30-60	39.08	16.35	13.82	32.18
25	NP-13	0-30	62.12	17.06	6.45	14.94
26		30-60	25.54	4.04	1.36	9.20
27	NP-14	0-30	55.67	18.26	5.76	11.15
28		30-60	40.47	16.51	3.65	7.70
29	NP-15	0-30	88.96	22.16	7.63	32.30
		30-60	67.80	18.42	1.25	9.95

Table 6.19: Concentrations of available metals in soil samples of Njeliamparamba

Sl.No	Sample ID	Depth (cm)	Fe (mg/kg)	Mn (mg/kg)	Cu (mg/kg)	Zn (mg/kg)
31	NP-16	0-30	58.66	6.40	5.65	12.56
32		30-60	42.71	1.37	5.24	7.38
33	NP-17	0-30	76.24	39.76	7.52	22.98
34		30-60	59.36	18.21	5.36	21.53
35	NP-18	0-30	56.9	7.11	13.11	15.53
36		30-60	46.2	3.36	9.11	9.58
37	NP-19	0-30	61.81	21.59	10.03	15.57
38		30-60	48.65	7.37	6.39	8.82
39	NP-20	0-30	88.09	3.56	8.87	8.29
40		30-60	82.92	3.34	5.44	5.24
41	NP- 21	0-30	89.67	15.83	12.24	34.87
42		30-60	62.99	12.81	8.64	12.16
43	NP-22	0-30	47.58	14.13	5.34	22.82
44		30-60	31.51	5.92	4.95	7.18
45	NP-23	0-30	31.9	22.46	38.07	29.12
46		30-60	50.28	22.37	37.38	28.78
47	NP-24	0-30	56.32	26.66	11.55	35.77
48		30-60	53.93	75.55	9.87	39.89
49	NP-25	0-30	54.88	31.02	5.67	36.05
50		30-60	22.67	2.84	4.97	4.70

The results of the concentrations of available metals in the soil samples were found to be high concentrations for iron, copper, zinc and manganese. The range and mean values of micronutrients are presented in Table 6.20 and the critical level of micronutrients in soil is given in Table 6.21. By comparing the extractable micronutrients (Fe, Cu, Zn and Mn) contents with the accepted criteria revealed that all the analysed soil samples were found to be higher concentration. Accumulation of micro nutrients is higher in the top soil than the substratum, where OC percentage is higher. The concentrations of available metals such as Fe, Mn, Cu and Zn ranges from 10.05mg/kg to 97.80mg/kg, 1.24mg/kg to 75.55mg/kg, 1.14mg/kg to 43.4mg/kg and 2.01mg/kg to 39.89mg/kg, respectively in soils which exceeds the critical limits.

Table 6.20: Minimum - maximum concentrations and mean values of micronutrients

Parameters(mg/kg)	Minimum-Maximum	Mean
Fe	10.05 to 97.77	57.0
Mn	1.24 to 75.55	14.50
Cu	1.14 to 43.41	9.09
Zn	2.01 to 39.89	15.43

Table 6.21: Critical levels of soil micronutrients (Kerala State Planning Board, 2013 adapted)

Micro nutrients	**Deficiency**	**Sufficiency**
Fe (*HCl)	<5.0 mg/kg	≥5.0 mg/kg
Fe (**DTPA)	<5.0 mg/kg	≥5.0 mg/kg
Mn(*HCl)	<1.0 mg/kg	≥1.0 mg/kg
Mn (**DTPA)	<1.0 mg/kg	≥1.0 mg/kg
Cu(*HCl)	< 1.0 mg/kg	≥1.0 mg/kg
Cu(**DTPA)	< 0.12 mg/kg	≥0.12 mg/kg
Zn(*HCl)	< 1.0 mg/kg	≥1.0 mg/kg
Zn (**DTPA)	<0.6 mg/kg	≥0.6 mg/kg

**0.1 N HCl for acid soil, **DTPA for neutral to alkaline soils*

6.3.9.1 Correlation of available micronutrients with physico-chemical characteristics of the soils

Micro nutrients behavior is more or less similar to the heavy metals in soils, therefore, showing an affinity to some basic soil properties such as CEC, OM, clay content and pH. The correlation analysis of physico-chemical properties viz; soil pH, organic matter, sand, clay, silt and CEC with available micronutrients such as Fe, Mn, Cu and Zn were analysed and are presented in Table 6.22. The results revealed that pH of the soils showed significant negative correlation with available Fe (r = - 0.456) non-significant negative correlation with available Mn (r= -0.051), Cu (r= -0.084) and Zn (r= -0.119). Similar results were obtained by Kumar & Babel (2011) and Bhat et al. (2017).The soil organic matter showed positive and significant correlation with available Cu (r = 0.690) and Zn (r = 0.607), but showed non-significant and positive correlation with Fe (r = 0.078) and Mn (r = 0.273). The available Fe, Mn, Cu and Zn showed positive and significant correlation with organic matter and also found to be negatively correlated with pH of soils. Similar results were obtained by Kumar & Babel, 2011; Bhat et al., 2017.The data given in Table 6.22 shows that Cu was positively correlated with organic matter, clay, silt and CEC with (r) value 0.690, 0.401, 0.151 and 0.690 respectively. Accumulation of micro nutrients is high in relation with CEC and clay content. In addition, Fe, Mn, Zn, and Cu have a common character to form chelate with organic matter (Sikder et al., 2016) and OM data shows a significant relationship with the micro nutrients.

Table 6.22: The correlation matrix between micronutrients and some soil properties

Parameters	Fe	Mn	Cu	Zn	pH	OM	Sand	Clay	Silt	CEC
Fe	1									
Mn	0.045	1								
Cu	0.03	-0.012	1							
Zn	0.095	0.152	0.811	1						
pH	-0.456	-0.051	-0.084	-0.119	1					
OM	0.078	0.273	0.69	0.607	0.013	1				
Sand	0.121	-0.028	-0.384	-0.211	-0.179	-0.553	1			
Clay	-0.107	0.053	0.401	0.245	0.184	0.573	-0.978	1		
Silt	-0.117	-0.075	0.151	-0.01	0.079	0.235	-0.637	0.461	1	
CEC	0.003	0.232	0.69	0.557	0.106	0.948	-0.706	0.717	0.353	1

A significant positive correlation between Zn with organic carbon (r = 0.607) and CEC(r= 0.557) indicate that complexing agents generated by organic matter promote zinc availability in soils. The r-value obtained between Zn and clay was 0.245 which indicates that Zn and clay content were positively correlated. The negative correlations were observed between Zn with silt and sand with r value of -0.010 and -0.211 respectively. Non significant positive correlation were observed between Mn with OM(r=0.273), clay(r=0.053) and

CEC(r=0.232) and negatively correlated to sand and silt. Fe was non-significant and positively correlated with OM (r=0.078), sand (r=0.121), CEC(r=0.003) and non-significant negative correlation to clay (r=-0.107) and silt (r=-0.117).

6.3.9.2 Relationship between soil pH and the relative availability of nutrients

Generally, soil pH has a major contribution factors that influences the mobility, bioavailability and leaching capability of heavy metals to plants (Ginocchio et al., 2002; Cheng, 2003; Chimuka et al., 2005, Wang et al., 2006; Adamczyk-Szabela, 2015). Soils with pH values below 7 are very prone to migration of heavy metals from soil solid components into the soil solution, as has been observed for Cu, Mn and Zn (Alam et al., 1999; Zeng et al., 2011; Adamczyk-Szabela et al., 2015). Figure 6.7 shows the relationship between soil p^H and the relative availability of nutrients in soil.

Increasing acidity or alkalinity corresponds to logarithmic increase in concentration of H^+ and OH^- respectively, as shown in vertical bars. Horizontal bars indicate the relative availability or toxicity at any particular pH. The availability of different nutrients at different pH is indicated by the width of the white bar; the wider the bar, the more available is the nutrient. Under alkaline conditions, Fe and Mn are generally present in Fe^{3+} and Mn^{3+} states. Thus in soils with pH 7.5 and above, they become unavailable and occasionally produce deficiency diseases likes chlorosis in plants. In acidic soils with pH<5.5, manganese oxides are simply reduced to Mn^{2+} ions which are available for plants (Adriano, 2001; Watmough et al., 2007; Adamczyk-Szabela, 2015). The soil with high pH (pH>8.0), chemical Mn^{2+} auto-oxidation may lead to the formation of MnO_2, Mn_2O_3, Mn_3O_4, or even Mn_2O_7, which are not easily available to plants (Ducic & Polle, 2005). Additionally, these oxides can readily absorb on soil particles, further decreasing the bioavailability of manganese (Fageria et al., 2002). The availability of Cu and Zn gradually decreases as the soil pH increases and their availability also decreases when the pH is below 5.0. Zn availability in alkaline soils form insoluble zinc salts (calcium zincate) which reduces its availability. Zn and Cu adsorbed on the clay colloids and are not easily displaced and therefore not available for plant growth.

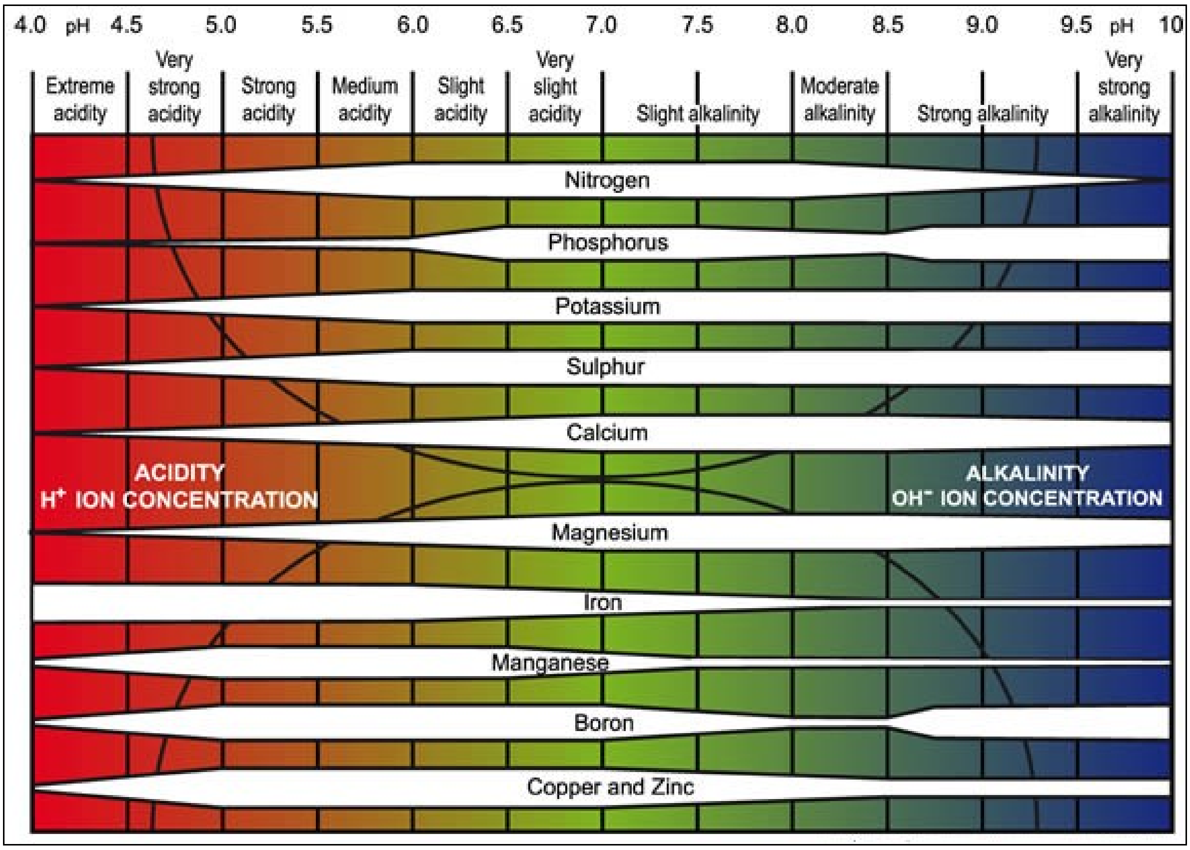


Figure 6.7: The relationship between soil pH and the relative availability of nutrients (Adapted from Truog, 1946)

The results of the present study revealed that the higher concentration of all the available metals analyzed were found to be within a pH range of 5.60 to 6.60 and their availability decreased with increase in pH. In the alkaline condition (above 7.5) all the metals were found to be low.

6.3.10 Cation Exchange Capacity (CEC)

Cation exchange capacity of a soil is the ability to hold or bind exchangeable cations or to assess the number of negatively charged binding sites in soil (Olorunfemi et al., 2016). The CEC of a soil is mostly influenced by soil organic matter and texture. High percentage of clay and organic matter in the soil leads to elevated CEC values because both have large number of negative charges on their surfaces, which attract and hold cations. Among the mineral components of soil, clay particles have the highest CEC value followed by silt and sand.

The higher CEC content in soil possibly indicates more clay, poor internal drainage, limited structure and soil compaction. The soil with low CEC value is an indicative of sandy textured, prone to drought that desires more organic matter to improve water holding capacity but have open grainy structure that resist compaction. The higher the CEC of a soil can also have the ability to retain high amount of metals. The CEC is a general indicator of soil constituents that restraint the solubility and mobility of cationic trace elements in soils. Results of the CEC analysis of the soil samples are discussed in Table 6.23 and Table 6.24.

High cation exchange capacity value (31.97 milli equivalents/100g soil) is observed in the surface soil sample of NP- 18 and low CEC value (1.37 milli equivalents/100g soil) observed in the sub-surface soil sample of NP-03. The sample NP-18 is a clay type soil (45%) and it contains a substantial amount of organic matter (8.28%). 56% of the analysed soil samples were found to be within the CEC range of 3 to 10meq/100g soil, which indicated sandy loam soils.

Table 6.23: Cation exchange capacity of soil samples

Sl.No	Sample ID	Depth (cm)	CEC (meq/100g)
1	NP- 01	(0-30)	2.59
2		(30-60)	1.92
3	NP- 02	(0-30)	16.50
4		(30-60)	6.46
5	NP- 03	(0-30)	2.39
6		(30-60)	1.30
7	NP- 04	(0-30)	10.77
8		(30-60)	4.22
9	NP- 05	(0-30)	15.23
10		(30-60)	7.50
11	NP- 06	(0-30)	5.19
12		(30-60)	2.05
13	NP- 07	(0-30)	12.22
14		(30-60)	7.08
15	NP- 08	(0-30)	10.70
16		(30-60)	5.61
17	NP- 09	(0-30)	6.43
18		(30-60)	2.38
19	NP- 10	(0-30)	3.58
20		(30-60)	1.60
21		(0-30)	13.67
22	NP- 11	(30-60)	7.26
23		(0-30)	16.37
24	NP- 12	(30-60)	10.47
25		(0-30)	11.88
26	NP- 13	(30-60)	4.50
27		(0-30)	11.59
28	NP- 14	(30-60)	5.56
29		(0-30)	4.40
30	NP- 15	(30-60)	6.04
31		(0-30)	16.07
32	NP- 16	(30-60)	4.47
33		(0-30)	8.49
34	NP- 17	(30-60)	7.83
35		(0-30)	31.97
36	NP- 18	(30-60)	28.22

meq/100g -milli equivalents per100g of soil

Table 6.24: Cation exchange capacity of soil samples

Sl.No	Sample ID	Depth	CEC(meq/100g)
37	NP- 19	(0-30)	12.15
38		(30-60)	6.43
39	NP- 20	(0-30)	7.36
40		(30-60)	5.54
41	NP- 21	(0-30)	6.09
42		(30-60)	4.37
43	NP- 22	(0-30)	8.05
44		(30-60)	4.23
45	NP- 23	(0-30)	7.68
46		(30-60)	4.44
47	NP- 24	(0-30)	10.37
48		(30-60)	4.18
49	NP- 25	(0-30)	6.23
50		(30-60)	7.58

meq/100g -milli equivalents per100g of soil

6.4 Summary

Deteriorating soil quality is a grave consequence of MSW dumping which have resulted in growing public concern. One of the objectives of the study was to evaluate the soil quality and assessment of soil contamination at Njelianparamba. The physicochemical characteristics of most of the samples revealed acidic nature and we obtained mainly three types of texture (sandy loam, loam and clay loam). The mean value of the major ions (cations and anions) in soil samples is in the following order: exchangeable calcium>sodium>potassium> magnesium> inorganic phosphorous and sulphate>chloride>alkalinity. The results revealed that the concentrations of all the physico-chemical parameters decrease from surface to sub-surface soil in all the stations, which confirmed the increased anthropogenic activities with time. The monitoring of pesticide residues indicated that out of twenty four sampling sites, only one sample reported the presence of lindane and three samples reported the presence of aldrin.

The heavy metals such as Fe, Cu, Ni, Pb and Zn were detected in all the analysed soil samples and were found to be within the CCME soil quality limit except Pb. The presence of lead indicated the disposal of Pb batteries, Pb based paints and pipes at the landfill site, chemicals for photograph processing. The results of the enrichment factor for surface soils revealed that the most of the soils samples could be considered as deficiency or minimal enrichment for all the studied metals, while the values of Pb demonstrated to have significant enrichment. The results of the contamination factor also demonstrated low contamination levels for Cu, Ni, Zn, Cd and moderate contamination levels for Pb. The pollution load index calculated for each sampling sites were found to be low in all the studied samples except one sampling site which indicates low pollution considering the total of the studied metals. The principal component analysis and correlation study revealed that that, anthropogenic inputs derived from leachate are the contamination sources. The concentrations of available metals in the soils of Njeliamparamba were found to be above the critical limit for micronutients. The maximum concentration of all the available metals was higher in the top soil than the substratum, where percentage of organic matter is higher. 55% of the analysed soil samples were found to be within the CEC range of 3 to 10meq/100g soil.

The results of the study indicated that the samples collected within the buffer zone had more contamination than those collected outside the zone. The site, NP-18 is considered to be more polluted, which is located at the vicinity of a steel factory and also near the discharge point of drainage system coming from Njeliamparamba. The higher contamination might be due to the leachate migration from Njeliamparamba or industrial wastes from number of small and medium scale industries which interact with the soil and thereby enriching metal concentration. The results can also be used as an indicator in the identification of pollution sources and can assist the decision-makers to evaluate the soil pollution status around Njeliamparamba dumping.

JASEELA C.”A STUDY ON THE SOIL AND WATER QUALITY OF SELECTED SITES AROUND SOLID WASTE DUMPING AREAS IN KERALA STATE”. THESIS. CWRDM (CENTRE FOR WATER RESOURCES DEVELOPMENT AND MANAGEMENT), UNIVERSITY OF CALICUT, 2018.

Chapter 7

APPLICATION OF GIS AND DRASTIC MODEL FOR EVALUATION OF GROUNDWATER VULNERABILITY

7.1 Introduction

Groundwater vulnerability is the basis for evaluating the risk of groundwater contamination and to develop a management option to preserve the quality of groundwater. The groundwater vulnerability to contamination is based on the concept that physical environment can provide protection to groundwater against natural and human impacts with respect to contaminants in the groundwater (Prasad & Shukla, 2014). Groundwater vulnerability deals with the hydrogeological parameters which plays an important role in the transport and the transformation of groundwater pollutants. Groundwater vulnerability assessment has become a useful tool for groundwater pollution prevention (Awawdeh & Jaradat, 2010).

The DRASTIC model was developed by the US Environmental Protection Agency, which is an overlay and index method and is one of the most popular standardized methods for evaluating groundwater vulnerability to contamination (Aller et al., 1987). The DRASTIC method in a Geographic

Information System (GIS) environment has been widely used in many countries because the required inputs for its application are easy to use, requirement of minimum data and can explain the groundwater vulnerability (Awawdeh & Jaradat, 2010). It is based on seven hydrogeological parameters which controls the movement of contaminants from the ground surface to the saturated zone (Aller et al., 1987). Groundwater vulnerability maps provide is used to identify areas that are more vulnerable to contamination than others and to give preference to areas to evaluate the potential for water quality improvement. Landfill leachate is considered as the main cause of groundwater contamination in the nearby areas of the dumpsite due to the percolation of leachate (Kale et al., 2010). A number of studies have been reported related to impact of leachate on surrounding groundwater (Kelley, 1976; Kumar & Alappat, 2003; Akinbile & Yusoff, 2011). There is a need for groundwater monitoring around the landfill sites to understand the degree of contamination. The most important hydrogeological factors that affect and control groundwater contamination were incorporated into the DRASTIC model, to produce groundwater vulnerability and risk maps. Geographical Information System was also used to create a groundwater vulnerability map by overlaying the available hydrogeological data.

One of the main objectives of the study was to assess the groundwater vulnerability in the vicinity of a two municipal solid waste disposal sites, Njeliamparamba in Kozhikode district and Laloor in Thrissur district, Kerala, India using DRASTIC model using Geographic Information System environment and to validate the model using real time data collected on water quality from the field.

7.2 Materials and Methods

7.2.1 DRASTIC model

A GARMIN GPS was used to record the latitude and longitude of sampling points which were imported into the GIS platform. The DRASTIC model was used to prepare a vulnerability map for the study area using ArcMap 10.1. Groundwater vulnerability map identifies the region, most potent to groundwater contamination on the basis of hydrogeologic and anthropogenic factors. The map was developed by using Geographic Information System to combine the seven data layers. It is determined by using the weighted sum overlay method under the spatial analyst tool in the ArcMap tool box. The seven hydrogeological raster inputs were compiled in the weighted sum overlay method specifying the weight for each input, which is then processed into the final vulnerability map. The flow chart of methodology for groundwater vulnerability analysis is given in Figure 7.1.

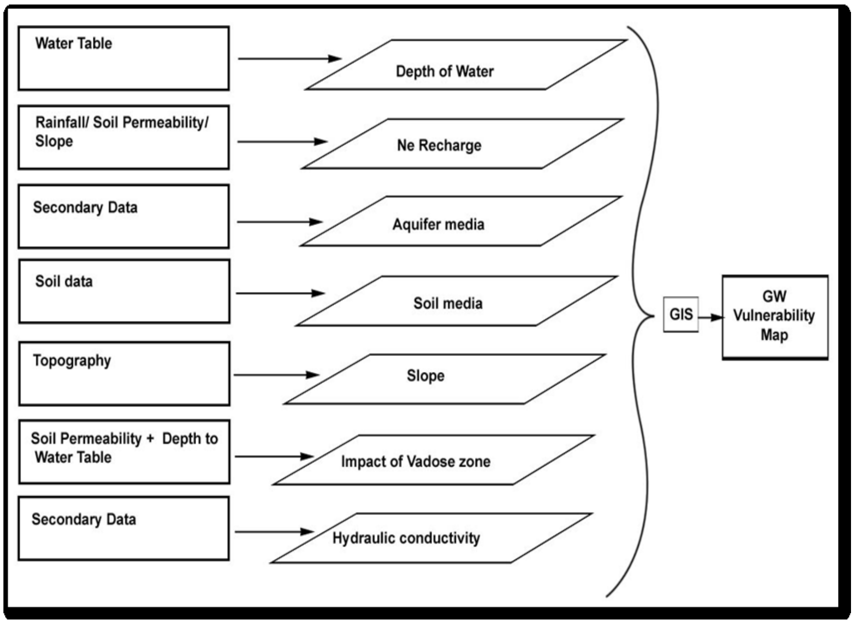


Figure 7.1: Methodology for groundwater vulnerability study (Adapted from Prasad & Shukla, 2014)

The DRASTIC model is based on seven parameters, corresponding to seven layers to be used as input parameters for modelling. The **DRASTIC** model is considered for seven hydrogeological parameters which are **D**epth to water, net **R**echarge, **A**quifer media, **S**oil media, **T**opography, **I**mpact of vadose zone media, and hydraulic **C**onductivity of the aquifer (Aller, 1987). The parameters would be weighted and rated according to their relative susceptibility to the pollutant according to their relative contribution to the potential contamination (USEPA, 1987). DRASTIC assigns that the weights and ratings would be given to each of the seven parameters, each is classified in to classes on the scale of 1-10, in which 1 denotes least vulnerable while 10 is for the most vulnerable areas. This rating would be further scaled into weights based on the importance of the parameter in determining aquifer characteristics, which are scaled from 1 to 5, where, 1 is least significant and 5 is most significant. The DRASTIC vulnerability index can be calculated by linear addition of the weights and rating. The equation for calculating the DRASTIC Index is given in equation (7.1)

$$\text{DRASTIC Index} = \mathrm{DrDw} + \mathrm{RrRw} + \mathrm{ArAw} + \mathrm{SrSw} + \mathrm{TrTw} + \mathrm{IrIw} + \mathrm{CrCw} \qquad (7.1)$$

where *D* the is depth to water table, *R* the net recharge, *A* the aquifer media, *S* the soil media, *T* the topography, *I* the impact of vadose zone, *C* the hydraulic conductivity, *r* is the rating value assigned to units of parameters and *w* is the weight assigned to each parameter.

Table 7.1: Standard assigned ratings and weights for DRASTIC parameters; depth to water, net recharge and aquifer media (USEPA, 1987)

Depth to water		**Net recharge**		**Aquifer media**	**Rating**
Range	**Rating**	**Range**	**Rating**	**Massive Shale**	**2**
0-5	10	0-2	1	Metamorphic/Igneous	3
5-15	9	2-4	3	Weathered Metamorphic/Igneous	4
15-30	7	4-7	6	Glacial Till	5
30-50	5	7-10	8	Bedded Sandstone, limestone and Shale	6
50-75	3	>10	9	Massive sandstone	6
75-100	2			Massive Limestone	6
>100	1			Sand and Gravel	8
				Basalt	9
				Karst Limestone	10
Weight 5		Weight 4		Weight 3	

Table 7.2: Standard assigned ratings and weights for soil media

Soil media	
Range	**Rating**
Thin or absent	10
Gravel	10
Sand	9
Peat	8
Shrinking and /or aggregated	7
Sandy loam	6
Loam	5
Silty loam	4
Clay loam	3
Muck	2
Non shrinking and non	1
Weight 2	

Table 7.3: Standard assigned ratings and weights for soil media

Topography	
Slope	Rating
0-2	110
2-6	9
6-12	5
12-18	3
>18	1
Weight 1	

Table 7.4: Standard assigned ratings and weights for Impact of the vadose zone

Impact of the vadose zone	
Ranging	**Rating**
Confinig layer	1
Silt/clay	3
Shale	3
Limestone	6
Sandstone	6
Bedded limestone, sandstone,	6
Sand and gravel with significant	6
Metamorphic/igneous	4
Sand and gravel	8
Basalt	9
Karst limestone	10
Weight 5	

Table 7.5: Standard assigned ratings and weights for Hydraulic conductivity

Hydraulic conductivity	
Ranges (GPD/ft2)	**Ranges**
1-100	1
100-300	2
300-700	4
700-1000	6
1000-2000	8
>2000	10
Weight 3	

Table 7.6: Standard range and rating for rainfall and soil permeability (Piscopo, 2011)

Rainfall(mm)		**Soil Permeability**	
Range	**Rating**	**Range**	**Rating**
>850	4	High	5
700–850	3	Moderate to high	4
500–700	2	Moderate	3
<500	1	Slow	2
		Very slow	1

7.2.2 Hydrogeological characteristics of Njeliamparamba and Laloor

Hydrogeological characteristics of Njeliamparamba and Laloor area are explained in chapter 4.

7.2.3 Sampling and analysis of Njeliamparamba

Sampling and analysis of the groundwater samples were conducted according to the Standard Methods for Examination of Water and Wastewater (APHA, 2012). A random sampling method was followed to study the impact of solid waste leachate on groundwater quality. A total of 29 sampling sites were randomly chosen with a buffer zone of 1 km radius from the Njeliamparamba landfill site and analysed for its physico-chemical and bacteriological parameters. Out of these sites, 20 groundwater samples were collected within the buffer zone and 9 samples from outside of the zone. To validate the vulnerability map, a total of 29 groundwater samples were collected and analysed for total dissolved solids and *E.coli.* The total dissolved solids was analysed by gravimetric method and the bacteriological analysis was done by the Multiple Tube Dilution technique.

About 25 soil samples were collected, out of which, 19 samples were collected within the buffer zone and 6 samples from outside the buffer zone. These samples were analysed for texture analysis using hydrometer method to determine the soil media map (Baruah & Barthakur, 1997). All the chemicals used in this study were of analytical reagent grade. To ensure standard quality control/quality assurance procedures, replicates were analyzed for each sample.

7.2.4 Sampling and analysis of Laloor

A total number of 20 groundwater samples were collected from the study area and analysed for its physico-chemical and bacteriological parameters.

Sampling and analysis of the groundwater samples were conducted according to the Standard Methods for Examination of Water and Wastewater (APHA, 2012). The characteristics of groundwater samples from Laloor indicated that the nitrate is the major contaminant; therefore the DRASTIC model was validated using the nitrate concentrations. UV- visible spectrophotometer (Thermo, Evolution 201) was used to determine the concentration of nitrate. A total of ten soil samples were collected from different distanced from the study area and analysed for texture analysis using hydrometer method to prepare the soil media map. All the chemicals used in this study were of analytical reagent grade. To ensure standard quality control/quality assurance procedures, replicates were analyzed for each sample.

7.3 Results and Discussion

7.3.1 Input parameters of DRASTIC vulnerability map for Njeliamparamba

7.3.1.1 Depth to water table

The depth to water determines the depth of material through which a contaminant must travel before reaching the aquifer, and it may help to determine the amount of time during which contact with the surrounding media is maintained. The deeper water table levels imply lesser chance for contamination to occur. Locations of 29 wells were selected from the study area to calculate the average depth to water table. Depth of groundwater ranged from 5-15 m. The depth to water table map was then classified into ranges defined by the DRASTIC model and assigned rates ranging from 1 (minimum impact on vulnerability) to 10 (maximum impact on the vulnerability) are shown in Figure 7.2.

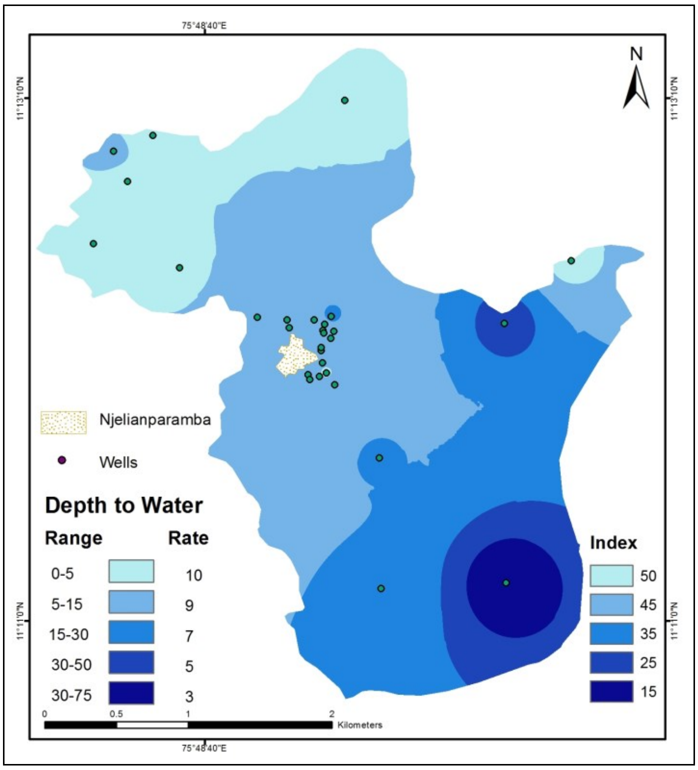


Figure 7.2: Depth to groundwater range, rating and index map

7.3.1.2 Net Recharge

Net recharge is the amount of water which infiltrates through the ground surface and reaches the water table; recharge water represents the medium for transporting pollutants. Recharge water is thus available to transport a contaminant vertically to the water table and horizontally within the aquifer. Rainfall is an important factor which transports surface pollutants and landfill leachate by infiltration. Recharge data were not available for the study area. Therefore, net recharge was calculated by a combination of ratings for slope, soil permeability and rainfall following the method given by (Piscopo, 2001).

$$\text{Recharge value} = \text{Slope (\%)} + \text{Rainfall} + \text{Soil permeability} \qquad (7.2)$$

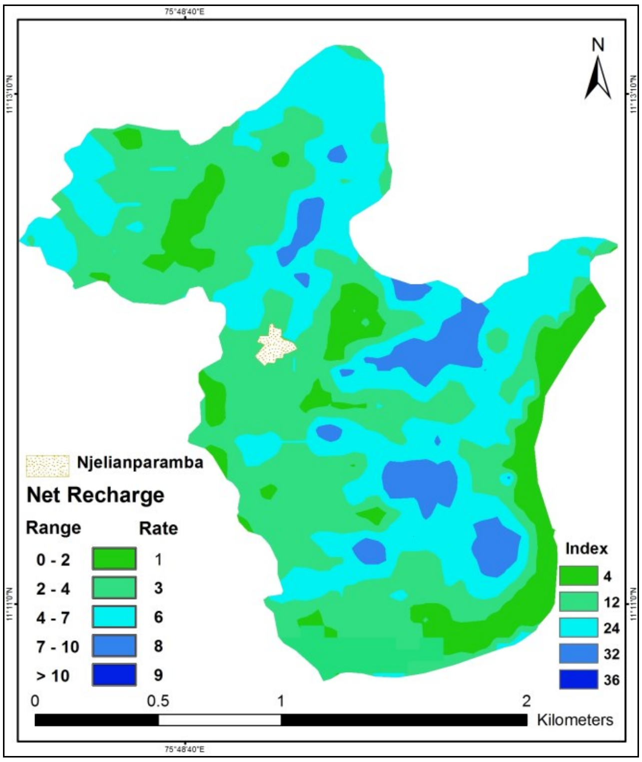


Figure 7.3: Net recharge range, rating and index map

The net recharge map was generated by superimposing the net recharge parameters, according to the values given in Table 7.7. The range, rating and index of net recharge are given in Figure 7.3.

Table 7.7: Data used for measurement of net recharge in the study area

Slope %	**Rating**	**Rainfall (mm)**	**Rating**	**Soil Permeability**	**Rating**	**Net recharge**	**Rating**
0-2	10	3200	4	1-100	1	0-2	4
2-6	9					2-4	12
6-12	5					7-7	24
12-18	3					7-10	32
>18	1					>10	36

The slope (%) in the study area was derived from the NASA SRTM (Shuttle Radar Topographic Mission) data that provides the digital elevation model (DEM) obtained from the USGS ftp site. The soil permeability map was generated from soil texture data. The CWRDM rainfall stations maintained by the meteorological observatory were used to measure the average annual rain fall (3200 mm) in the study area.

7.3.1.3 Aquifer media

Aquifer media refers to consolidated or unconsolidated rock which serves as an aquifer. It is the saturated zone material, which controls the pollutant attenuation processes which determine the flow rates and types of contamination. The sand and gravel are the basic rock formation in the study area. The assigned rating for aquifer media is found to be 8. The range, rating and index of aquifer media given in Figure 7.4.

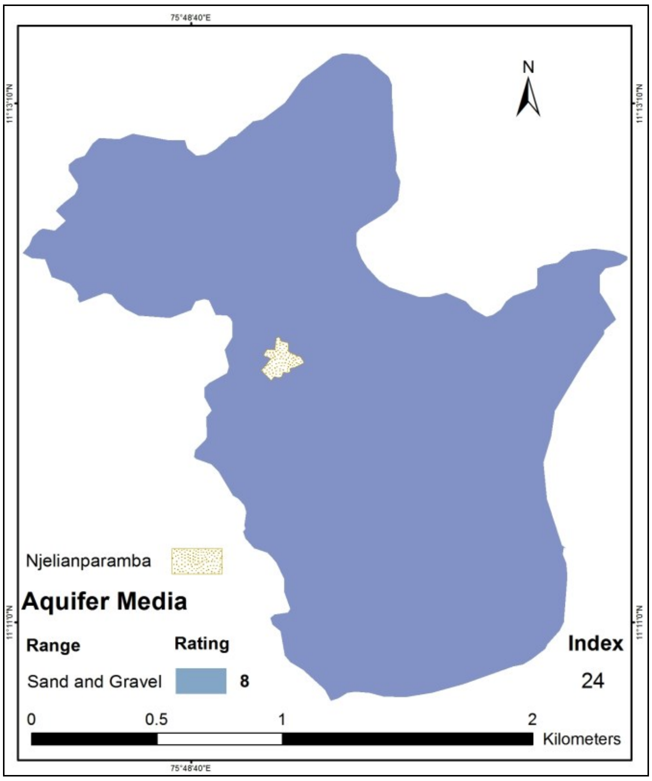


Figure 7.4: Aquifer media range, rating and index map

7.3.1.4 Soil media

Soil media refers to the weathered portion of the earth surface characterised by considerable biological activity. Soil acts as a transport media for contaminants to travel vertically into the groundwater because of its ability to infiltrate impurities through rainfall recharge. Soil pollution potential is mostly affected by the soil types. Soil types were analysed and identified from different sampling stations using soil texture analysis. Based on soil texture, the soil map was classified into three classes- sandy loam, loam and clay loam with ratings 6, 5 and 3 (Figure 7.7). The rating value of 6 covered the largest area. This result was then compiled in to a soil media map using the USEPA DRASIC system. The range, rating and index of soil media of the study area are shown in Figure 7.5.

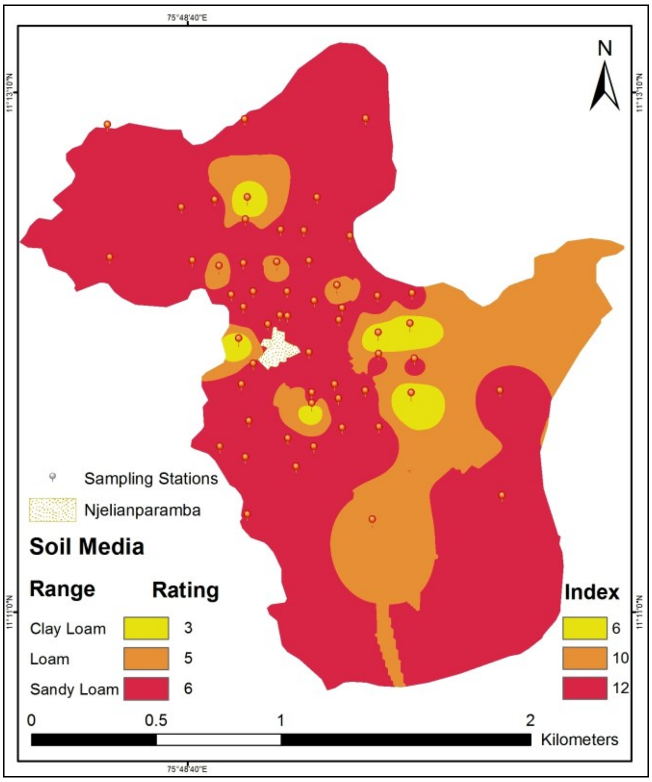


Figure 7.5: Soil media range, rating and index map

7.3.1.5 Topography

Topography refers to the slope of the land surface. It indicates that plain surfaces will let the runoff water to remain on the surface and permit percolation of contaminants to the saturated zone and also indicates that steeper slopes can be a sign of higher groundwater velocity. Slope classes with their range, rating and index of the study area are shown in Figure 7.6. A digital elevation model (DEM) was used to extract the slope of the study area.

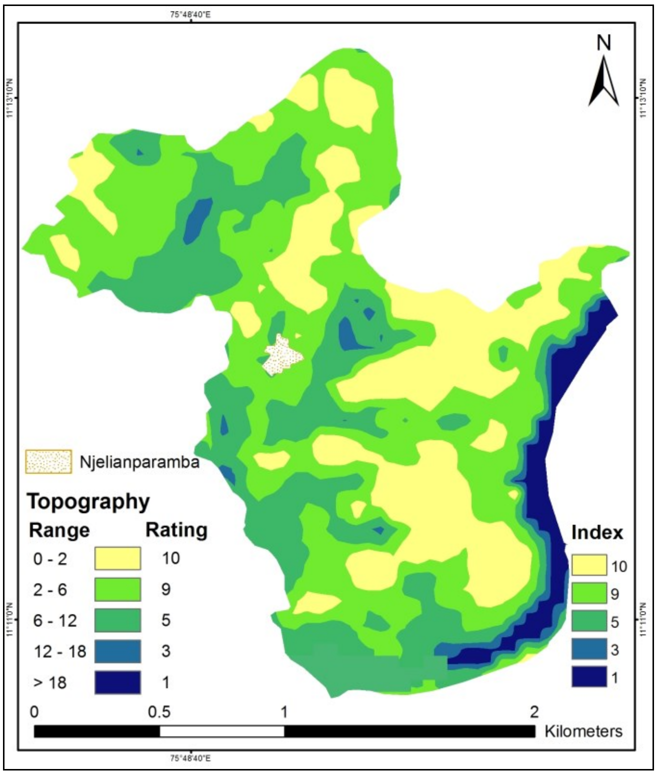


Figure 7.6: Topography range, rating and index map

7.3.1.6 Impact of vadose zone

The vadose zone range, rating and index are shown in Figure 7.7.

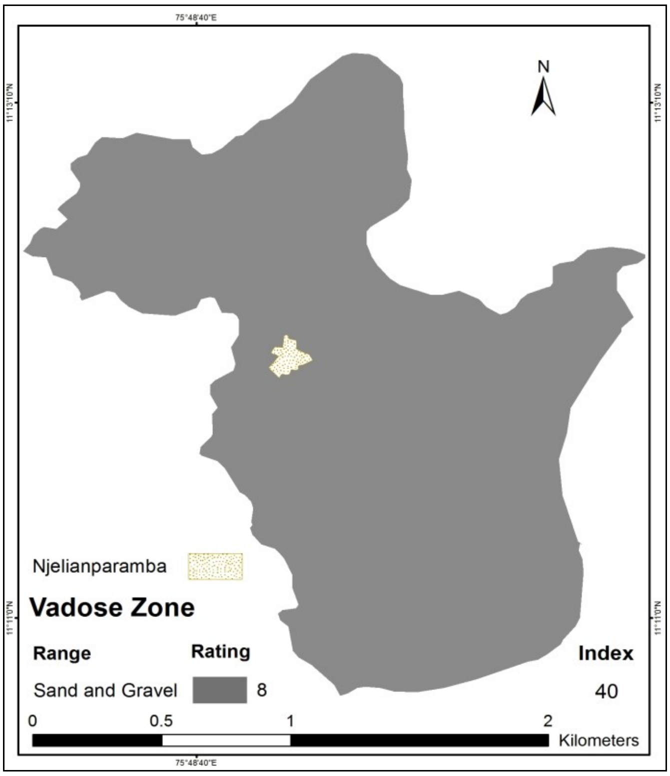


Figure 7.7: Vadose zone range, rating and index map

The vadose zone is mainly the unsaturated zone is above the water table which controls the passage and filters the contaminants into the saturated zone. The vadose zone in the study area is mainly composed of sand and gravel. It is rated as 8 according to the USEPA-DRASTIC method.

7.3.1.7 Hydraulic Conductivity

Hydraulic conductivity is the ability of an aquifer to transport water and control the groundwater flow rate under a constant hydraulic gradient. It determines the rate of flow of contaminant material through groundwater, as it is controlled by the amount and void spaces, porosity, fracturing etc. A low conductivity means high resistance against contamination and high conductivity indicates high vulnerability while transportation. Hydraulic conductivity value was obtained from the soil permeability class based on the United State Department of Agriculture (USDA, 1994) as shown in Table 7.8. The texture analysis data from the soil media layer was used to determine soil permeability for the study area. The indigenous value for hydraulic conductivity was found to be within the range of 1-100gpd/ft^2 with a rating of 1 (Aller, 1987). The range, rating and index for hydraulic conductivity of the study area are shown in Figure 7.8.

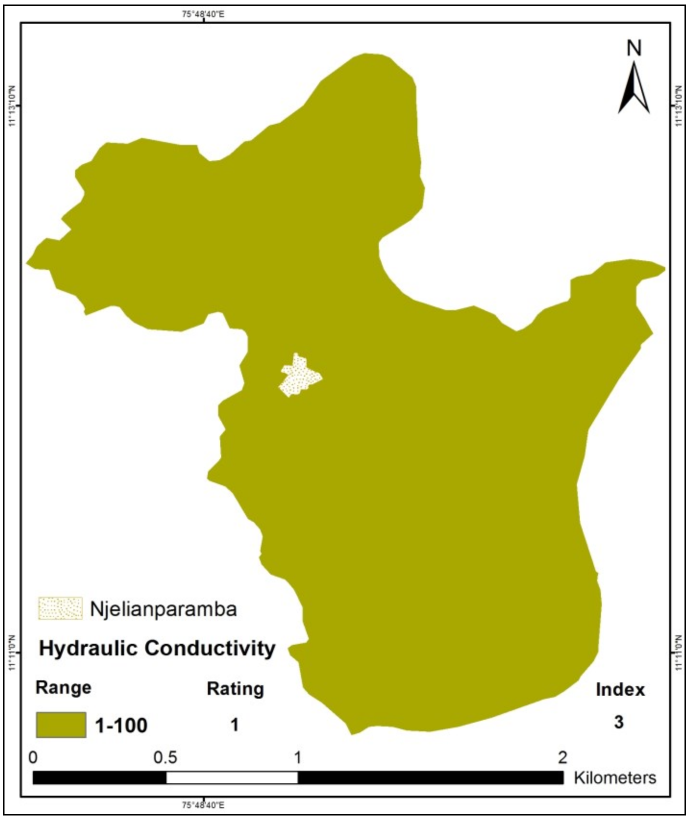


Figure 7.8: Hydraulic conductivity range, rating and index map

Table 7.8: Soil permeability class (USDA, 1994)

Texture class	Texture	Permeability rate	Permeability class
Coarse	Gravel, coarse sand Sand, loamy sand	> 20 inches/h 6.20 inches/h	Very rapid Rapid
Moderately coarse	Coarse sandy loam, sandy loam, fine sandy loam	2–6 inches/h	Moderately rapid
Medium	Very fine sandy loam, loam, silt loam, silt	0.60–2 inches/h	Moderate
Moderately fine	Clay loam, sandy clay loam, silty clay loam	0.20–0.60 inches/h	Moderately slow
Fine	Sandy clay, silty clay, clay (<60%)	0.06–0.20 inches/h	Slow
Very fine	Clay (>60%), clay pan	<0.06 inches/h	Very slow

7.3.1.8 Vulnerability map

To create the vulnerability map, all the seven parameter index map layers were overlaid using the Geoprocessing tool, weighted sum overlay falling under the Spatial Analyst extension in the Arc toolbox. This method overlay the resultant map layers, multiplying each by their given weight with their corresponding rate (as per the USEPA), summing them together to get the index. The study area was divided into three vulnerability classes ranging between a minimum value of 120 and a maximum value of 243. These classes are moderate vulnerable, high vulnerable and very high vulnerable as shown in the vulnerability zone map in Figure 7.9. The vulnerability classes were categorized according to the USEPA DRASTIC Index and vulnerability class (Aller, 1987) as given in the Table 7.9.

Table 7.9: DRASTIC Index and vulnerability class

DRASTIC index	Vulnerability class
1–100	Low
101–140	Moderate
140–200	High
>200	Very high

According to vulnerability map of the study area, the eastern and south eastern portion of Njeliamparamba dump site was very highly vulnerable to groundwater contamination. This is probably due to the lower slope terrains towards the eastern part that is mostly covered with loam and sandy loam which allows enhanced percolation of contaminants into the groundwater. About 75% of the study area falls under high vulnerability class including the areas close to Njeliamparamba dump site.

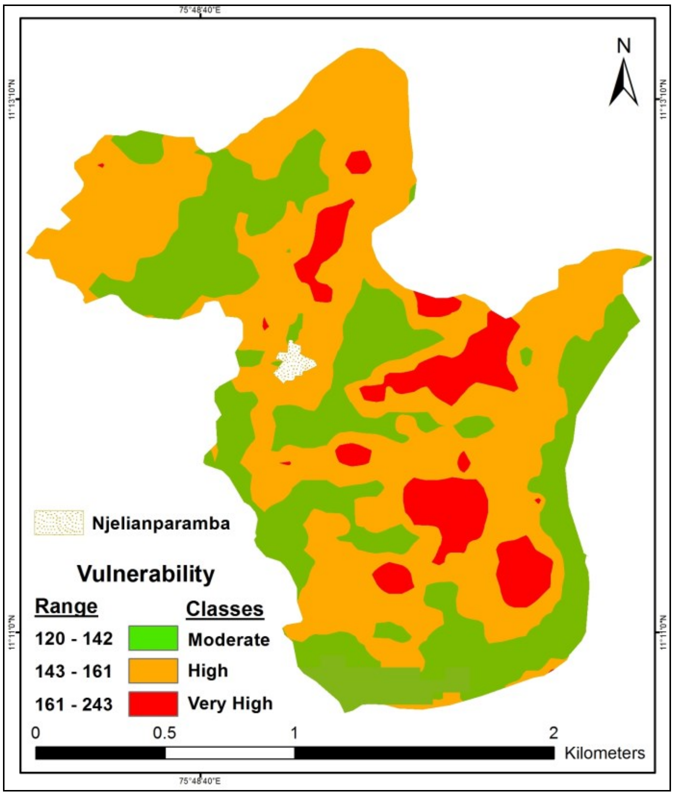


Figure 7.9: Groundwater vulnerability map of the study area

7.3.1.9 Validation of DRASTIC model

A total of 29 groundwater samples were collected from different vulnerability zones of the study area. A buffer zone of 1 km from the Njelianparamba dumping site was considered to assess the correlation between distance and the selected contamination detection factors. For validation of the vulnerability index map, a chemical and bacteriological parameter was considered to justify with the USEPA DRASTIC vulnerability index. The samples were analyzed for the estimation of total dissolved solids and *E.coli* as per the standard procedure (APHA, 2012) and the results were produced in the form of maps as shown in Figure 7.10 and Figure 7.11. These maps along with the buffer zone were then correlated with the vulnerability map to interpret the problematic areas.

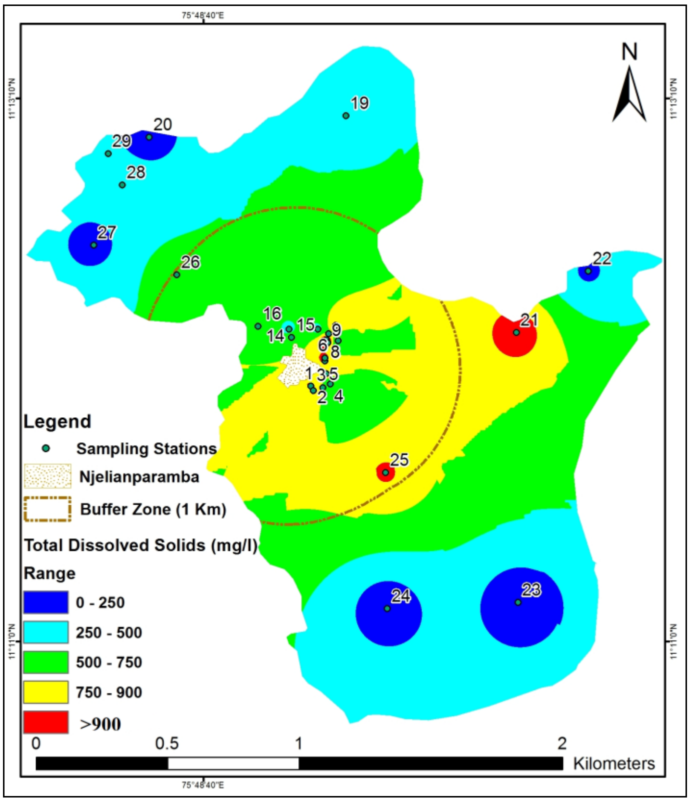


Figure 7.**10:** Concentration of total dissolved solids in different vulnerability zones

In the case of validation using total dissolved solids, a total of 20 groundwater samples were found to be within the buffer zone and 9 samples laid outside the buffer zone. The dissolved solids concentration in samples that laid inside the buffer zone, were detected between a range of 500 to 1200mg/L which is above the permissible limit as prescribed by Bureau of Indian Standards (BIS, 2012). This indicates that leachate percolation is maximum at 1 km distance from the dumping site. The samples collected from outer portion of buffer zone were within the permissible limit of 500 mg/L except the sample 21, which falls under very high vulnerable zone. The samples collected at greater distances from the dumping site had lower concentration of dissolved solids.

The *E.coli* bacteria were found to be present in samples in vicinity to the dumping site particularly within the buffer zone of 1 km. Most of the samples within the buffer zone had the presence of *E.coli*. This validates that the area surrounding the dumpsite is contaminated in correlation to the highly vulnerable area present in the vulnerability map. But an exception of 3 samples (NP-26, NP-13 and NP-14) within the buffer zone did not have the presence of *E.coli* bacteria which can be due to the presence of residual chlorine detected in these samples; indicating the presence of regular chlorination of the wells. The samples outside the buffer zone were free from *E.coli* except sample NP-21and NP-19 lying towards the eastern portion of the study area. Both of these samples fall under the very high vulnerable class in the vulnerability map which explains the presence of bacteria.

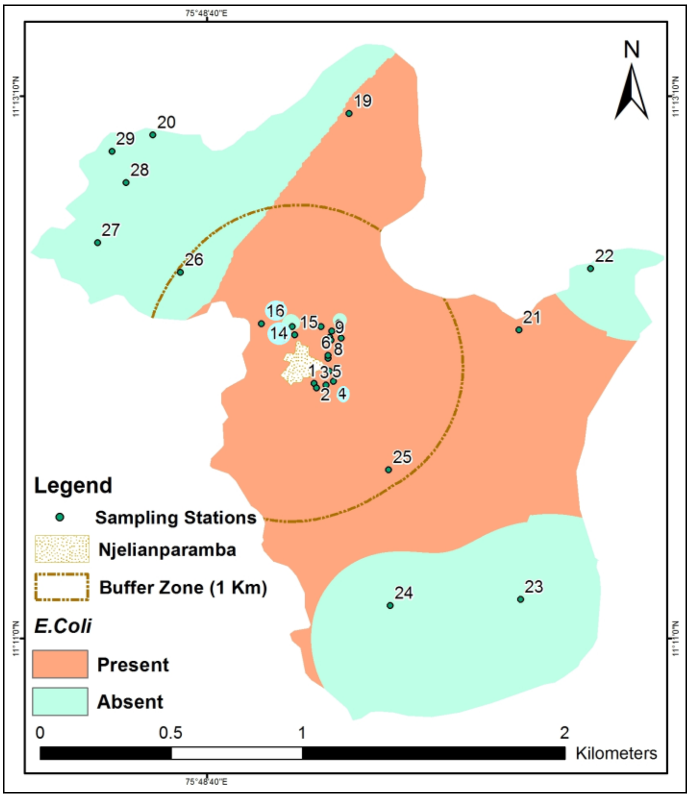


Figure 11: *E.coli* in different vulnerability zones

7.3.2 Input parameters of DRASTIC vulnerability map for Laloor

7.3.2.1 Depth to water

The depth to water is the distance from the ground surface to the water table. It determines the depth of material through which a contaminant must travel before reaching the aquifer. The depth of groundwater data were obtained from the field. The range, rating and index map is shown in Figure 7.12.

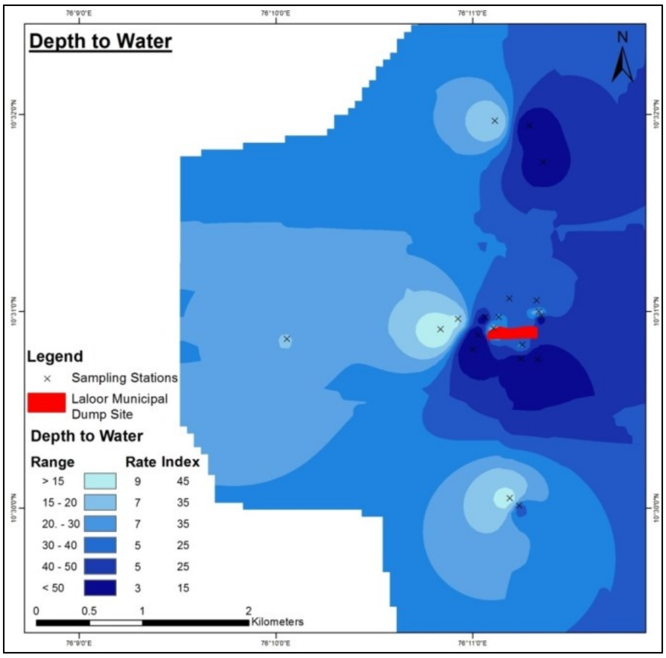


Figure 7.12: Depth to Groundwater range, rating and index map

7.3.2.2 Net Recharge

Recharge is the principal medium for leaching and transporting contaminants to the water table. The higher the recharge value, the chance for contaminants to reach the water table is high. Net recharge data were not available for the study area. Therefore, it is calculated through a combination of slope, soil permeability and rainfall following the method of Piscopo (2001). The resultant recharge range, rating, index map is shown in Figure 7.13. Recharge was calculated using the formula equation (7.2)

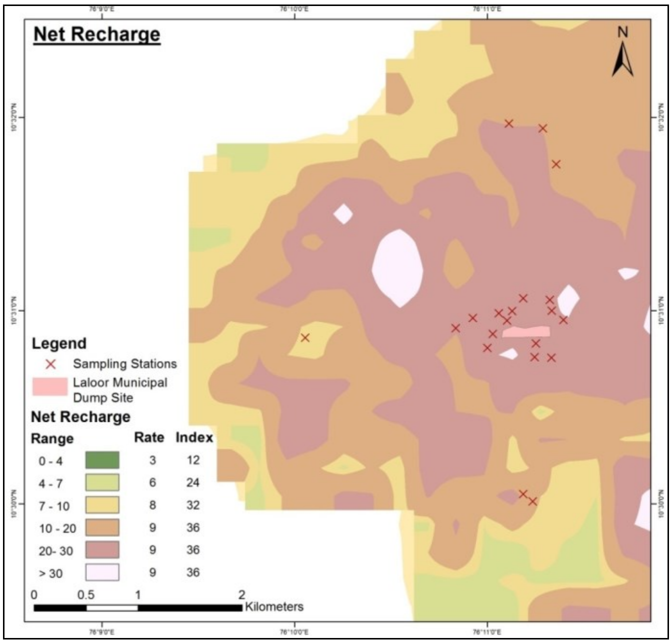


Figure 7.13: Net Recharge range, rating and index map

7.3.2.3 Aquifer media

The aquifer media exerts a major control over the flow path, hydraulic conductivity and gradient. Gneissic Charnockite is the basic rock formation in the study area. This area mainly consists of sandy and gravel as aquifer medium which is given a rating of 8. The map showing aquifer media range, rating, and index map is given in Figure 7.14

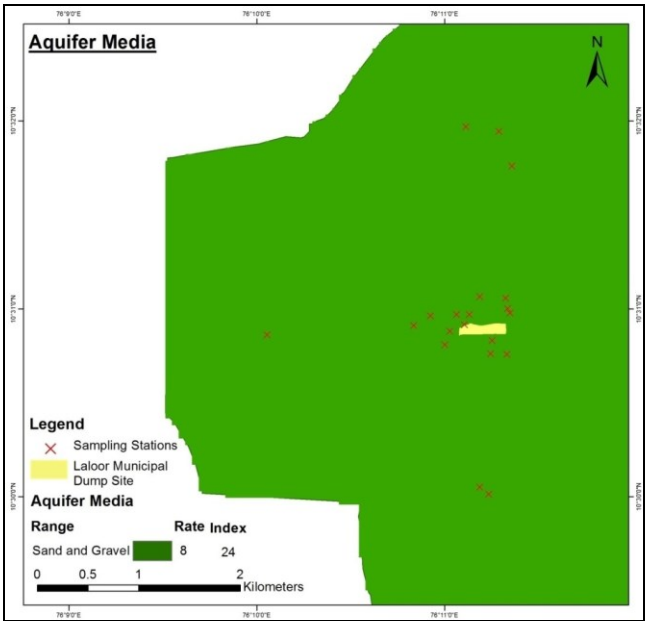


Figure 7.14: Aquifer media range, rating and index

7.3.2.4 Soil media

The range, rating and index of soil media map is shown in Figure 7.15.

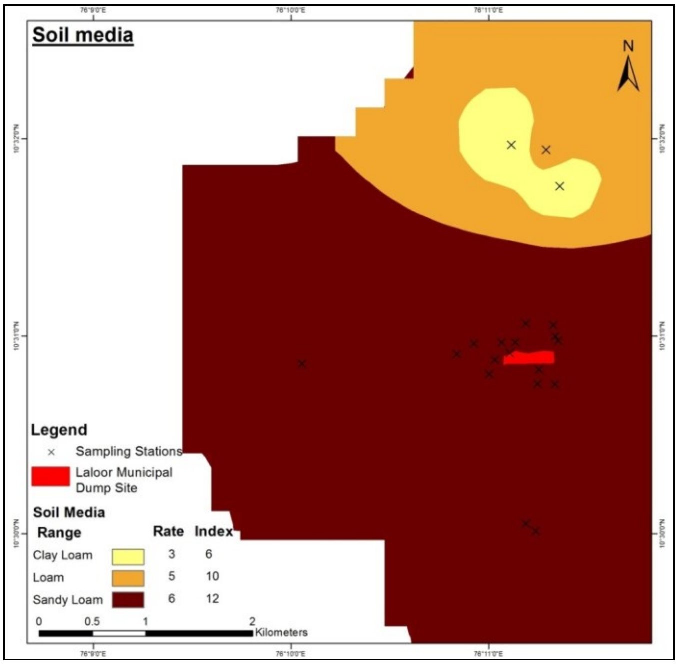


Figure 7.15: Soil media range, rating and index map

The soil data for preparing the soil media map were obtained from Soil Survey of India, Thrissur. The soils in this area were classified as clay loam, loam and sandy loam based on the results of texture analysis of soil samples collected from the study area.

7.3.2.5 Topography

Topography refers to the slope of the land surface. The slope map was prepared from the SRTM data using ‘Extraction Tools’ in ‘Spatial Analyst Tool’ in ArcGIS 10.1. The topography range, rating and index map is shown in Figure 7.16.

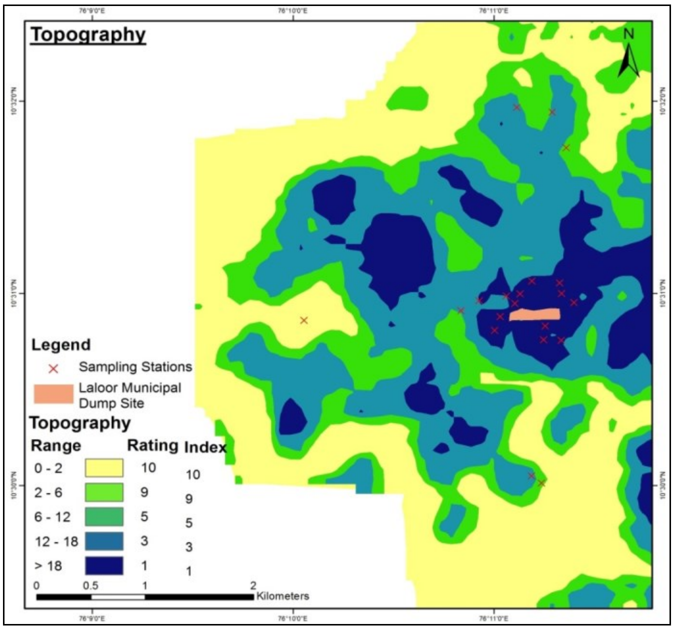


Figure 7.16: Topography range, rating and index map

7.3.2.6 Impact of the vadose zone media

The vadose zone is the unsaturated zone above the water table. The texture of the vadose zone determines the time of travel of the contaminant through it. The vadose zone in the study area mainly consists of laterite soil of sand and gravel type which was assigned as rating of 8. The range, rating and index map for impact of vadose zone is shown in Figure 7.17.

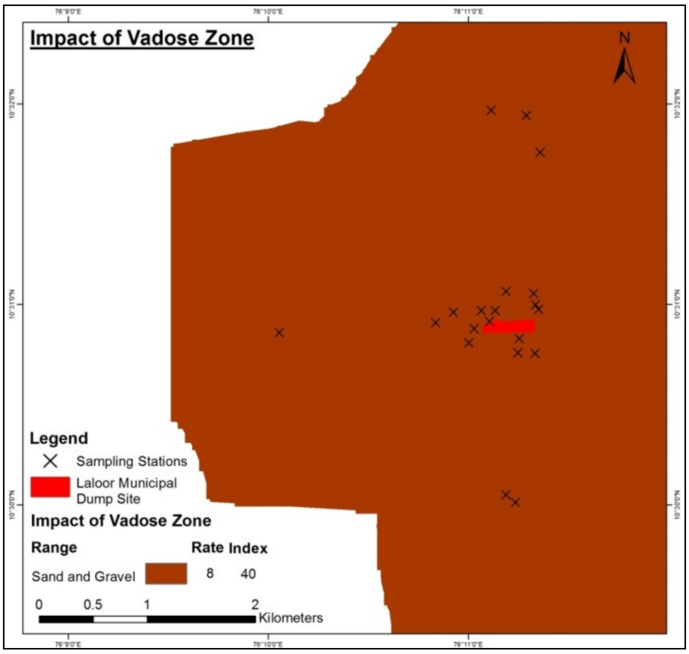


Figure 7.17: Impact of vadose zone range, rating and index map

7.3.2.7 Hydraulic Conductivity of the aquifer

Hydraulic conductivity refers to the rate at which water flows horizontally through an aquifer. It is controlled by the amount and interconnection of void spaces and inter-granular porosity, fracturing etc. The higher the conductivity, the chance for aquifer vulnerability is more. The hydraulic conductivity value of the study area was in the range of 0-5 m/day and the assigned rating was given as 2 and the index map is shown in Figure 7.18.

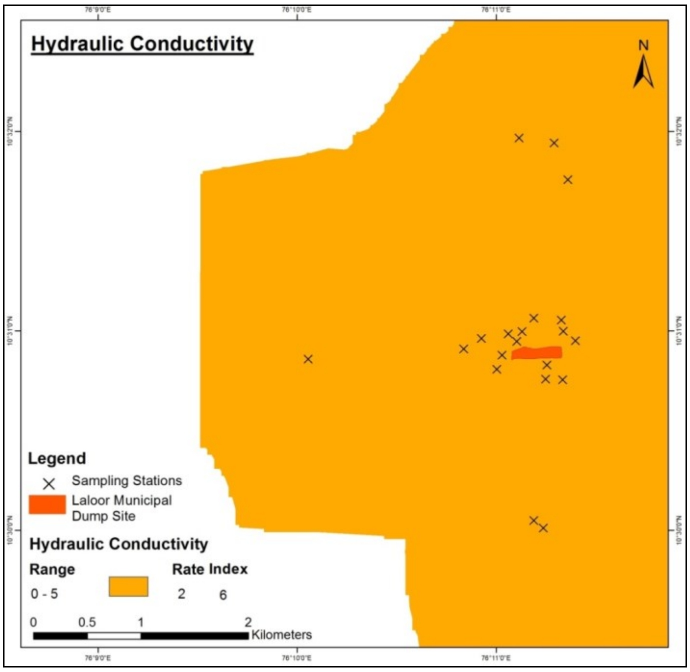


Figure 7.18: Hydraulic conductivity range, rating and index map

7.3.2.8 Vulnerability map

The DRASTIC index, a measure of the pollution potential, was calculated using the Arc View GIS environment to prepare the groundwater vulnerability map of the study area. From the DRASTIC index map, it is possible to identify areas which are more likely to be polluted. According to the index value obtained, the vulnerability index ranges from 184 – 398 were classified into three classes i.e, 184-253, 253-320 and 320-398 corresponding to low, medium and high vulnerability zones respectively. The vulnerability map obtained by DRASTIC method is shown in Figure 7.19.

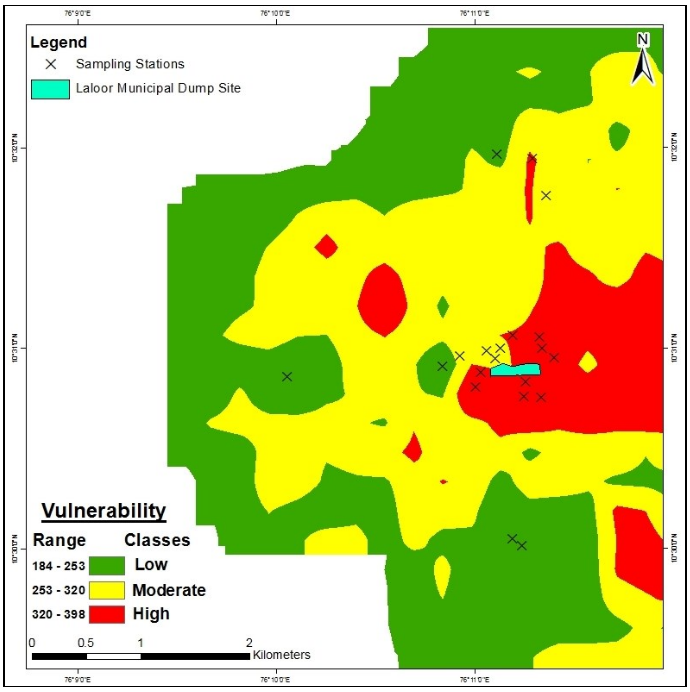


Figure 7.19: Groundwater vulnerability map for Laloor

7.3.2.9 Validation of DRASTIC model

A total of twelve groundwater samples were collected from different vulnerability zones of the study area and analyzed for its nitrate concentration. The concentration of nitrate exceeded in 25% of the groundwater samples and 75% of the samples are within the permissible limit prescribed by the Bureau of Indian Standards for drinking water (BIS, 2012). Figure 7.20 shows that the variation of Nitrate–N concentrations in different distances from the landfill site. The nitrate concentration of the groundwater samples were spatially represented and analyzed in the form of GIS maps, and then super imposed with the resultant vulnerability map. The vulnerability map indicated that eight groundwater samples were laid down in highly vulnerability zone, 5 samples in low vulnerable zone and 7 samples in the moderate vulnerable zone.

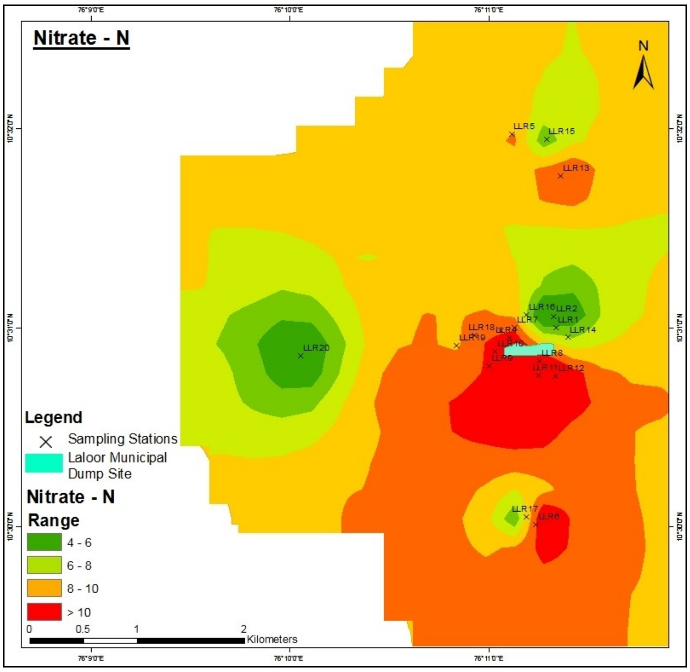


Figure 7.20: Map showing variation of Nitrate–N

7.4 Summary

The DRASTIC model in a geographical information system environment was used to determine the groundwater vulnerability to contamination in the vicinity of a two solid waste disposal sites, Njeliamparamba and Laloor, municipal dumping sites in Kozhikode and Thrissur district, Kerala, India. DRASTIC is an index model composed of several hydrogeological parameters. The ArcMap 10.1 was used to prepare a vulnerability map for the study area. According to the vulnerability map in the Njeliamparamba, the study area was divided into three vulnerability classes ranging between a minimum value of 120 and a maximum value of 243. The vulnerability classes are moderate vulnerable, high vulnerable and very high vulnerable. It can be concluded from the vulnerability map, that the eastern and south eastern portion of Njeliamparamba dump site was very highly vulnerable to groundwater contamination. This is probably due to the lower sloped terrains towards the eastern portion which allows percolation of contaminants into the groundwater. The resulting vulnerability map was then validated using a chemical and bacteriological analysis of samples collected from nearby wells of the dumping site to assess the area which is of more potential risk to pollution. From the results of the study, it is clear that the concentrations of total dissolved solids and *E.coli* were correlated in different vulnerable zones; which validated the results obtained.

The vulnerability index map in the Laloor dumping site were identified into three categories of groundwater vulnerable zones of contamination - 184 to 253, 253 to 320 and 320 to 398 corresponding to low, medium and high vulnerability zones respectively. At Laloor high vulnerable zone is dominant near the dump site, so that dumping of any type of waste in that area will directly accelerate the pollution potential of groundwater at that area regardless of the amount of waste. The results revealed that the vulnerability index value was found to be higher in Laloor compared to Njeliamparamba; but more groundwater contamination was observed in Njeliamparamba due to high leachate percolation. The characteristics of groundwater samples from Laloor indicated that the nitrate is the major contaminant; therefore the DRASTIC model was validated using the nitrate concentrations. The vulnerability map indicates that 80% of the nitrate contaminated samples were coming under the region of high vulnerable zone.

The results provided a preliminary tool to identify potential areas or vulnerability zones with high risks of groundwater contamination due to the leachate percolation from solid waste dumping sites. The vulnerability map obtained from the DRASTIC method provides information about the locations that should be avoided waste dumping and also highlight the importance of showing high priority in terms of protection and contamination prevention. DRASTIC method results are useful in the design of aquifer protection and management strategies and the scenario also provides significant benefits in relation to time and economy for local authorities concerned in managing groundwater resources.

JASEELA C.”A STUDY ON THE SOIL AND WATER QUALITY OF SELECTED SITES AROUND SOLID WASTE DUMPING AREAS IN KERALA STATE”. THESIS. CWRDM (CENTRE FOR WATER RESOURCES DEVELOPMENT AND MANAGEMENT), UNIVERSITY OF CALICUT, 2018.

Chapter 8

REMOVAL OF ORGANIC AND INORGANIC CONTAMINANTS IN MSW LANDFILL LEACHATE BY ELECTRO-COAGULATION TECHNOLOGY

8.1Introduction

Electro-coagulation (EC) process has been proven as a feasible, economical and ecological alternative technique for the treatment of wastewater containing organic and inorganic compounds with promising results (Gengec et al., 2012; Al-Shannag et al., 2014; Chakchouk et al., 2017). Electro-coagulation has been successfully used to treat different wastewaters such as textile wastewater (Zaroual et al., 2006; Chithra et al., 2008), oily wastewater (Chen et al., 2000; Kobya et al., 2003; Abdelwahab et al., 2009; Safari et al., 2016), dairy wastewater (Sengil & Ozacar, 2006), petroleum refinery wastewater (El-Naas et al., 2009), paint manufacturing wastewater (Akyol, 2012), laundry wastewater (Janpoor et al., 2011), restaurant wastewater (Chen et al., 2000), pharmaceutical wastewater (Zaidi et al., 2015; Kermet-Said & Moulai-Mostefa, 2015), heavy metals containing wastewater (Al-Shannag et al., 2015; El-Taweel et al., 2015), potato chips manufacturing wastewater (Kobya et al., 2006), olive mill wastewater (Inan et al., 2004; Khoufi et al., 2007) and oily bilge water (Asselin et al., 2008).

Generally, landfill leachate has complex structure and high pollutant load, therefore its treatment is quite difficult to meet the discharge standards. Leachate contains high concentration of organic or inorganic pollutants such as COD, ammonia, heavy metals. Hence, many treatment methods such as biological, chemical, physical, wetland and advanced oxidation processes, have been performed to treat leachate (İnanç et al., 2000; Apaydın & Ozkan, 2017). Electro-coagulation method, which is frequently preferred among the electrochemical treatment methods, was performed for the treatment of organic and inorganic contaminants in landfill leachate.

8.1.1 Theoretical background on EC process

Electro-coagulation is the in situ production of coagulants in water by passing electrical charge using sacrificial electrodes resulting in the formation of hydroxide ions and hydrogen gas at the cathode. Three main processes occur during electro-coagulation: coagulant formation, contaminant destabilization and flocculation (Liu et al., 2010). First, the anode is electrochemically oxidized to release cations in solution:

$$M^0_{(s)} \rightarrow M^{z+}{}_{(aq)} + z \cdot e^-$$

Where, M is the metal comprising the sacrificial electrode(s). These cations combine with hydroxide ligands to form coagulant in solution. Simultaneously, hydrogen gas is formed at the cathode by electrolytic reduction of water. Then the coagulant destabilises dissolved or colloidal contaminants and aggregates to form flocs. Flocs may enmesh bubbles of hydrogen gas and rise to the surface to form flotation layer or simply settle by gravitation. The Figure 8.1 shows the schematic diagram of two-electrode EC processes.

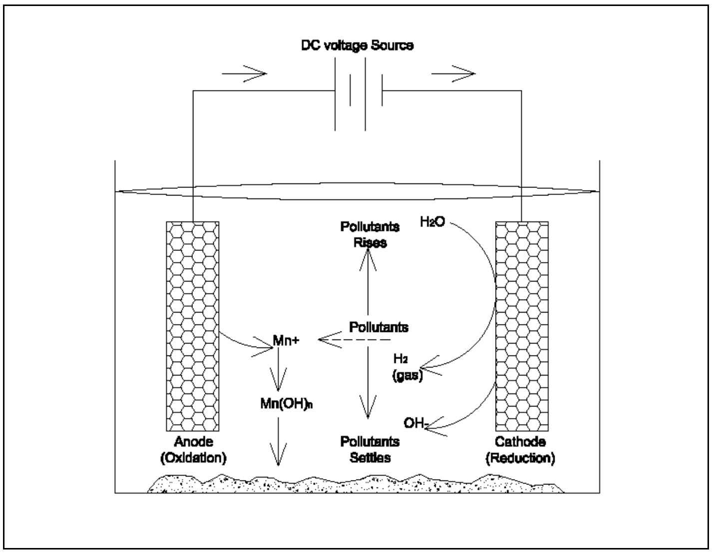


Figure 8.1: Schematic diagram of bench-scale two-electrode electro-coagulation cell (Adapted from Pak, 2015)

8.1.2 Mechanism of EC

In this process, many mechanisms are used to remove pollutants from the aqueous effluents. Anodic oxidation and production of adsorbents (hydrated aluminum hydroxides in the case of aluminum electrodes) occurred simultaneously with cathodic reactions and the evolution of hydrogen gas responsible of absorbent flotation. The metal hydroxides that formed have a large surface and can quickly adsorb pollutants. Consequently, the formed flocs can be removed by flotation or sedimentation. The mechanisms of reactions that happen in the electrochemical units are studied well enough (Antropov, 1977; Inan et al., 2004). The electrodes used in EC process are usually made of aluminium, iron or stainless steel, because these metals are cheap, readily available, proven effective and non-toxic. Some chemical reactions, which occur on electrodes and in the wastewater, are shown in Table 8.1.

8.1.3 Reactions and mechanisms

The main reaction occurs at the anode when aluminum electrode is applied in the EC process is as follows:

$$Al_{(s)} \longrightarrow Al^{3+}_{(aq)} + 3e^{-} \qquad (8.1)$$

Also, oxygen evolution can compete with aluminum dissolution at the anode by the following reaction

$$2H_2O_{(l)} \longrightarrow O_{2\,(g)} + 4H^+_{(aq)} + 4e^- \qquad (8.2)$$

At the cathode, hydrogen evolution reaction occurs (equation 8.3). It contributes to floatation of the flocculated particles to the surface of the wastewater.

$$3H_2O_{(l)} + 3e^- \longrightarrow 3/2\ H_{2\,(g)} + 3OH^-_{(aq)} \qquad (8.3)$$

At high pH, generated OH^- at the cathode attacks the cathode by the reaction (equation 8.4) (Gengec et al., 2012; Safari et al., 2016)

$$2Al + 6H_2O + 2OH^- \longrightarrow 2Al\,(OH)_4^- + 3H_{2\,(g)} \qquad (8.4)$$

Electrode reactions generate Al^{3+}(aq) and hydroxyl ions [equations (8.1) and (8.4)] to form different monomeric polymeric species, which convert primarily into $Al(OH)_{3(s)}$ and ultimately polymerize to $Al_n(OH)_{3n}$ [equations (8.5) and (8.6)] in the solution (Safari et al., 2016)

$$nAl\,(OH)_3 \longrightarrow Al_n(OH)_{3n} \qquad (8.5)$$

$$Al^{3+} + 3H_2O \longrightarrow Al\,(OH)_{3(s)} + 3H^+ \qquad (8.6)$$

Formed amorphous $Al(OH)_{3(s)}$ have large surface areas and contribute to rapid adsorption of soluble contaminants and also trapping the colloidal particles which are simply separated from aqueous medium by H_2 flotation or sedimentation (Kobya et al., 2006). The concentration of hydrolyzed aluminum species depends on the pH and aluminum concentration (Gengec et al., 2012)

Iron produces Fe $(OH)_n$ upon oxidation in an electrolytic system. The first mechanism includes the following reactions

At the anode:

$$Fe_{(s)} \longrightarrow Fe_{(aq)}^{2+} + 2e^- \quad (8.7)$$

$$Fe_{(aq)}^{2+} + 2OH^- \longrightarrow Fe(OH)_{2(S)} \quad (8.8)$$

At the cathode:

$$2H_2O_{(l)} + 2e^- \longrightarrow H_{2\,(g)} + 2OH^-_{(l)} \quad (8.9)$$

Overall reaction:

$$Fe_{(s)} + 2H_2O_{(l)} = Fe(OH)_{2(s)} + H_{2\,(g)} \quad (8.10)$$

Fe^{2+} ions will undergo further spontaneous reactions to produce monomeric ions, ferric hydroxo complexes with hydroxyl ions and polymeric species. The formed gelatinous suspension of Fe $(OH)_{n(s)}$ that remains in the aqueous medium removes the contaminants from wastewater either by complex formation or electrostatic attraction, and followed by coagulation (Mollah et al., 2011).

The objective of the work was to investigate the removal of nitrate, COD and heavy metals from MSW landfill leachate by electro-coagulation method and to determine the optimum operational conditions.

8.2 Materials and Method

8.2.1 Experimental set up

Experiment was performed in an electro-coagulation reactor composed of electrolysis cell, DC power supply, and magnetic stirrer and is shown in Figure

8.2. The electro-coagulation reactor consists of a circular cylindrical reactor with 10cm in diameter made of glass with 1L capacity of aqueous solution and two pairs of electrodes placed at a distance of 2cm apart. Two trial experiments were carried out to investigate the performance of electrode materials on higher removal efficiency of organic and inorganic pollutants. In the first step, electro-coagulation was conducted using Al as both anode and cathode with dimensions of 100mm length, 70mm width and 0.2mm thickness. While in the second step, Fe was used as anode and cathode with dimensions of 100mm length, 70mm width and 0.4mm thickness. The electrodes were arranged parallel to each other and connected to the negative and positive outlets of the digital Direct Current power supply (Model Spectrum 9551) that regulates the electricity. The pairs of electrodes in each step were submerged in the electrolysis reactor which contained leachate sample of 1L. A magnetic stirrer was placed on the bottom of the reactor in order to achieve proper mixing in the leachate sample.

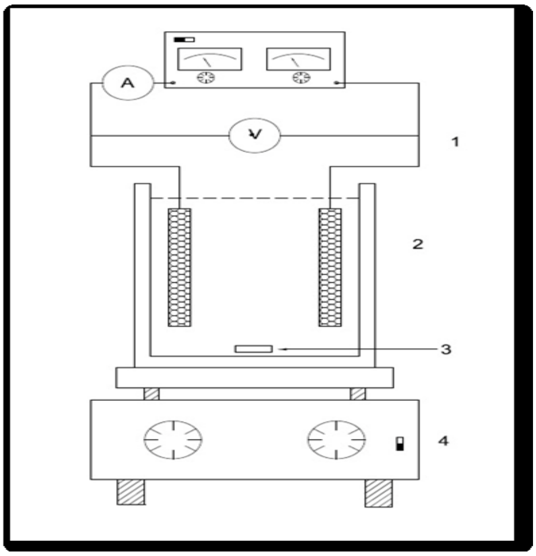


Figure 8.2: Schematic diagram of experimental setup (1) DC power supply (2) Electro-coagulation cell (3) Magnetic bar stirrer (4) Digital magnetic stirrer

The electrodes were connected to a DC power supply providing voltage in the range of 0 to 8 V and electrical current in the range of 0 to 2 A. In each value of electric potential, the sample of electrolysed leachate was taken in different EC time of 20, 40, 60, 80 and 100 min. pH was monitored and maintained by the addition of concentrated HCl (0.1N) or NaOH (0.1N). 0.2 to 1.0g/L of NaCl was added to increase the conductivity of solution. The electrodes were washed with dilute HCl, followed by distilled water to remove surface grease or other impurities on the metal surface. Before analyzing the concentrations, the treated sample was filtrated using whatman filter paper grade No 1 (size 110mm). Temperature was maintained at constant temperature of 30°C. Power supply was started at time $t = 0$ and the corresponding time taken as the starting time of the EC process.

8.2.2 Method of analysis

The physico-chemical characteristics of the leachate were carried out based on standard methods for the examination of water and wastewater (APHA, 2012). pH, electrical conductivity and dissolved solids of the leachate sample were measured with a multi-parameter PCSTestr35. The chemical oxygen demand in the leachate was measured by open reflux digestion method, and nitrate was estimated by cadmium reduction method and determined using UV-VIS Spectrophotometer (Thermo Scientific-Evolution 201). The concentrations of analysed heavy metals except Pb in the leachate were found to be below the permissible limits of MoEF standards for discharge in public sewer (MoEF, 2000). Thus for determining the electro-coagulation efficiency of heavy metals, a synthetic heavy metal solution of Zn^{2+}, Ni^{2+}, Cu^{2+}, Pb^{2+}, Cr^{3+} and Cd^{2+} were prepared using $CuSO_4.5H_2O$, $Ni(NO_3)_2·6H_2O$, $Pb(NO_3)_2$, $Zn(NO_3)_2·4H_2O$, $CdSO_4.8H_2O$, $Cr (NO_3)_3$ and $Mn (NO_3)_2$. The synthetic wastewater containing all the heavy metals was freshly prepared by diluting appropriate volume of each stock solution with distilled water up to 1L. Method of analysis of the heavy metals is given in chapter 3. Concentrations of heavy metals were determined using Inductively Coupled Plasma-Optical Emission Spectroscopy (Thermo Scientific iCAP 7000 series).

The efficiency of the EC process was determined in terms of the initial and treated sample. The RE of various parameters is calculated (Daneshvar et al., 2006: Ni'am et al, 2007) using the following equation.

$$C_R = (C_0 - C_1) / C_0 \times 100\% \qquad (8.11)$$

Where C_0 = initial concentration (mg/L), Ce = final concentration (mg/L) and C_R is the removal efficiency.

8.3 Results and Discussion

The process of electro-coagulation is not so complex and can be examined by the optimization of several parameters like pH, contact time and current density. In the present study, the process of electro-coagulation has been explored as a treatment technology for the removal of heavy metals, nitrate and COD. Removal efficiency of these parameters in different operating conditions has been evaluated.

8.3.1 Characteristics of leachate used

The analysed parameters for electro-coagulation are pH, TDS, nitrate and heavy metals such as Zn^{2+}, Ni^{2+}, Cu^{2+}, Pb^{2+}, Cr^{3+}, Cd^{2+} and the characteristics are discussed in Table 8.1.

Table 8.1: Characteristics of leachate used

Parameters	Concentrations
pH	4.54±0.20
TDS, (mg/L)	14300.0±1.0
COD, (mg/L)	3401.0±2.20
NO_3^-, (mg/L)	101.0±1.50
Cu^{2+}, (mg/L)	5.05±1.0
Zn^{2+}, (mg/L)	5.14±0.16
Cd^{2+}, (mg/L)	5.02±0.20
Ni^{2+}, (mg/L)	5.25±0.50
Pb^{2+}, (mg/L)	5.22±0.60
Cr^{3+}, (mg/L)	5.13±0.18
Mn^{2+}, (mg/L)	5.30±0.45

8.3.2 Selection of electrode materials

The appropriate selection of electrode material is very important for electro coagulation process. The electrode materials used in this study are aluminium and stainless steel; these are cheap, readily available and proven effective. Thus both electrodes were tested in the study. The study included using two types of materials for electrode, firstly, using Al as both cathode and anode and secondly, using Fe as both anode and cathode. The effect of electrode material on the removal efficiency of COD, nitrate and heavy metals content of the leachate sample and the results are shown in Figure 8.3. The highest removal efficiency of COD and nitrate was obtained when Al was used as sacrificial anode with an initial concentration of COD and nitrate as 101.0±1.50mg/L and 3401.0±2.20mg/L, respectively. Those results are in agreement with other studies conducted by El-Shazly et al. (2011) and Safari et al. (2016). The maximum removal efficiency for heavy metals was obtained when Fe was used as sacrificial anode. The results are in agreement with Al-

Shannag et al. (2015). They also achieved the higher removal efficiencies for Cu^{2+}, Cr^{3+}, Ni^{2+} and Zn^{2+} from metal plating wastewater using Fe as sacrificial electrode.

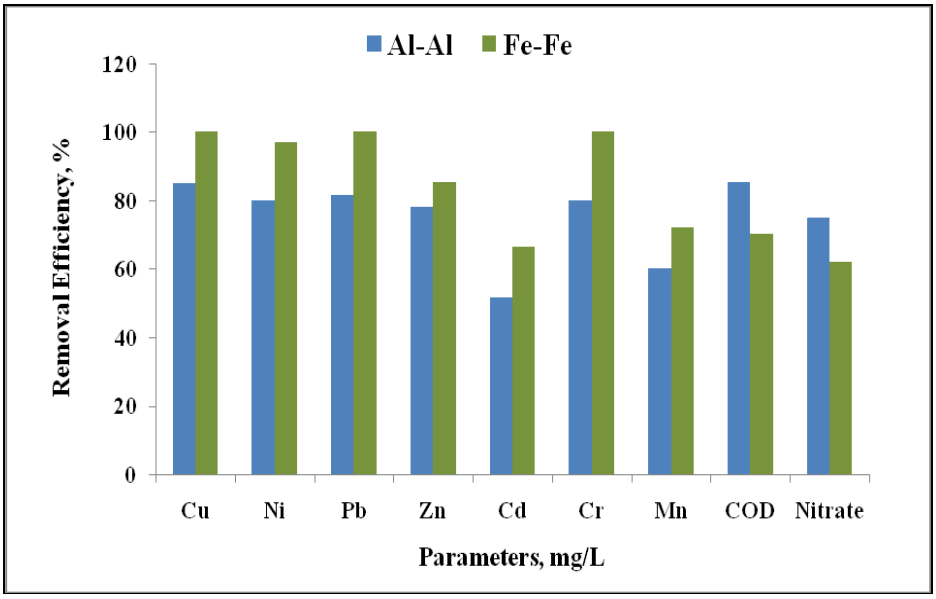


Figure 8.3: Effect of electrode materials on removal efficiency of various parameters (pH 7, 80 min, 8 V, NaCl concentration of 0.50g/L, initial concentrations of heavy metals 5.0mg/L, COD 3401.0±2.20mg/L and nitrate 101.0±1.50mg/L)

8.3.3 Removal of Nitrate by electro-coagulation method

Nitrate is stable and highly soluble ion with low potential for co-precipitation or adsorption, hence it is difficult to be removed from wastewater. Existing methods for removing nitrate from wastewater includes ion exchange, biological decomposition, chemical treatment, reverse osmosis, electrodialysis and catalytic denitrification. This methods for treating nitrate is usually very complicated and expensive (El-Shazly et al., 2011). Among these methods, electro-coagulation proved to be effective and economic method for treating nitrate contaminated wastewater. Inorder to evaluate the performance of electro-coagulation system for the removal of NO_3^-, the following variables such as solution pH (3 to 12), electrolysis time (ranged from 10 to 100 minutes), initial

NO_3^- concentration (100mg/L to 300mg/L) and current density (ranged from 2 to 10 V) were investigated.

8.3.3.1 Effect of initial pH

pH is a significant operating factor influencing the performance of electro-coagulation (Chen et al., 2000; Daneshvar et al., 2006; Ni'am et al., 2007). Depending on the pH of the solution, other ionic species like dissolved Al $(OH)^{2+}$ and $Al_2(OH)_2^{4+}$ hydroxo complexes possibly present in the system. Anodic metal ions and hydroxide ions produced at the electrode surfaces react in the bulk wastewater to form various hydroxides and build up polymers (Cañizares et al., 2006; El-Shazly et al., 2011).

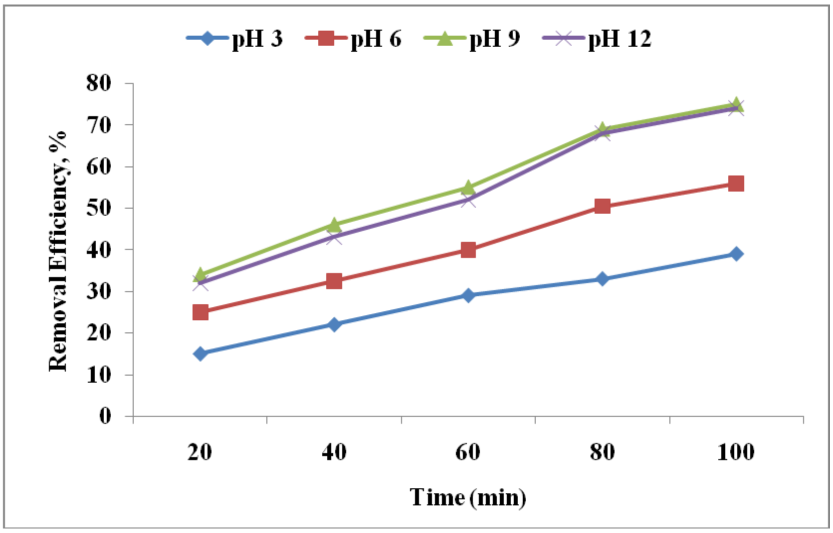


Figure 8.4: % Removal efficiency vs electrolysis time at different solution pH

The suspended aluminium hydroxides are able to remove nitrate from wastewater by sorption, co-precipitation or electrostatic attraction, and coagulation (Hua et al., 2003).The effect of pH on the removal of nitrate by electro-coagulation was studied for pH 3, 5, 9 and 12 and the results are shown in Figure 8.4. The results revealed that maximum concentration of nitrate (75.1±

0.2%) was achieved at pH=9. At pH=3 the removal efficiency of nitrate (39± 2.2 %) was very low. The study revealed that the removal efficiency is increased by increasing initial pH of the solution (Figure 8.4). This can be ascribed to the fact that, increasing the solution pH can destroy the passive aluminium oxide layer which is formed at lower pH

8.3.3.2 Effect of initial NO_3^- concentration

To assess the effect of initial concentration on the removal efficiency of nitrate, experiments were carried out using different initial nitrate concentrations in the range from 100 to 300 mg/L, and the results are shown in Figure 8.5. The results showed that increasing nitrate concentration, at fixed other parameters, causes decrease in the removal efficiency of nitrate. The nitrate was decreased from 75.10±0.20% to 59.2±2.50% as initial concentration was increased from 101.0±0.80 to 300.0±1.30mg/L. This can be ascribed to the fact that when increasing nitrate concentration more ions will present in the wastewater and this need more time to remove these ions. Increasing the NO_3^- concentration will block the adsorption sites of $Al\ (OH)_3$ rapidly and decreases its ability to adsorb more NO_3^- ion. This is consistent with the study of (El-Shazly et al., 2011) for the nitrate removal efficiency from wastewater by using monopolar vertical aluminum electrodes in a batch electrochemical unit.

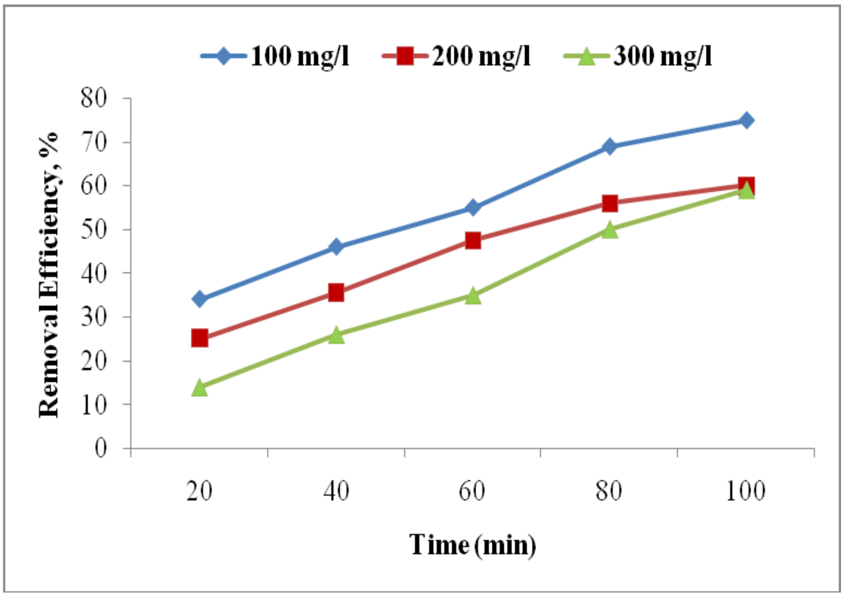


Figure 8.5: Removal efficiency vs electrolysis time for different initial NO_3^- concentration

8.3.3.3 Effect of voltage

The current applied is an important parameter that influences the performance and economy of the electro-coagulation process (El-Taweel et al., 2015). In order to investigate the effect of applied voltage on electro-coagulation efficiencies, experiments were conducted at voltage range from 2V to 10V.

The effect of voltage on the removal efficiency of nitrate is shown in Figure 8.6. The removal efficiencies of nitrate are increased with the voltage (2 to 8 V) from 36.70±2.0% to 75.1±0.2%. The results revealed that the increasing the applied voltage results in increasing the removal efficiency of nitrate. This result can be explained as follow: according to Faraday’s law, when increasing the current density the aluminium released from the anode is increased and hence increases the nitrate removal. These results can be explained by the fact that, increasing current density will increase the dissolution rate of aluminium electrode according to Faraday's law with the formation of $Al(OH)_3$ coagulant

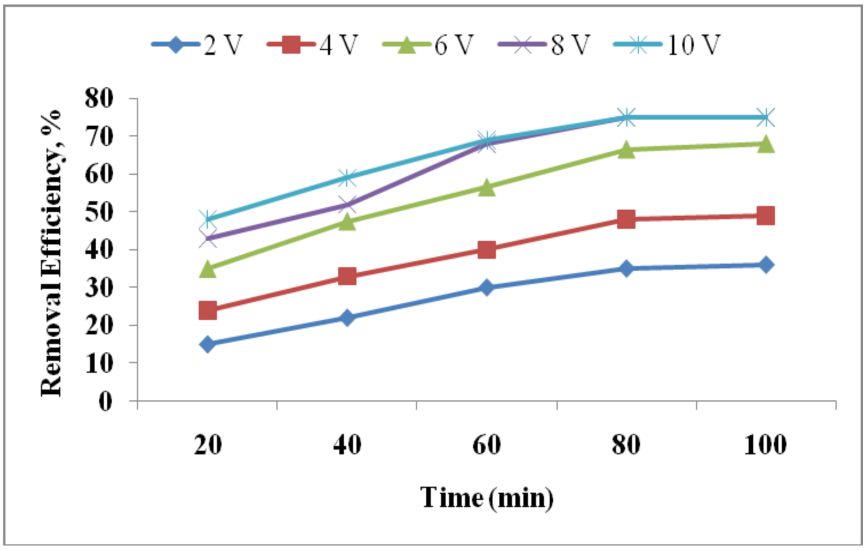


Figure 8.6: Removal efficiency vs voltage for different electrolysis time

Increasing the rate of amorphous Al $(OH)_3$ formed, which have large surface area on rapid adsorption of soluble nitrate and trapping of colloidal particles occurs with resultant removal of NO_3^- from wastewater. In addition, the cathodically evolved H_2 bubbles float Al $(OH)_3$ along with the adsorbed NO_3^- compounds to the upper surface of the solution. Increasing the current density above 8V had decreased the removal efficiency of nitrate, which may be ascribed to the possible passivation of anodic surface due to higher potential applied. Figure 8.6 shows that increasing the electrolysis time has increased the removal efficiency of nitrate, which can be attributed to fact that increasing the electrolysis time will certainly increase the available Al^{+3} according to Faraday's law, and consequently increase the amount of $Al(OH)_3$ which is responsible for NO_3^- removal.

8.3.3.4 Effect of NaCl concentration

The effect of NaCl concentration on removal efficiency of nitrate was studied by adding different concentrations (0.20 to 1.0g/L) of NaCl to the electrolyzed sample. The removal efficiency of nitrate with increase of NaCl concentration is illustrated in Figure 8.7.

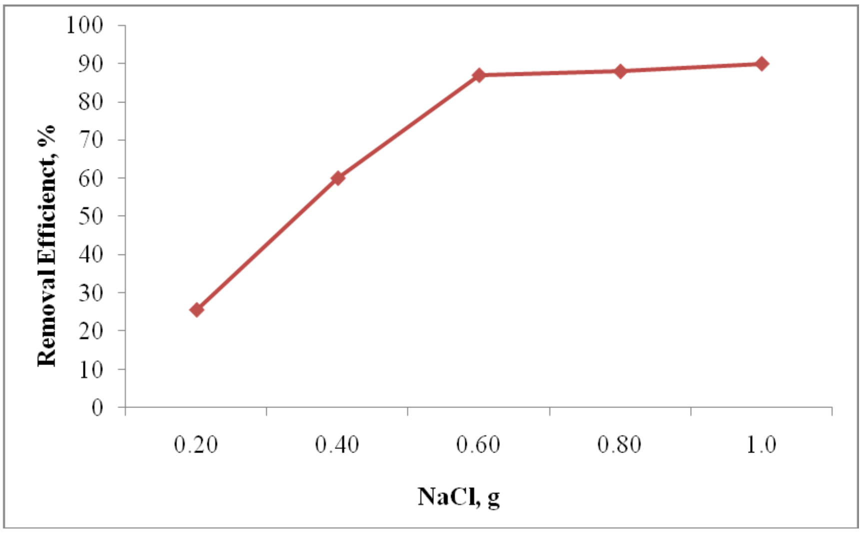


Figure 8.7: Removal efficiency at different NaCl concentration

8.3.4 Removal of COD by Electro-coagulation Method

The electro-coagulation of COD from leachate was experimentally investigated by using aluminum as sacrificial anode, the reactor voltage (2 to 8V), pH (3, 5, 7 and 9), 20 to 100 minutes of electro-coagulation time and supporting electrolyte (NaCl) of 0.50g/L. The results of the study are explained in the following sections.

8.3.4.1 Effect of pH on the COD reduction of leachate

In this experiments, various values of pH=3, 5, 7 and 9 were investigated to assess the effect of pH on the electro-coagulation performance. The COD concentration and the estimated maximum removal efficiency resulted after 60 minutes of EC treatment were plotted against the corresponding pH values as shown in Figure 8.8.

The results from Figure 8.8 indicated that the minimum COD concentration and the corresponding maximum COD removal occur at pH=7.

At this pH value, the COD value and the removal efficiencies were 0.50g/L and 85.29%, respectively. For strongly acidic and alkaline medium (pH 3 and 9), the COD values were 2.50 and 1.30g/L and the corresponding removal efficiencies were 26.49% and 61.78%, respectively. This indicates that the electro-coagulation of leachate is highly pH-dependent. This result agrees with those of Al-Shannag et al. (2014) for the COD removal from baker's yeast wastewater. The effect of pH on the EC processes could be attributed to the interaction of the hydronium ion (H_3O^+) with the hydroxyl iron (III) complexes formed at these pH conditions (Al-Shannag et al., 2014).

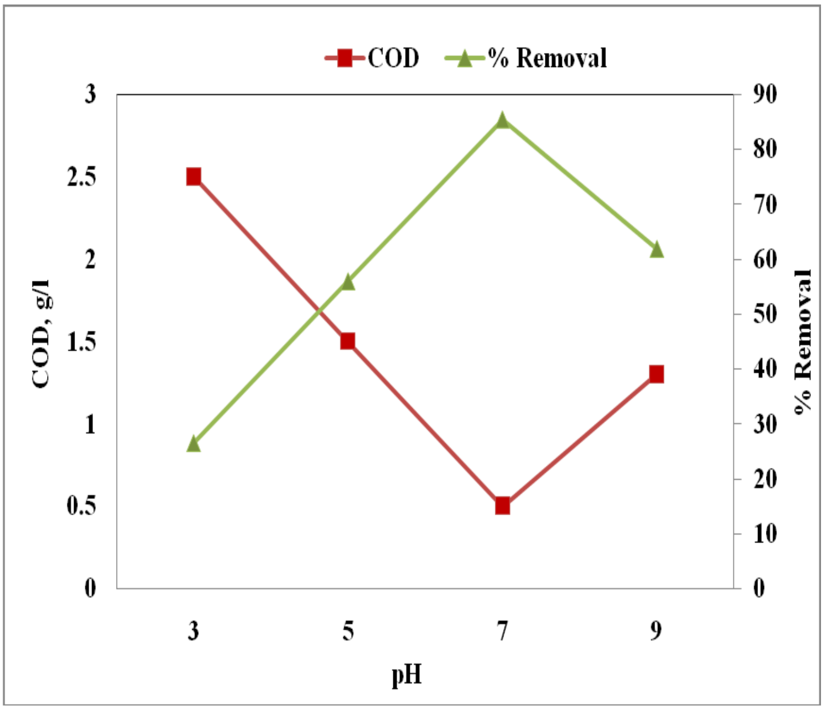


Figure 8.8: Effect of pH on COD concentration and its removal percentage (pH =3 to 9, initial COD=3.40g/L, NaCl=0.60g/L, applied voltage=6V and electrolysis time = 80min)

During the EC process, a pH increase is observed when the initial pH is acidic. The interpretation for this phenomenon is that this increase is due to the release of over-saturated CO_2 because of hydrogen evolution at cathodes (Safari et al., 2016). It is also found that in the alkaline mediums, pH of the solution decreases through the treatment, which is due to precipitation of hydroxide ions with cations. These results show that EC can act as pH buffer. The COD removal efficiencies decreased in acidic and alkaline conditions.

8.3.4.2 Effect of voltage on electro-coagulation

In order to investigate the effect of applied voltage on electro-coagulation efficiencies, a series of experiments were conducted at the voltage ranged from 2 to 8V and applied for initial COD concentrations of 3.40g/L. The effect of applied voltage on the removal efficiency of COD is shown in Figure 8.9. From the figure, it was found that as the value of voltage increased, the residual COD concentration decreased with maximum removal of COD obtained at 6V. The applied voltage determines the rate of coagulant dosage, bubble production and size of flocs growth resulting in a faster removal of pollutants (Li et al., 2011; Farhadi et al., 2012).

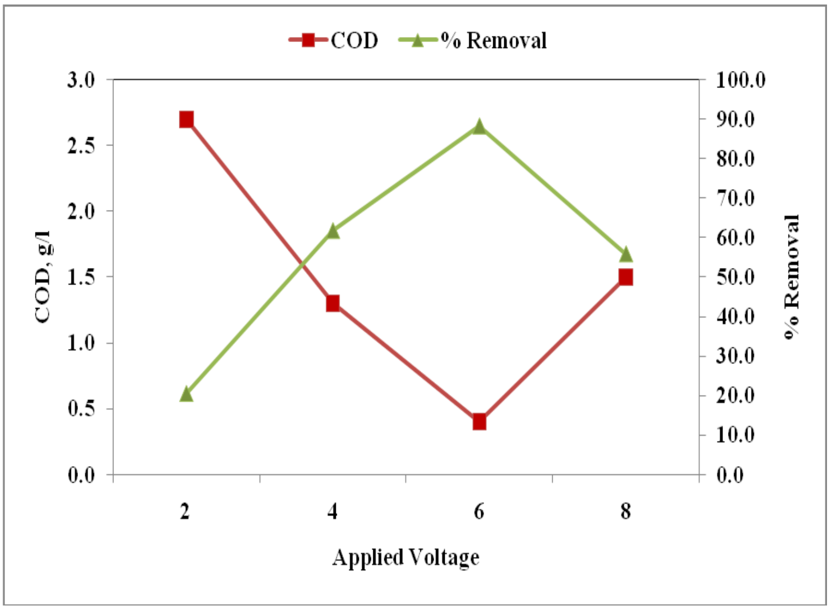


Figure 8.9: Effect of applied voltage on COD concentration and its removal percentage (applied voltage = 2 to 8V, initial COD=3.40g/L, NaCl=0.60g/L, pH=7 and electrolysis time = 80min)

8.3.4.3 Effect of supporting electrolyte on electro-coagulation

The effect of supporting electrolyte on the removal efficiency of COD is shown in Figure 8.10. Inorder to evaluate the effect of NaCl concentration on electro-coagulation, different concentration of sodium chloride ranges from 0.20 to 1.0g/L were used. It can be seen from Figure 8.10 that as sodium chloride concentration increases from 0.50 to 1.0g/L the removal efficiency of COD increases from 25.50 to 90.0mg/L because as the initial concentration of sodium chloride increases the conductivity of the cell increased and the percentage removal increases. It is also obviously shown that beyond sodium chloride concentration of 0.60g/L there was small increase on conductivity. This is probably due to the fact that at high salt concentrations the salting out effect appears. But for lower concentration of sodium chloride (<0.60g/L), there was a decrease in the rate of removal, probably because there were not enough ions to conduct the current so efficiency of the process would decrease (El-Taweel et al., 2015).

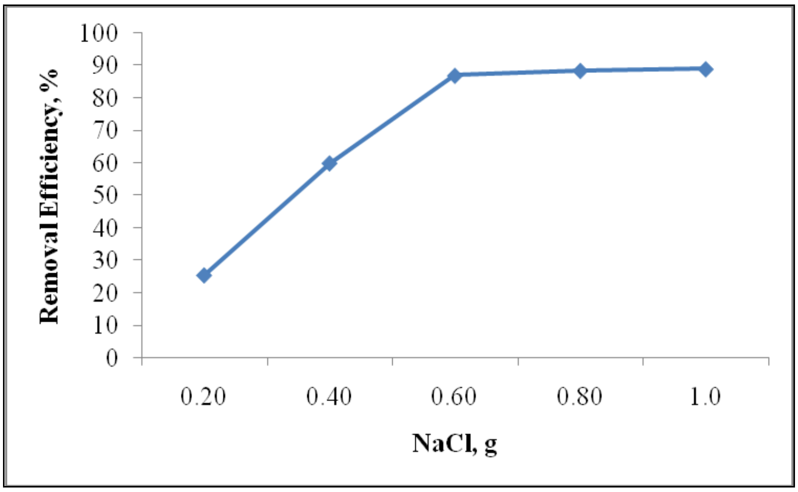


Figure 8.10: Effect of supporting electrolyte on COD concentration (concentration of NaCl =0.2 to 1.0g/L, applied voltage = 6V, initial COD = 3.40g/L, pH =7 and electrolysis time = 80min)

Conductivity causes an increase in current density; thus, more amount of coagulant can be introduced to the media. In addition, NaCl causes an increase in Cl- ions that chloride ions can remove the formed passivation layer on electrode surface. Thus, availability of metal hydroxide in the solution leads to an increase in the COD removal efficiency. Molecular chlorine is produced during the electrolysis of chloride salts.

$$2Cl^- \rightarrow Cl_2 + 2e^- \qquad (8.13)$$

The produced molecular chlorine can then be hydrolyzed to hypochlorous acid and hypochlorite ions that these species are responsible for pollutants removal due to their high oxidative potentials (Janpoor et al., 2011).

$$Cl_{2\,(g)} + H_2O \rightarrow HOCl + H^+ + Cl^- \qquad (8.14)$$

$$HClO \rightarrow ClO^- + H^+ \qquad (8.15)$$

8.3.4.4 Effect of initial COD concentration

The effect of initial COD concentration on COD reduction was investigated from 3401±2.20 to 9000±2.50mg/L, and the results are shown in Figure 8.11. The COD removal was decreased from 88.0±0.2 to 42.0±2.5%, as the COD concentration is increased. Removal efficiency for higher concentration of COD is lower compared to its lower concentrations when using the conditions, which are optimized for lower concentrations. Since the formation amounts of the coagulant are insufficient, the EC process needs more time and voltage to achieve the same removal efficiency as concentrations is lowered

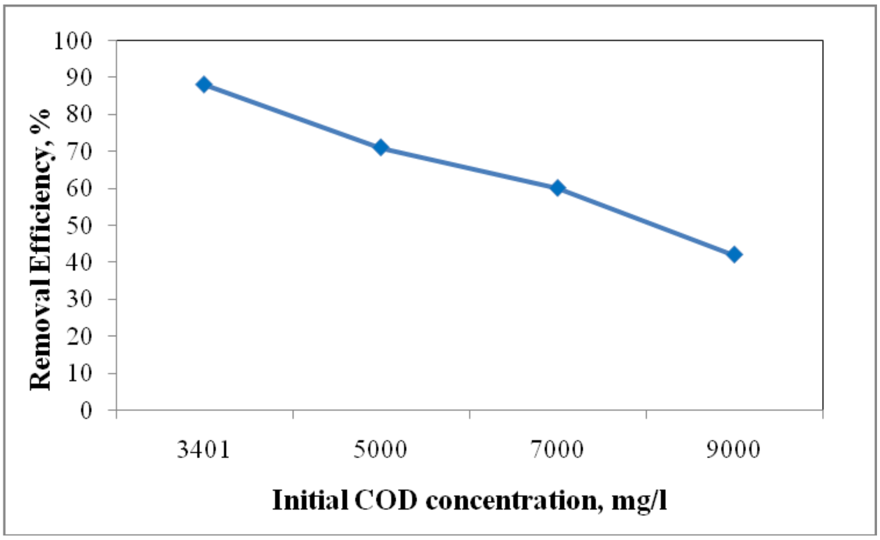


Figure 8.11: Effect of initial COD concentration on COD reduction (initial COD concentration = 3401.0±2.20 to 9000.0±2.50mg/L, applied voltage= 6V, NaCl =0.60g/L, pH =7 and electrolysis time=80min)

8.3.4.5 Effect of time on electro-coagulation

Time of electro-coagulation is one of the most important parameter because finding the required time for desired removal is necessary. Electrolysis time determines the rate of production of metal ions from electrodes. The effect of time on the removal efficiency of COD was investigated and is shown in Figure 8.12.

At the beginning of the EC process, the rate of production of metal ions from electrodes is slow, therefore removal efficiencies of COD is also low. However, when the electrolysis time increases, the concentration of metal ions and their hydroxide flocs increases and thus removal efficiencies also increase. The removal efficiencies of the COD was nearly constant after 80 minutes of operating time since metal ions and their hydroxide flocs cover the electrode surface. Moreover, this has caused electrode passivation and the concentration of metal ions and their hydroxide flocs became constant and therefore the removal efficiencies did not change significantly. Hence 80 minutes process time was taken as optimum time for further experiment.

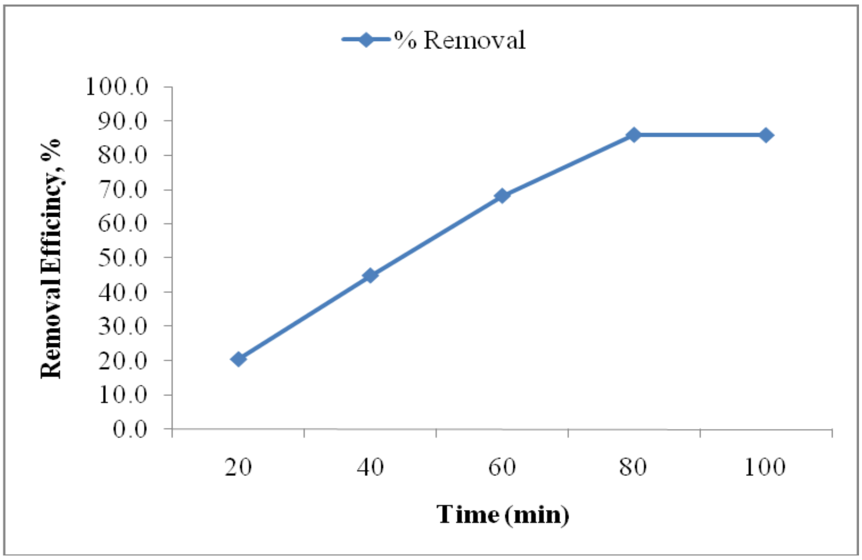


Figure 8.12: Effect of electrolysis time on COD reduction (electrolysis time=20 to 100min, pH=7, initial COD concentration = 3401.0±2.2mg/L, applied voltage= 6V, NaCl =0.60g/L)

At the beginning of the EC process, the rate of production of metal ions from electrodes is slow, therefore removal efficiencies of COD is also low. However, when the electrolysis time increases, the concentration of metal ions and their hydroxide flocs increases and thus removal efficiencies also increase. The removal efficiencies of the COD was nearly constant after 80 minutes of operating time since metal ions and their hydroxide flocs cover the electrode surface. Moreover, this has caused electrode passivation and the concentration of metal ions and their hydroxide flocs became constant and therefore the removal efficiencies did not change significantly. Hence 80 minutes process time was taken as optimum time for further experiment.

8.3.5 Removal of heavy metals by electro-coagulation method

Numerous approaches such as physical, chemical and biological processes including adsorption, biosorption, precipitation, ion-exchange, reverse osmosis, filtration and other membrane separations are employed to treat heavy metals in wastewaters (Al-Shannag et al., 2015). Precipitation of heavy metals in an insoluble form of hydroxides is the most effective and economical method to treat wastewater containing heavy metals. The main idea of precipitation method is to adjust the pH of wastewater and to add chemical coagulants like aluminum or iron salts to remove pollutants as colloidal matter (Agridiotis et al., 2007). Although the chemical coagulation technique is considered to be effective in treating industrial wastewater effluents, but it has quite high cost and it may produce side-products that are considered as secondary pollutants (Clark & Stephenson, 1998). Alternatively, electro-coagulation was found to be an effective technique for precipitating industrial wastewater pollutants (Mollah et al., 2001; Al-Shannag et al., 2015). The present work investigated simultaneous removal of Cu^{2+}, Ni^{2+}, Pb^{2+}, Zn^{2+}, Cd^{2+}, $Cr^{3+}$and Mn^{2+} ions from synthetic wastewater using electro-coagulation technique.

8.3.5.1 Effect of pH on the removal of heavy metal ions

In this work, effect of pH on the removal efficiencies of heavy metals by electro-coagulation were studied for considering three pH values (3, 6 and 9). Figure 8.13 illustrates the effect of pH on the removal efficiency of Pb^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Cr^{3+} and Mn^{2+}after 30 minutes of EC treatment with initial concentration of 5.0mg/L and voltage of 8V.

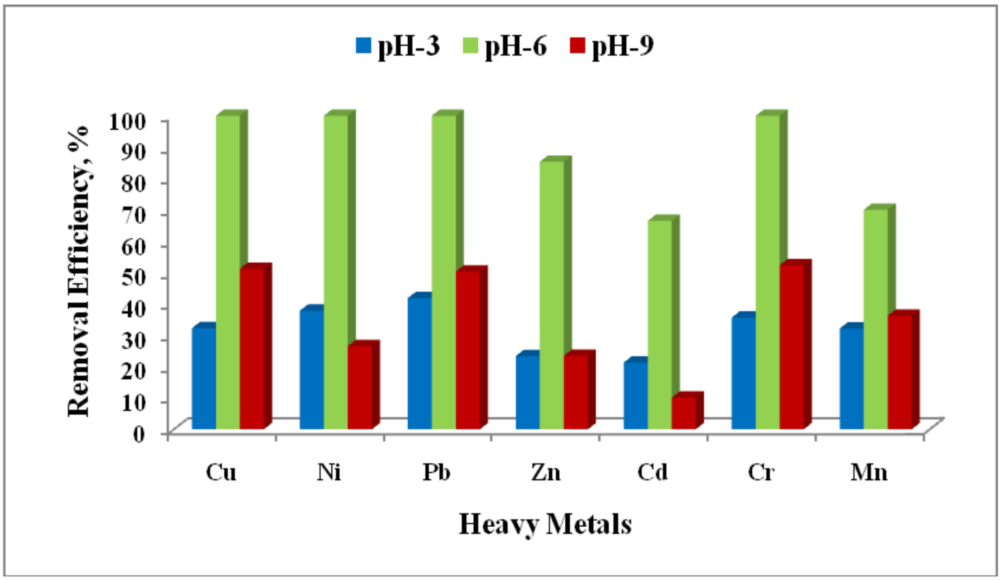


Figure 8.13: Effect of pH on initial concentration of heavy metals (applied current =8V, NaCl concentration=0.60g/L, the electrolysis time =30 min)

It is clear in the figure that the maximum removal efficiencies for all heavy metal ions occur at pH=6 and lower removal efficiencies were obtained at pH=3 and 9. This indicates pH 6 is the optimum pH level at which maximum heavy metal ions are removed. In alkaline medium, the oxidation of hydroxyl ions at the anode and the formation of Fe $(OH)^{4-}$ and $Fe(OH)_6^{3-}$ anions lowered the removing capacity (Al-Shannag et al., 2015). In strongly acidic medium, the protons in the solution were reduced to hydrogen gas at the cathode and the same proportion of hydroxyl ions could not be produced (Mollah et al., 2001). In addition, the pH affects the EC performance through varying the solution physiochemical properties, such as the solubility of metal hydroxides and the electrical conductivity, and the size of colloidal particles of iron (III) complexes that are strongly reactive agents with the heavy metal ions (Mollah et al., 2001; Gurses et al., 2002).

8.3.5.2 Effect of applied voltage

The effect of applied voltage on heavy metal removal was investigated by running the EC experiments at different direct current fields with applied voltage of 2, 4, 6 and 8V. It was clearly observed that increasing the applied voltage led to a significant removal of heavy metal ions concentrations. Figure 8.14 shows the heavy metal ions removal efficiencies after 30 minutes of EC treatment at different voltages.

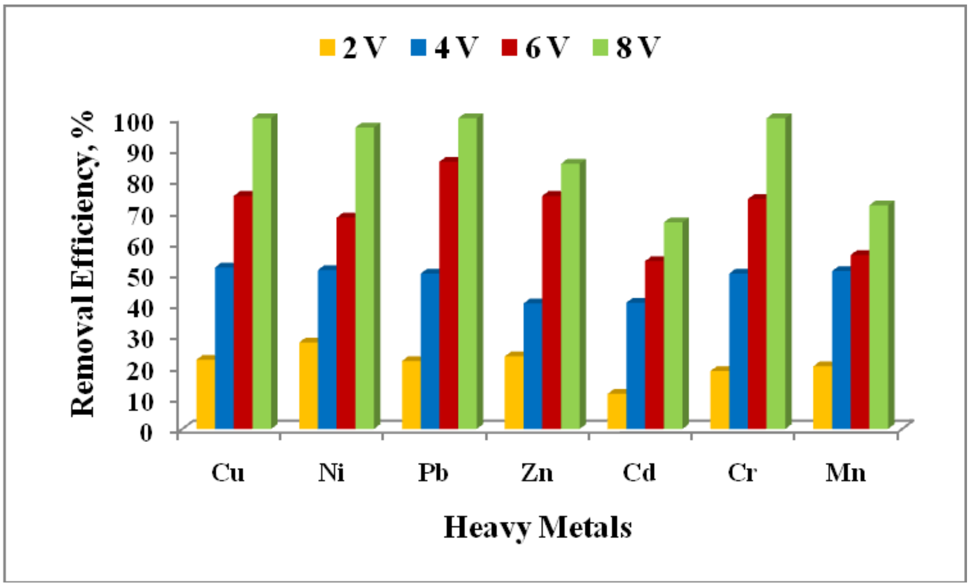


Figure 8.14: Effect of applied current on residual heavy metal concentration (initial heavy metal concentration=5.0mg/L, NaCl concentration=0.60g/L, pH=6.0, the electrolysis time =30min)

It is clear that the removal efficiency has values in the ranges of 11to 28%, 40 to 52%, 54 to 75% and 66 to 100% for applied voltage of 2, 4, 6 and 8V, respectively. In other words, the applied voltage represents a key parameter in enhancing heavy metal ions removal. This can be attributed to the direct proportionality between direct current field and potential electrolysis which implies more release of ferric ions, and thereby more generation of iron hydroxides necessary to form coagulants (Zaroual et al., 2006).

8.3.5.3 Effect of supporting electrolyte

The conductivity of the solution can influence the electro-coagulation process because it facilitates the passage of current. In fact, to investigate the effect of NaCl on heavy metal removal, a set of experiments was conducted with 30 minute EC time at applied voltage of 8V, at initial pH of 4.0 and initial concentration of heavy metal ions of 5.0mg/L by adding 0.20 to 1.0g/L NaCl to the electro-coagulation cell and the results are depicted in Figure 8.15.

The maximum removal efficiency of different metals was observed when 0.60g/L NaCl was used as the electrolyte. Beyond, sodium chloride concentration of 0.60g/L there was no effect on the conductivity. This is probably due to the fact that at high salt concentrations, the salting out effect appears. But for lower concentration of sodium chloride (<0.60g/L), there was a decrease in the rate of removal, probably because there were not enough ions to conduct the current so the efficiency of the process would decrease (El-Taweel et al., 2015).

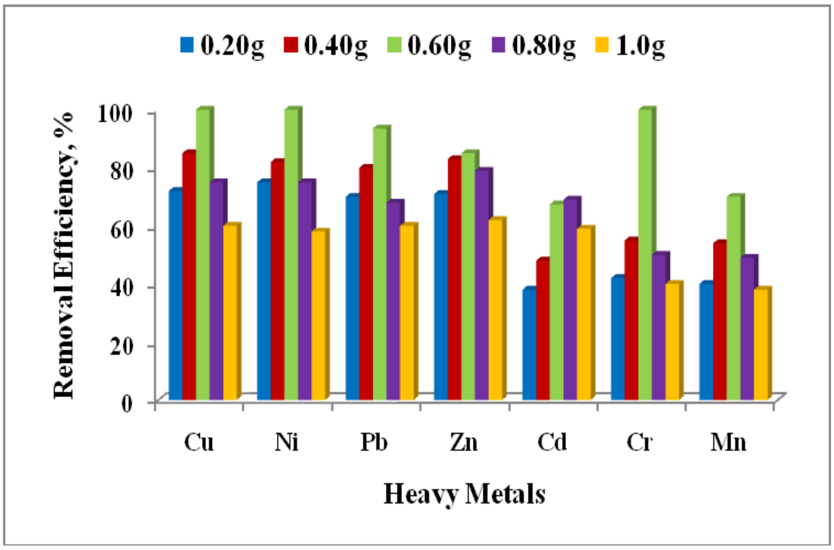


Figure 8.15: Effect of NaCl concentration on residual heavy metal concentration (initial heavy metal concentration= 5.0mg/L, applied voltage = 8V, pH= 6.0, electrolysis time = 30 min)

8.3.5.4 Effect of electro-coagulation time

Reaction time influences the efficiency of the electro-coagulation process. It determines the rate of production of iron (II) ions from iron electrode (Guo et al., 2006; El-Taweel et al., 2015). To investigate the effect of electro-coagulation time on heavy metal removal, experiments were carried out using solutions containing initial concentrations of different heavy metals (5.0mg/L) at applied voltage (8V) and subjected to different time of electro-coagulation (15, 30 and 60min). The results obtained after the electro-coagulation indicated that there was a decrease in the final concentration with an increase in EC time for the different heavy metals.

It is depicted in Figure 8.16 that there is dramatic reduction in the heavy metal ion concentrations within the first 30min. As shown in Figure 8.16, by increasing the electro-coagulation time after 15 min, the removal efficiency of heavy metals increased from 70 to100 % for Cu, 62 to 98% for Ni, 70 to 99% for Pb, 52 to 85% for Zn, 50 to 67% for Cd, 65 to100% for Cr and 40 to 70% for Mn, respectively. However, the removal efficiency was found to be very low when electrolysis time was increased beyond 30 min. This can be attributed to the fact that at short electrolysis time, the amount of ferric ions released from anode will not be adequate to generate iron hydroxide complexes necessary for destabilization and aggregation mechanisms involved in the electro-coagulation process (Kobya et al., 2006; El-Taweel et al., 2015).

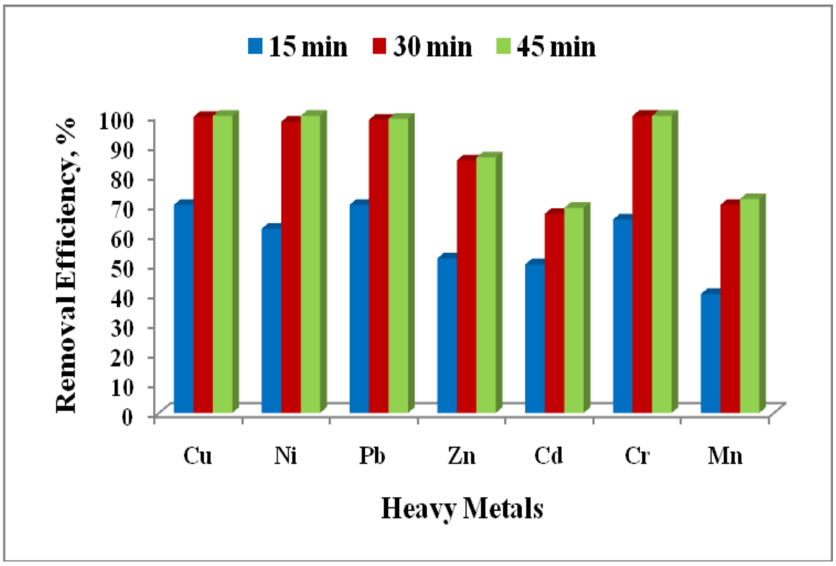


Figure 8.16: Variations of removal efficiencies of heavy metal ions with different electrolysis time (initial heavy metal concentration = 5.0mg/L, current = 8V, pH= 6.0, NaCl= 0.60g/L)

8.3.5.5 Energy and electrodes consumptions

In the electro-coagulation process, consumption of electrical energy and sludge production or the amount of electrode dissolved in solution demonstrate significant economical factor. The electrical energy consumption per unit volume of treated wastewater was calculated using the following equation (Martınez-Huitle & Brillas, 2009):

$$E = \frac{(P)\,(I)\,(t)}{V} \qquad 8.16$$

Where, E is the specific energy consumption in kWh/m^3, P is the voltage in V, I is the direct electrical current in A, t is EC time in hour and V is the volume of the wastewater in litres.

The amount of electrodes dissolved per unit volume of treated wastewater, was calculated theoretically using Faraday's law as follows (El-Taweel et al, 2015).

$$m_{Fe/Al} = \frac{1000\ (I)\ (t) \times Mwt_{Fe/Al}}{(Z_{Fe/Al})\ (F)\ (V)} \qquad 8.17$$

where $m_{Fe/Al}$ is the specific amount of dissolved electrode in kg/m^3, I is the current in A, t is the EC time in seconds, $Mwt_{Fe/Al}$ is the molecular weight of iron (55.845 g/mol) or Al (26.982 g/mol), $Z_{Fe/Al}$ is the chemical equivalence of Fe or Al (Z_{Fe} = 2), F is the Faraday constant (F = 96500 C/mol) and V is the volume of the treated wastewater in m^3.

Table 8.2: Electrical energy consumptions, amounts of electrodes dissolved, and removal efficiencies of heavy metals at different current density and electrolysis time with solution volume = 1L, pH = 6 and voltage= 8V

Current density (mA/m^2)	**t (min)**	**E (kWhr/m^3)**	**m_{Fe} (kg/m^3)**	**Removal of heavy metals (%)**						
				Cu^{2+}	**Ni^{2+}**	**Pb^{2+}**	**Zn^{2+}**	**Cd^{2+}**	**Cr^{3+}**	**Mn^{2+}**
1.5	15	3.0	0.623	72	71.12	70.5	65.40	60.63	70.5	60.70
1.5	30	6.0	0.979	81.60	84.0	82.6	79.5	68.50	80.9	70.55
1.8	15	3.60	0.807	78.5	78.80	78.40	75.25	66.90	78.60	69.0
1.8	30	7.20	1.251	100	97.01	100	89.34	69.47	100	78.5

Table 8.3: Electrical energy consumptions, amounts of electrodes dissolved, and removal efficiencies of nitrate at different current density and electrolysis time with solution volume = 1L, pH = 9 and applied voltage= 8V

Current density (mA/m^2)	**t (min)**	**E ($kWhr/m^3$)**	**m_{Al}(kg/m^3)**	**Nitrate**
1.5	60	12.0	1.920	60.20
1.5	80	15.96	2.152	70.5
1.8	60	14.4	2.08	69.50
1.8	80	19.152	2.310	75.60

Table 8.4: Electrical energy consumptions, amounts of electrodes dissolved, and removal efficiencies of COD at different current density and electrolysis time with solution volume = 1L, pH = 7 and applied voltage= 6V

Current density (mA/m^2)	**t (min)**	**E ($kWhr/m^3$)**	**m_{Al} (kg/m^3)**	**COD**
1.5	60	9.0	1.720	75.50
1.5	80	11.97	1.915	82.50
1.8	60	10.8	1.850	80.0
1.8	80	14.364	2.162	88.0

Table 8.2 to Table 8.4 explains the consumption of electrical energy and the amount of dissolved electrodes per one cubic meter of treated wastewater and the corresponding removal efficiencies of heavy metals, nitrate and COD, respectively at different current densities and treatment times. From the tables, it is clear that increasing current density and electro-coagulation time increases the removal efficiency, which is correlated with increasing both the specific electrical energy consumption and the dissolution of electrodes. In

order to maximize the removal efficiency at the operating conditions of this study, the current density must not be less than 1.8mA/cm^2 and EC treatment time should be in the range of 15 to 30 min for heavy metals and 60 to 80 min for nitrate and COD. These operating conditions reduce the specific energy consumption to the level of 3.60-7.20 kWh/m^3, 14.4-19.15 kWh/m^3, 10.8-14.36 kWh/m^3 for heavy metals, nitrate, COD, respectively and the specific amount of dissolved electrodes to the level of 0.81-1.25 kg/m^3, 2.08-2.31 kg/m^3, 1.85-2.16 kg/m^3 for heavy metals, nitrate, COD, respectively

The sludge generated in the electro-coagulation process might contain a variety of components which will harm the environment if no suitable treatment is considered. Hence, viable end-use of the sludge generated from EC reactor is an important problem in order to reduce its harmful impact on the environment. Landfill is the common used method for sludge disposal, however, sludge management and reuse became an interesting area in recent times, mainly when the sludge contains economic compounds like metallic hydroxides as in the present study.

8.4 Summary

This study investigated the removal of nitrate, COD and heavy metals such as Pb^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Cr^{3+} and Mn^{2+} from MSW landfill leachate by electro-coagulation technique. Experiments were conducted in a 1L reactor using aluminum and iron electrodes. Effects of different parameters including pH (3, 7, 9 and 12), electro-coagulation time (20, 40, 60, 80 and 100min), applied voltage (2, 4, 6 and 8V), supporting electrolyte, NaCl (0.20, 0.40, 0.60, 0.80 and 1.0g/L), electrode material (Fe and Al) and initial concentration of different parameters were studied in order to evaluate the efficiency of electro-coagulation. The highest removal efficiency of nitrate (75.10±0.20%) was observed under the following conditions: pH: 9, voltage: 8V, time: 80 minutes, NaCl concentration of 0.60g/L, initial nitrate concentration of 101.0±1.50mg/L and Al as sacrificial anode. For higher removal of COD, the optimal conditions were pH: 7, voltage: 6V, time: 80 minutes, NaCl: 0.60g/L, initial COD concentration of 3.40g/L, and Al as sacrificial anode. The highest removal efficiency for heavy metals was observed at pH 6, 8V, 30 minutes of electrolysis time, NaCl concentration of 0.60g/L, initial heavy metals concentration of 5.0mg/L and Fe as sacrificial anode. In addition, for optimal heavy metal removal, the pH of the leachate should be adjusted to neutral conditions. In order to minimize the energy consumption while maintaining higher removal efficiency, the current density must not be higher than 1.8mA/cm^2, with EC time in the range of 15 to 30 minutes for heavy metals and 60 to 80 min for nitrate and COD. This process consumes low amount of energy, making the process economically feasible technique and possible to scale up. The results indicated that the, electro-coagulation is a feasible technique for the treatment of multi-pollutants (e.g., organic, inorganic and heavy metals) from landfill leachate.

JASEELA C.”A STUDY ON THE SOIL AND WATER QUALITY OF SELECTED SITES AROUND SOLID WASTE DUMPING AREAS IN KERALA STATE”. THESIS. CWRDM (CENTRE FOR WATER RESOURCES DEVELOPMENT AND MANAGEMENT), UNIVERSITY OF CALICUT, 2018.

Chapter 9

TREATMENT OF WASTEWATER USING PHYTOREMEDIATION AND CONSTRUCTED WETLAND TECHNOLOGY

9.1 Introduction

Contamination of water by toxic pollutants has become a worldwide problem by the discharge of untreated municipal and domestic wastes, industrial wastewater, landfilling sites, etc., due to its harmful effects on human health and to the fauna and flora of receiving water. Wastewater mainly consists of organics with different biodegradable matter and inorganic matters such as ammonia, sulfate, cationic metals and heavy metals etc (Yalcuk & Ugurlu, 2009). The lack of proper wastewater treatment disposal methods and absence of environmental awareness are the important factors causing contamination in surface as well as water. Today, various wastewater treatment technologies are available; but most of the technologies have their own limitations because of the high capital, operational cost and generation of secondary wastes (Aksu, 2002; Herath & Vithanage, 2015). Thus considerable attention has been made in the potential use of a variety of natural biological systems to purify wastewater in a controlled manner during the past 20 years. Phytoremediation is a cost-effectiveness and eco-friendly technology, which uses green plants to remove pollutants from the environment or to render them harmless (Raskin et al., 1994; Herath & Vithanage, 2015). Phytoremediation through aquatic plants for the removal of pollutants and contaminants from various wastewaters is a well established environmental protection technique (Priya & Selvan, 2017).

9.1.1 Constructed wetlands for phytoremediation

Constructed wetlands are a plant-based cleanup technology for the remediation of wastewater by acting as a sink for various contaminants discharged from sewage, landfill leachate, agricultural and industrial wastewaters, and storm water runoff (Vymazal, 2005; Sheoran & Sheoran, 2006; Rai, 2008; Imfeld et al., 2009; Jomjun et al., 2010). It offers a low-energy, land-intensive, and less operational requirements substitute to conventional treatment methods (Wu et al., 2015). CWs are complex ecosystems designed to utilize the natural processes for treating wastewater. This system mainly comprised of vegetation, substrates, soil, water chemistry, and microorganisms, utilize complex processes involving physical, chemical, and biological mechanisms to assist in treating wastewaters (Vymazal, 2010; Saeed & Sun, 2012). The principal mechanisms by which wetlands remove pollutants includes sedimentation, sorption, filtration, biological processes and biochemical interactions. More than 150 macrophyte species have been used in CWs globally, but only a limited number of these plant species are very frequently planted in CWs (Vymazal, 2013). Currently, several studies have reported that CWs could be efficient for removing wide variety of pollutants including organic matter, nutrients, trace elements, pharmaceutical contaminants, pathogens, etc. from wastewater (Cui et al., 2010; Saeed & Sun, 2012).

9.1.2 Phytoremediation of heavy metals using aquatic plants

Contamination of the aquatic environment by heavy metals is a serious environmental problem, which threatens human health and aquatic ecosystems (Sasmaz et al., 2008). Phytoremediation of heavy metal from wastewater offers a promising technology and it utilizes the potential of plants to degrade, detoxify and inactivate the toxic contaminants (Miretzky et al., 2004; Mishra & Tripathi, 2008). Conventional metal removal techniques are quite costly, energy intensive and metal specific which includes sedimentation, adsorption, complexation, reverse osmosis, ion exchange, electrodialysis etc (Mishra & Tripathi, 2008). Aquatic macrophytes have high potential to accumulate heavy metals from the aquatic environments, hence these macrophytes have been used for heavy metal removal from wastewater (Singh & Sinha, 2005; Kumar et al., 2011).

Here we report our study on the recycling of wastewater with the objectives of: (1) to identify removal efficiency of horizontal flow constructed wetland planted with *Eichhornia Crassipes* and *Marsileaceae for* treating leachate, dairy effluent and canteen wastewater (ii) Phytoremediation of heavy metals such as Pb, Cd and Ni from synthetic wastewater using aquatic plants such as *Salvinia molesta, Azolla Caroliniana* and *Marsileaceae.*

9.2 Materials and Methods

Part I

9.2.1 Treatment of different types of wastewaters by constructed wetland technology

9.2.1.1 Method of sampling and analysis

Leachate sample was collected from Njeliamparamba MSW treatment plant in Kozhikode; and two types of effluents from dairy plant in Kozhikode and wastewater from CWRDM canteen, were used in this study. In addition, synthetic wastewater was prepared by artificially with spiking known concentration of heavy metals. The physico-chemical characteristics of influent samples were analysed and then the sample was added to CWS system for treatment. The leachate sample was diluted before applying into the wetland unit to avoid clogging of the soil pores and reduce the treatment efficiency.

The physico-chemical and bacteriological parameters of the influent and effluent samples were analyzed as per the standard methodology for the characterization of wastewater (APHA, 2012) and are explained in detail in chapter 3. The pH of the leachate was measured electrometrically with glass electrode pH meter. The chemical oxygen demand (COD) was measured by open reflux digestion method and concentration of sulphate was determined by turbidimetric method using Systronics Digital Nephelo-Turbidity meter 132. The analysis of nitrate and phosphorous was determined using UV Visible spectrophotometer (Thermo Scientific-Evolution 201). The synthetic heavy metals solution was prepared from reagent grade chemical by diluting 1000ppm stock standards solutions. The concentrations of heavy metals in water and plant samples were determined by Thermo M5 series Atomic Absorption Spectrophotometer. Escherichia coli (*E.coli*) and thermotolerant coliforms (TC) were determined by multiple tube fermentation technique.

9.2.1.2 Plants used in constructed wetlands

The plants used in CWs increases the residence time of water by reducing velocity and increase sedimentation of the suspended particles. Furthermore, they add oxygen and provide a physical site for microbial bioremediation. Wetland plants have been used to remove suspended solids, nutrients, heavy metals, toxic organic compounds, and bacteria (Sudarsan et al., 2015). The plants species such as *Eichhornia Crassipes* and *Marsileaceae* were used in this study.

9.2.1.2.1 Eichhornia Crassipes

Eichhornia crassipes or water hyacinth is a free-floating plant, growing plentifully in the tropical water bodies. It is an herbaceous perennial plant that belongs to the family pontederiaceae. It has the great reproduction potential and commonly forms dense, interlocking mats due to its rapid reproductive rate and complex root structure. It has a deep and resistant root system, extending up to 3m in depth with fast growth. It has fine purple flowers and an architectural aesthetic that can be well incorporated in landscape designs. Generally, *Eichhornia Crassipes* can tolerate pH values from 4.0 to 10.0. It has a huge potential for removal of the vast range of pollutants from wastewater and has the ability to grow in severe polluted waters. It is also used to improve the quality of water by reducing the levels of organic, inorganic nutrients and heavy metals. Presence of its fibrous root system and broad leaves help them to absorb higher concentrations of heavy metals. This capability makes them a potential biological alternative to secondary and tertiary treatment of wastewater.

9.2.1.2.2 *Marsileaceae*

*Marsilea minuta (*Marsileaceae), commonly called water clover or clover fern grows in low elevations. The *Marsileaceae* is a small family of heterosporous aquatic and semi-aquatic ferns. The group is commonly known as the pepperwort family or water-clover family because the leaves of the genus *Marsilea* superficially resemble the leaves of a four-leaf clover (a flowering plant). Members of the *Marsileaceae* are aquatic or semi-aquatic. Plants often grow in dense clumps in mud along the shores of ponds or streams, or they may grow submerged in shallow water with some of the leaves extending to float on the water surface. They grow in seasonally wet habitats, but survive the winter or dry season by losing their leaves and producing hard, desiccation-resistant reproductive structures.

9.2.1.3 Experimental design and sampling strategy

A laboratory scale horizontal flow constructed wetland (HFCW) was constructed using a rectangular tank with dimensions of 1m x 0.6m x 0.28m (L × W × H) with a total volume of 60 litres. A HFCW is large gravel and sand filled channel that is planted with aquatic vegetation and wastewater flows horizontally through the channel. The filter material filters out particles and microorganisms degrade organic materials that are present in wastewater (Herath & Vithanage, 2015). The wetland bed typically consisted of 4 layers and was filled with 36kg of large pebbles, 36 kg of small pebbles, 30 kg of sand, and 96 kg of soil. The top portion of the CW unit was filled with sandy clay loam soil to support vegetation. The maximum and minimum temperatures during the study period were 35°C and 25°C respectively. The inlet and outlet arrangement was performed and wastewater was fed manually into a storage container.

The experimental plants, water hyacinth (*Eichhornia crassipes*) and water clover (*Marsileaceae)* were collected from the wetlands in Kozhikode. The plants were cleaned using distilled water and were initially subject to acclimatization in tanks containing fresh water for one month and the second generations of the plants were used for the effluent treatment. Approximately 700g (fresh weight) of the *Eichhornia crassipes* and 300g of *Marsileaceae* plants were collected and planted in the constructed wetlands. The vegetation was planted by hand and normal water was used to grow plants. The constructed wetlands containing macrophytes were placed in the natural environment. The four water hyacinth plants were placed in two rows and in between these two rows of the plant *Marsileaceae* was planted. A one-week acclimatization period was set to stabilize the water hyacinth and *Marsileaceae*. The entire constructed wetlands containing macrophytes were placed in the natural environment. The Schematic representation of CW system is given in Figure 9.1.

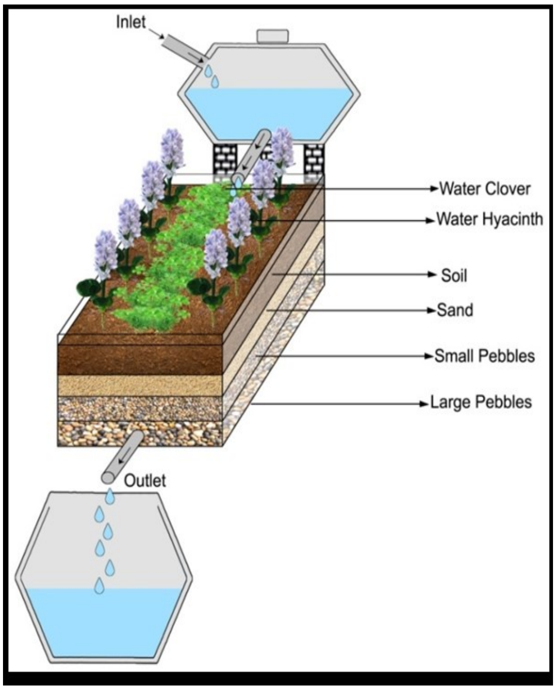


Figure 9.1: Schematic representation of CW **Plate 9.1:** Wetland constructed at CWRDM

The CW system was provided with 10^0 slopes with slight elevation at the bottom of backside of the tub. Sixty liters of the wastewater was added to CWs for treatment. The initial concentration of all the parameters in the wastewater samples were analyzed before introduction into the constructed wetlands. After 12 days of treatment, final concentrations in effluent samples were analyzed for pH, COD, TDS, TSS, nitrate-N, chloride, sulphate, phosphate, oil and grease, heavy metals, total coliforms and *E.coli* according to the standard method (APHA, 2012). The reduction in concentration of various parameters during 0 to 12-day period was compared and analyzed. Triplicate of each experiments were done. Treatment efficiency was calculated from the percentage of removal for each parameter and was evaluated according to equation 9.1.

$$\text{Removal efficiency } \% = C_i - C_e / C_i * 100 \qquad (9.1)$$

Where Ci and Ce are the influent and effluent concentrations of a given pollutant (mg/L)

9.2.1.4 Metals Accumulation

After treatment, the plants were harvested and then separated into shoots and roots, and were analyzed for heavy metal accumulation. The plant parts were dried in an oven at 70°C for 72 hr and the dry weight were recorded by electronic balance. 0.20g of plant parts were digested at 150°C for 200 min with 10 ml mixtures of $HNO_3/HClO_4$ (4:1) (Qu et al, 2011). After complete digestion, the volumes of digested samples were adjusted to 20 ml with distilled water and the contents of metals were determined by Thermo M5 series Atomic Absorption Spectrophotometer. In addition, the metals remained in the solution were measured to confirm the removal efficiency.

9.2.1.5 Bioconcentration and translocation factors

The bioconcentration factor (BCF) was calculated as the ratio of the heavy metal concentration in the plant tissues at harvest to the concentration of the metal in the external environment (Liao & Chang, 2004). BCF is calculated using the equation (9.2)

$$BCF = (P / E)_i \qquad (9.2)$$

Where i denotes the heavy metal and BCF is the bioconcentration factor and is dimensionless. P represents the heavy metal concentration in plant tissues (mg/kg dry wt); E represents the heavy metal concentration in the water (mg/L). A larger ratio implies better phytoaccumulation capability.

Translocation ability (TA) was calculated by dividing the concentration of a heavy metal accumulated in the root tissues by that accumulated in shoot tissues (Liao & Chang, 2004; Wu & Sun, 1998). TA is calculated using the equation (9.3)

$$TA = (A_r / A_s)_I \qquad (9.3)$$

Where *i* denote the heavy metals, TA is the translocation ability and is dimensionless. A_r represents the amount of heavy metal accumulated in the roots (mg/kg dry wt), and A_s represents the amount of heavy metal accumulated in the shoots (mg/kg dry wt). A larger ratio implies poorer translocation capability.

Part II

9.2.3 Phytoremediation of Pb, Cd and Ni from synthetic solution using aquatic plants

9.2.3.2 Aquatic plants used for phytoremediation

The effectiveness of commonly available free floating aquatic plant species such as Giant Salvinia (*Salvinia molesta),* water Fern *(Azolla Caroliniana)* and also submerged aquatic species Water Clover (*Marsileaceae)* to remediate heavy metal contaminated water was investigated.

9.2.3.2.1 Salvinia molesta

Salvinia molesta, commonly known as giant salvinia or kariba weed. It is a free floating plant that does not attach to the soil, but instead remains buoyant on the surface of a body of water. The fronds are 0.5 to 4cm long and broad, with a bristly surface caused by the hair-like strands that join at the end to form eggbeater shapes. They are used to provide a waterproof covering. These fronds are produced in pairs also with a third modified root-like frond that hangs in the water. *Salvinia molesta* has been used to extract nutrients and pollutants from the water.

9.2.3.2.2 Marsileaceae

The details of *Marsileaceae* plant species are discussed in part 1.

9.2.3.2.3 Azolla Caroliniana

Azolla Caroliniana is a freshwater aquatic fern, with scale-like fronds 5-10 mm long, green to reddish, most often reddish in strong light and in winter. They are covered in fine hairs (with their roots hanging in the water) that give it the appearance of velvet. It is able to fix nitrogen from the air by means of symbiotic cyanobacteria. It is a better macrophyte for aquatic phytoremediation because of its short doubling time (2 to 3 days), easy harvest, nitrogen fixation ability and tolerance to accumulate heavy metals.

9.2.3.3 Experimental design and sampling strategy

Plastic dishes of same size were taken for setting the experiments and 10 litre of synthetic heavy metal solution was taken in each tank. The replicated wastewater was made by dissolving $Pb (NO_3)_2$, $Ni (NO_3)_2$, and $(3CdSO_4).8H_2O$ in tap water. In each case 100g of plants material were taken in the 10 liter solutions in the plastic dish and it was artificially spiked with 1.0mg/L of Pb and Ni, 0.50mg/L of Cd. Water samples were analyzed at different intervals (0, 3, 7, 14, and 21 days) to find out the removal capacity. Four tanks (45 × 30 × 15cm) were setup with different operating conditions (Plate 9.2 to Plate 9.5).

Tank 1**:** Control (synthetic heavy metal solution without plant)
Tank 2: Treatment 1 (synthetic heavy metal solution with Salvinia molesta)
Tank 3: Treatment 2 (synthetic heavy metal solution with Marsileaceae)
Tank 4: Treatment 3 (synthetic heavy metal solution with *Azolla Caroliniana*)

Plate 9.2: Control

Plate 9.3: Treatment 1

Plate 9.4: Treatment 2

Plate 9.5: Treatment 3

9.2.3.4 Heavy metal analysis in plant

After treatment, the plants of the four units (treatments) were sampled, harvested and rinsed with tap water twice and deionized water three times. Then the plant samples were separated into shoots and roots, and were analyzed for heavy metal accumulation. The procedure for the extraction and analysis of heavy metals in plant is given in part 1. The shoot and root of studied plants are depicted in Plates 9.6 to 9.8.

Plate 9.6: Leaf and Root of *Salvinia molesta*

Plate 9.7: Leaf, stem and root of *Marsileaceae*

Plate 9.8: Leaf of Azolla Caroliniana

9.3 Results and Discussions

Part 1

9.3.1 Treatment of different types of wastewaters by constructed wetland technology

Table 9.1 to Table 9.4 shows the reduction in concentration of various parameters of MSW landfill leachate, dairy effluent, canteen wastewater, and synthetic wastewater at different contact time.

Table 9.1: Reduction in concentration of various parameters in the leachate with respect to time

Parameters	Before treatment, C^i	Reduction in concentrations of leachate at different contact time		
		Day- 4	Day-8	Day-12
pH	4.54±0.20	4.90±0.1	5.20±0.15	5.80±0.12
TDS, (mg/L)	11250.0±24.50	7500.0±16.50	5250.0±12.2	2500.0±9.60
TSS, (mg/ l)	1760±9.0	1200.0±8.50	950.0±7.0	632.60±4.0
Sulphate, (mg/L)	792.0±4.50	550.0±4.50	380.0±5.0	270.0±5.50
Phosphate, (mg/L)	65.0±1.0	40.80±1.60	25.20±1.0	ND
Nitrate, (mg/L)	101.0±1.50	75.0±2.0	56.10±1.30	25.5±1.0
Chloride, (mg/L)	2454.0±6.50	1800.0±9.0	1100.0±8.60	760.0±7.0
Oil and grease, (mg/L)	1915.0±9.0	1300.0±5.0	850.0±9.0	450.0±8.0
COD, (mg/L)	3401.0±14.20	2400.0±16.50	1600.0±8.50	911.20±11.0
Fe, (mg/L)	30.0±3.2	20.5±0.10	10.6±1.20	6.50±1.0
Cd, (mg/L)	0.12±0.10	0.08±0.02	ND	ND
Ni, (mg/L)	1.12±0.20	0.70±0.01	0.20±0.01	ND
Pb, (mg/L)	0.22±0.12	0.10±0.01	ND	ND

ND-Not Detected

Table 9.2: Reduction in concentration of various parameters in the diary effluent with respect to time

Parameters	Before treatment, C^i	Reduction in concentrations of dairy effluent with respect to time		
		Day- 4	Day-8	Day-12
pH	8.9 ±1. 0	7.8±0.8	7.20±0.70	6.8±0.50
TDS, (mg/L)	637.0±4.50	300. 0±9.50	108.0±7.0	38.0±4.0
TSS, (mg/L)	90.0±1.3	32.0±1.50	30.5±1.0	8.0±0.80
Sulphate, (mg/L)	80.0±2.0	35.0±1.0	18.0±0.9	ND
Phosphate, (mg/L)	8.50±0.20	2.8±0.80	ND	ND
Nitrate, (mg/L)	1.20 ±1.0	ND	ND	ND
Chloride, (mg/L)	350.0±1.50	158.0±4.0	76.5±2.0	24.0±0.50
Oil and grease, (mg/L)	1250.0±9.0	350.0±6.0	150.50±4.50	40.20±3.10
COD, (mg/L)	1700.0±7.0	900.0±11.0	300.0±9.0	205.0±7.20
Total Coliforms, MPN/100ml	≥2400	1600.0	920.0	100.0
E. coli, MPN/100ml	Present	Present	Present	Absent

ND-Not Detected

Table 9.3: Reduction in concentration of various parameters in the canteen wastewater with respect to time

Parameters	Before treatment, C^i	Reduction in concentrations of canteen wastewater at different contact time		
		Day- 4	Day-8	Day-12
pH	6.0±0.10	6.25±0.20	6.40±0.2	6.60±0.10
TDS, (mg/L)	287.0±3.0	105.0±1.50	58.5±0.9	11.56±0.50
TSS, (mg/L)	220.0±2.1	106.5±2.0	40.0±1.0	15.0±0.80
Sulphate, (mg/L)	30.0±1.0	15.5±0.50	2.0±0.8	ND
Phosphate, (mg/L)	2.1±0.1	ND	ND	ND
Nitrate, (mg/L)	25.0±0.8	7.5±0.20	ND	ND
Chloride, (mg/L)	263.0±2.5	102.0±2.0	45.0±1.5	ND
Oil and grease, (mg/L)	102.8±1.3	45.6±0.80	6.5±0.20	ND
COD, (mg/L)	978.0±10.0	400.0±8.0	150.0±5.60	46.0±4.0
Total Coliforms, MPN/100ml	1100.0	100.0	ND	ND
E.coli, MPN/100ml	Present	Present	Absent	Absent

ND-Not Detected

Table 9.4: Percentage removal of synthetic wastewater spiked with heavy metals

Parameters	Before treatment, C^i	Reduction in concentrations of synthetic wastewater in different contact time		
		Day- 4	Day-8	Day-12
Pb, (mg/L)	0.998±0.01	0.597±0.20	0.356±0.20	0.125±0.10
Ni, (mg/L)	2.097±0.01	1.56±1.50	0.95±0.90	0.45
Cd, (mg/L)	0.499±0.001	0.306±2.0	0.192±1.0	0.098±0.60

9.3.1.1 Removal of various physico-chemical parameters

The results showed that the CWs system reduced the concentration of all parameters. pH is the most important parameter in the biosorptive process: it affects the solution chemistry of the metals, the activity of the functional groups in the biomass and the competition of metallic ions (Sukumaran et al., 2013). The average pH values obtained for leachate, dairy effluent and canteen wastewater were 4.54, 8.90 and 6.0, respectively (Table 9.1 to 9.3). After 12 days of treatment, the pH was changed at a regular interval to neutral or close to neutral pH values. The reduction in pH is due to the absorption of pollutants by plants. Also, the change in pH favoured microbial action to degrade BOD and COD contained in the wastewater (Mahmood et al., 2005). Figure 9.2 to 9.4 shows the percentage removal of various physio-chemical parameters of leachate, dairy effluent, and canteen wastewater at different contact time. The results indicated that as the detention time increases, the percentage removal is also increased.

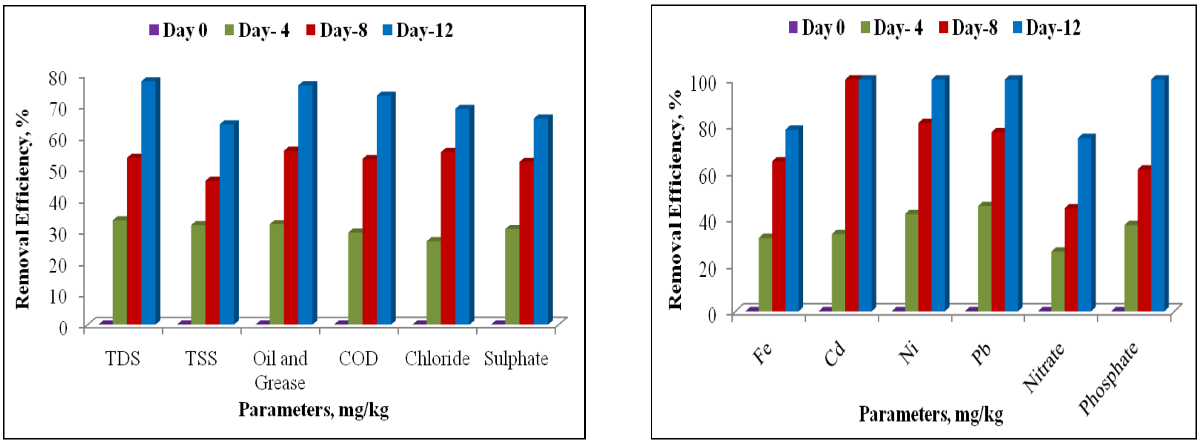


Figure 9.2: Percentage removal of various physico-chemical parameters of leachate at different contact time

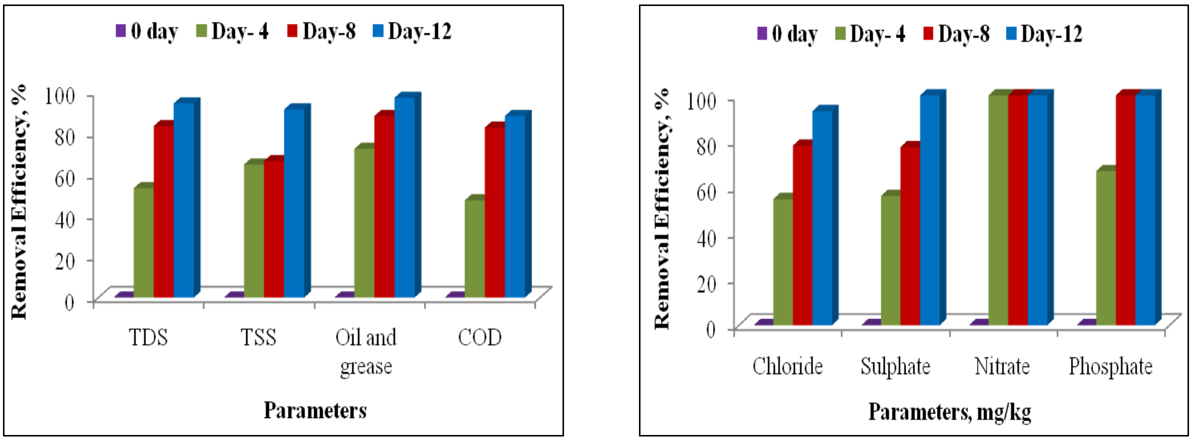


Figure 9.3 : Percentage removal of various physico-chemical parameters of the dairy effluent at different contact time

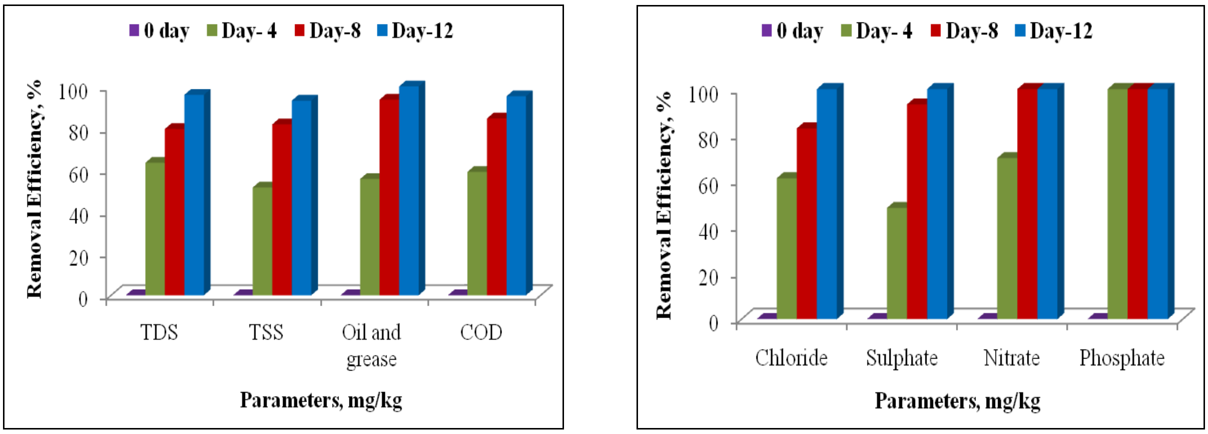


Figure 9.4: Percentage removal of various parameters of canteen wastewater at different contact time

Total dissolved solids are frequently used to express the degree of contamination or amount of solids in water and wastewater. TDS values obtained in the three types of wastewater after 12 days of treatment were reduced considerably by 77.77% (with C^i of 11250.0mg/kg) for leachate, 94.03% (with C^i of 637.0 mg/kg) for dairy effluent and 96.0% (with Ci of 287.0 mg/kg) for canteen wastewater. For suspended solids, the mean efficiency removal was about 64.0±1.3% (C^i of 1760.0mg/kg) for leachate, 91.0±1.0% (C^i of 90.0 mg/kg) for dairy effluent, and 93.01.2±% (C^i of 220.0mg/kg) for canteen wastewater. Reduction in TSS occurs mainly through physical mechanisms like filtration and sedimentation (Andreo-Martínez et al., 2016).

The presence of aquatic plants in wastewater can reduce dissolved CO_2 during the stage of high photosynthetic activity. This photo-synthetic activity increases the dissolved oxygen in wastewater; hence generate aerobic conditions in water which favor the aerobic bacterial activity to reduce the BOD and COD (Mahmood et al., 2005). The percentage removals of COD obtained for leachate, dairy effluent and canteen wastewater were 73.20% (C^i of 3401.0mg/kg), 87.94% (C^i of 1700.0mg/kg) and 95.29% (C^i of 978.00mg/kg), respectively. This reduction in COD mainly occurs through the absorption of organic matter physically or chemically by the soil particles and gravel surfaces, and subsequently decomposed by microorganisms (Latrach et al., 2015). Organic matter in the wastewater is an important carbon source for microorganisms. The percentage removal of oil and grease obtained were 76.50% (C^i of 1915.0mg/kg), 97.0% (C^i of 1250.0mg/kg) and 100% (C^i of 102.80mg/kg) for leachate, dairy effluent and canteen wastewater, respectively

The removal efficiency of NO_3-N obtained in the present study were 74.75% (C^i of 101.0mg/kg) for leachate, 100% for dairy effluent (C^i of 1.20mg/kg) and canteen wastewater (C^i of 25.0mg/kg) within 12 days. The nitrate removal mechanism takes place in constructed wetland by the uptake of nitrogen by plants and other living organisms followed by nitrification, denitrification, ammonia volatilization and cation exchange for ammonium (Yalcuk & Ugurlu, 2009). The complete removal of phosphate (100%) was obtained within 12 days for leachate; and 8 days for dairy and canteen wastewater. Phosphate abatement mechanisms takes place through physical (sedimentation), chemical (adsorption, precipitation with Fe, Al and Ca ions, complex formation with Ca and Mg ions) and biological process such as microbial and plant assimilation (Rossmann et al., 2012). The percentage removal of sulphate was 52.0±1.30% (C^i of 792.0mg/kg) for leachate; and 100% removals were obtained for dairy effluent and canteen wastewater.

9.3.1.2 Bacterial removal

Bacterial reduction in constructed wetland is normally attributed to diverse mechanisms. This includes physical (aggregation and adsorption, filtration and sedimentation), chemical (affected by oxidative destruction and other microorganisms or plants toxins), and biological (natural death, consumed by bacteriophages, lytic bacteria, and protozoa) (Al-Maliky et al., 2018). The percentage removal of total coliforms obtained in the dairy effluent and canteen wastewater is depicted in Figure 9.5 and 9.6. The total coliform level in the dairy influent was ≥2400 MPN/100ml, and after treatment, it was reduced by 100 MPN/100ml. *E.coli* was found to be absent after 12 days in dairy effluent and 8 days in canteen wastewater.

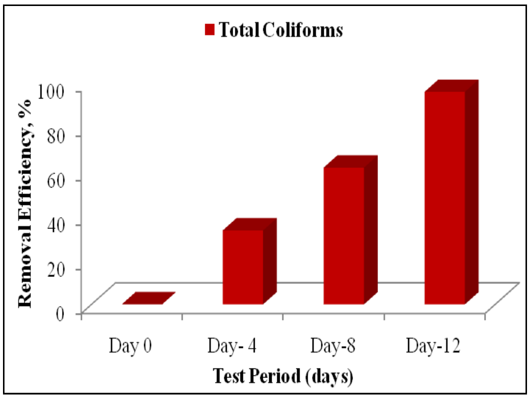


Figure 9.5: Percentage removal of total coliforms in canteen wastewater

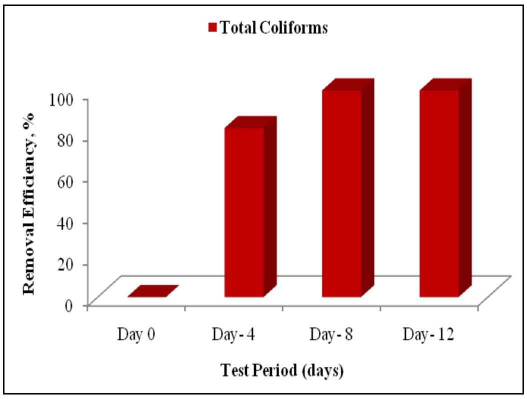


Figure 9.6: Percentage removal of total coliforms in dairy effluent

9.3.1.3 Heavy metal removal

The heavy metal removal in constructed wetlands is very complex processes comprising of a combination of biotic and abiotic reactions. This process includes sedimentation, flocculation, adsorption, precipitation, co-precipitation, oxidation and reduction, cation and anion exchange, complexation, microbial activity and plant up-take. The heavy metals in CWs cannot be destroyed, but their chemical and physical characteristics are modified (Ujang et al., 2005). The percentage removal of heavy metals in synthetic wastewater was; Pb (94.0 %), Ni (86.80%) and Cd (80.36%) with initial concentrations of 0.998 mg/kg of Pb, 2.097mg/kg of Ni and 0.499mg/kg of Cd. The percentage removal of artificially spiked heavy metals *viz*. lead, nickel and cadmium were given in Figure 9.7. Bioconcentration factor of the wetland plants used were also quantified.

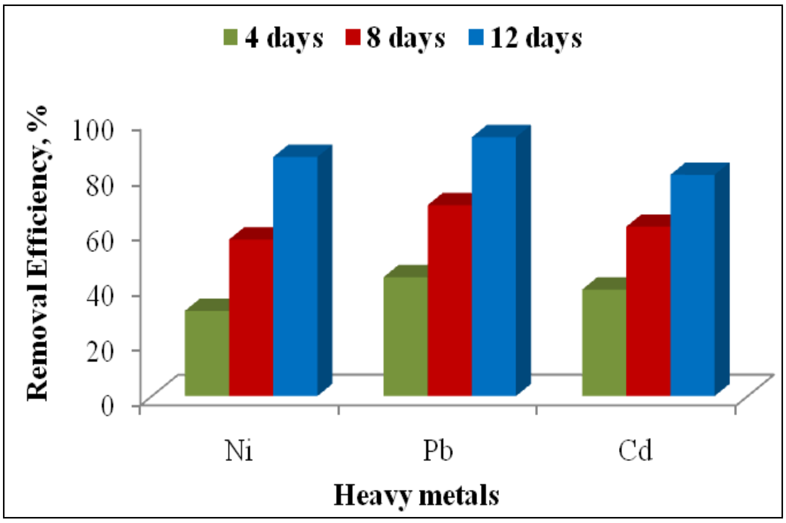


Figure 9.7: Percentage removal of heavy metals at different contact time

9.3.1.3.1 Accumulation of heavy metals by macrophytes

In the present study, *Eichhornia Crassipes* and *Marsileaceae* plants have accumulated Pb, Ni and Cd at varied levels in their tissues (Figure 9.8).

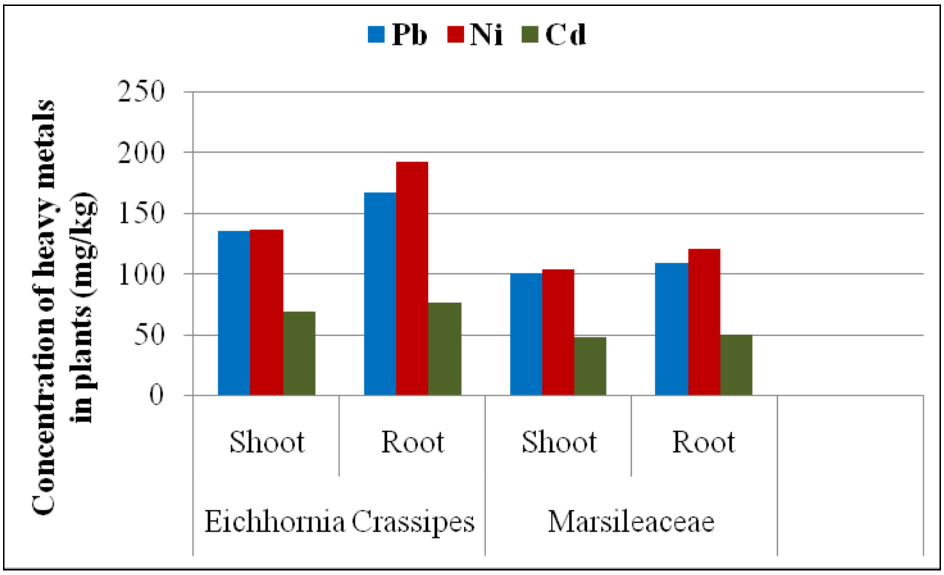


Figure 9.8: Concentration of heavy metals in the studied plant tissues

The experiment showed that the maximum accumulation of heavy metals were observed in *Eichhornia Crassipes* than in *Marsileaceae*. *Eichhornia Crassipes* accumulated the highest concentration of metals in roots than shoot. The higher removal efficiency of heavy metals by *Eichhornia Crassipes* could be due to extensive adventitious root system, which absorbs toxic substances from wastewaters. The concentration of Pb, Ni and Cd in the root tissues of *Eichhornia Crassipes* were 109.50mg/kg dry wt, 121.20mg/kg dry wt and 50.20mg/kg dry wt, whereas the corresponding shoot values were 101.20 mg/kg dry wt, 104.50mg/kg dry wt and 48.70mg/kg dry wt for Pb, Ni and Cd respectively.

Bioconcentration factor (BCF) is a useful parameter to evaluate the potential of plants for accumulating heavy metals. Higher BCF values reflect the higher phytoaccumulation capacity. The BCFs of metals in the studied plants are presented in Figure 9.9. The BCFs value obtained for *Eichhornia crassipes* were 303.71, 156.84 and 291.38 respectively for Pb, Ni and Cd; whereas the BCFs value of *Marsileaceae* were 211.12, 107.63 and 198.20 respectively for Pb, Ni and Cd. Maximum values of BCF was obtained in *Eichhornia crassipes* compared to *Marsileaceae.*

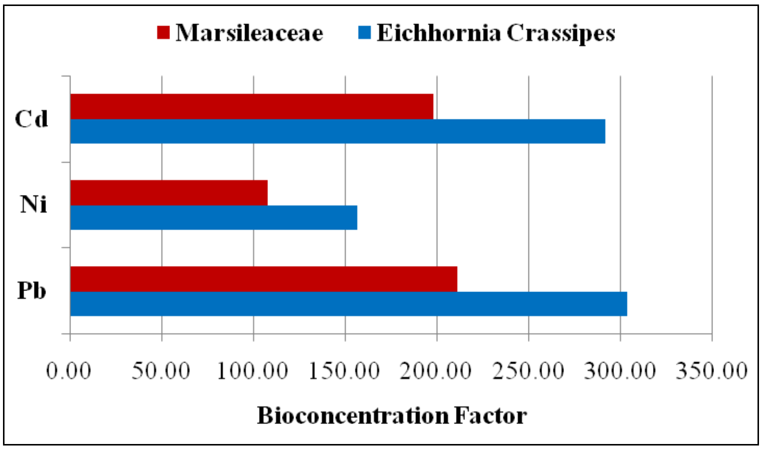


Figure 9.9: Bioconcentration factor of metals in the studied plants

Translocation ability was determined by dividing the concentration of a trace element accumulated in the root tissues by that accumulated in shoot tissues. Translocation of trace elements from roots to shoots is a limiting factor for the bioconcentration of elements in shoots (Lu et al., 2004). Larger ratio implies poorer translocation capability). Translocation ability of *Eichhornia crassipes* and *Marsileaceae* plants for Cd, Pb and Cu in the present study are graphically shown in Figure 9.10.

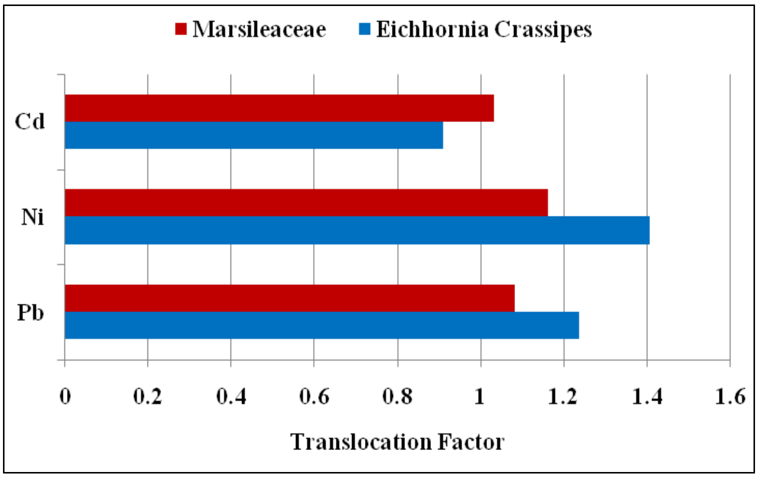


Figure 9.10: Translocation ability of *Eichhornia crassipes and Marsileaceae*

TF>1 indicates an efficient ability to transport metals from root to shoot, most probably due to efficient metal transporter system and possibly sequenstration of metals in leaf vacuoles and apoplast (Kumar et al., 2011; Lasat et al., 2000). In the present study, *Eichhornia crassipes and Marsileaceae* plants showed a root to shoot translocation factor of greater than 1 for all the metals except Cd in the case of *Eichhornia crassipes.This* indicated the lower translocation ability of Cd in *Eichhornia crassipes;* which shows that a small amount of Cd had moved into shoots. These can be explained by the fact that heavy metals were retained in the cation exchange sites of the vessel walls of xylem parenchyma cells in roots and immobilized in the vacuoles of the root cells (Qu et al., 2011). The normal TF values obtained for Pb and Ni in *Eichhornia crassipes* and *Marsileaceae* plants indicated the regular translocation ability of these heavy metals.

PART 2

9.3.2 Phytoremediation of lead, cadmium and nickel from synthetic solution using aquatic plants

This study investigated the phytoremediation potential of *Salvania molesta, Marsileaceae* and *Azolla Caroliniana* for the removal of lead, nickel and cadmium from synthetic wastewater. The characteristics of synthetic heavy metal solution are discussed in Table 9.5.

Table 9.5: Characteristics of synthetic heavy metal solution

Parameters	Values
pH	6.46±0.50
EC, (µS/cm)	258.0±1.30
TDS, (mg/L)	180.0±1.0
Pb, (mg/L)	0.9532±0.0221
Ni, (mg/L)	0.8016 ±0.011
Cd, (mg/L)	0.4837±0.001

9.3.2 .1 Effect of phytoremediation on heavy metal removal

The removal of Pb, Ni and Cd by phytoremediation techniques using aquatic plant species such as *Salvania molesta, Marsileaceae* and *Azolla Caroliniana* was investigated. The concentrations of metals remained in the water were significantly decreased when the contact times were increased. The concentration of heavy metals in the water was analyzed for each sample collected during the study period at an interval of 7 days using AAS. The result indicated that *Salvania molesta* and *Marsileaceae* could remove Pb, Ni and Cd efficiently.

9.3.2.2 Removal of Pb from synthetic heavy metal solution

Salvinia Molesta and *Marsileaceae* plants could remove Pb by 97% and 95% within 21 days. *Azolla Caroliniana* was also reduced Pb by 41.0% and found to decay within 14 days. The reduction in concentration of Pb remained in the solution after phytoremediation is presented in Table 9.6 and its percentage removal is graphically represented in Figure 9.11.

Table 9.6: Reduction in concentration of Pb by different aquatic plants

	Concentration of Pb in wastewater, mg/L			
Days	**Control**	***Salvinia Molesta***	***Marsileaceae***	***Azolla Caroliniana***
0	0.9532±0.024	0.9522±0.022	0.9503±0.021	0.9529±0.024
3	0.8723±0.021	0.3012±0.02	0.3117±0.021	0.6890±0.024
7	0.8228±0.02	0.1539±0.009	0.1720±0.008	0.60±0.008
14	0.6049±0.021	0.0380±0.006	0.0494±0.005	0.3563±0.006
21	0.6002±0.021	0.0195±0.002	0.0249±0.001	decay

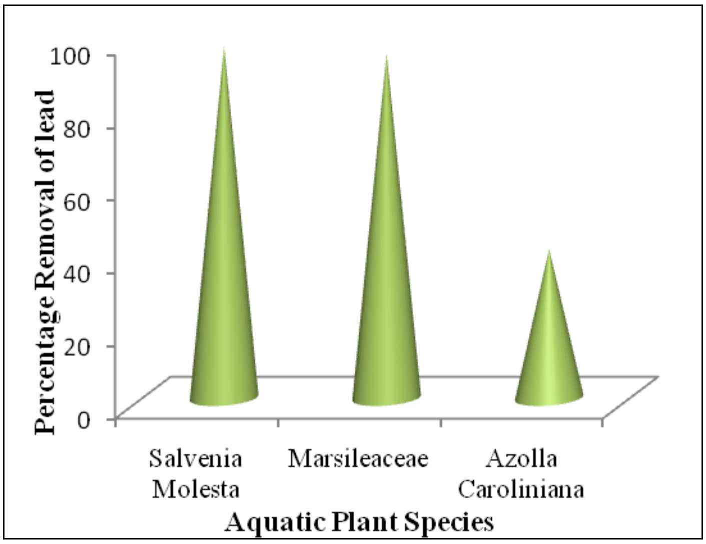


Figure 9.11: Comparison of lead removal efficiencies using different aquatic plant species

9.3.2.3 Removal of Ni from synthetic heavy metal solution

The phytoremediation using Salvinia Molesta reduced nickel by 94% and *Marsileaceae* by 93% within 21 days, and the plants were found to decay after 21 days. *Azolla Caroliniana* was found to decay after 14 days. The reduction in concentration of Ni remained in the solution after phytoremediation is presented in Table 9.7 and its percentage removal is graphically represented in Figure 9.12.

Table 9.7: Reduction in concentration of Ni by different aquatic plants

	Reduction in concentration of Ni, mg/L			
Days	**Control**	***Salvinia Molesta***	***Marsileaceae***	***Azolla Caroliniana***
0	0.8016±0.022	0.8013±0.021	0.80±0.022	0.8015±0.021
3	0.799±0.021	0.5930±0.02	0.5724±0.021	0.70±0.022
7	0.7095±0.02	0.3934±0.01	0.3386±0.011	0.5698±0.012
14	0.6116±0.02	0.1418±0.008	0.1372±0.009	0.3914±0.008
21	0.6012±0.01	0.0370±0.006	0.0410±0.007	decay

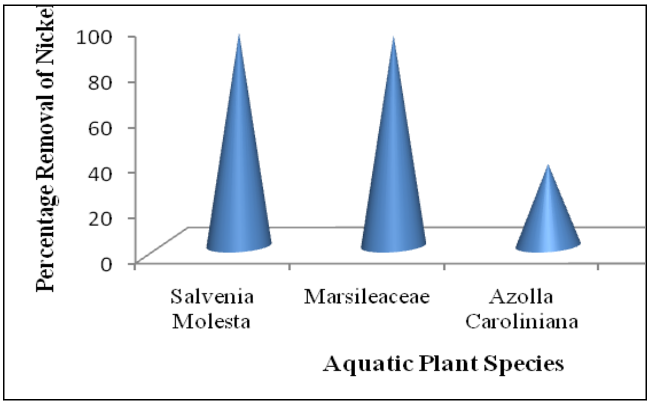


Figure 9.12: Comparison of nickel removal efficiencies of using different aquatic plant species

9.3.2.4 Removal of cadmium from synthetic heavy metal solution

Salvinia Molesta, Marsileaceae and *Azolla Caroliniana* removed cadmium by 92.0%, 87.0% and 26.0% respectively. Reduction in concentration of Cd by different aquatic plant species are presented in Table 9.8 and its removal efficiency are represented in Figure 9.13.

Table 9.8: Percentage removal of Cd by different aquatic plants

	Reduction in concentration of Cd in wastewater, mg/L			
Days	**Control**	***Salvinia Molesta***	***Marsileaceae***	***Azolla Caroliniana***
1	0.4837±	0.4835±0.008	0.4836±0.009	0.4830±0.007
3	0.4516±	0.3305±0.005	0.3502±0.0055	0.4265±0.006
7	0.4191±	0.1589±0.002	0.2265±0.002	0.3564±0.004
14	0.4012±	0.0885±0.001	0.0999±0.002	0.2968±0.005
21	0.40±	0.0336±0.001	0.0528±0.001	decay

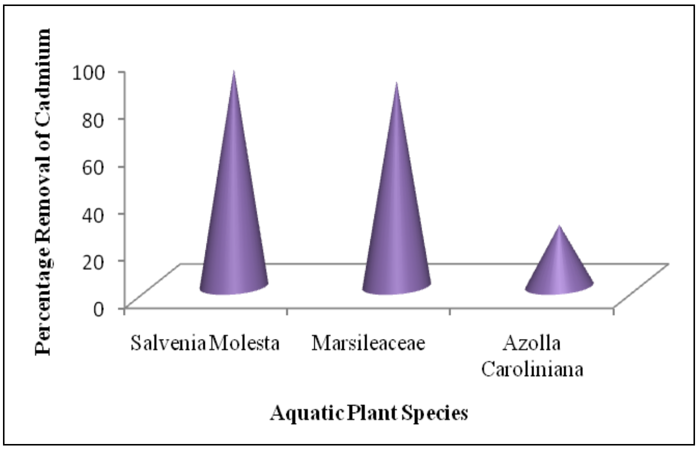


Figure 9.13: Comparison of cadmium removal efficiencies using different aquatic plant species

The uptakes of Pb, Ni and Cd by *Solvania molesta* were 97%, 94% and 92% respectively, and that of *Marsileaceae* were 95%, 93%, and 87%, respectively within 21 days of treatment. The experimental plant could not survive the high accumulation of the heavy metals and was found to decay after 21 days in the case of *Salvania molesta* and *Marsileaceae* after 14 days in the case of *Azolla Caroliniana.* Remediation of heavy metals in water using different aquatic plants showed that *Salvinia molesta* and *Marsileaceae* was more efficient than *Azolla Caroliniana.* The maximum removal efficiency of heavy metals were obtained within 21 days**.** Confirmation of the experiment was done by the extraction of different metals within the plant residue and the corresponding decrease of metals in the water.

9.3.2.5 Heavy metals accumulated in plant tissues

Figure 9.14 shows the concentration of heavy metals in the root and shoot of *Salvinia Molesta, Marsileaceae* and *Azolla Caroliniana*.

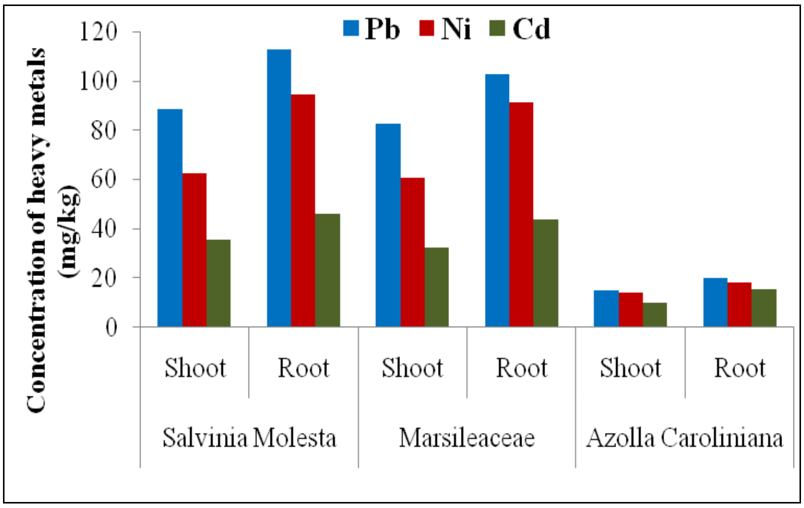


Figure 9.14: Concentration of heavy metals in different parts of the aquatic plants

The results indicated that all the aquatic plants have accumulated Pb, Ni and Cd at higher levels in their root than shoot. The Pb, Ni and Cd accumulation pattern in the studied plants was observed as *Salvinia Molesta*> *Marsileaceae* > *Azolla Caroliniana.*The concentration of Pb, Ni and Cd in the root tissues of *Salvinia Molesta* were 112.50mg/kg dry wt, 94.50mg/kg dry wt and 46.20mg/kg dry wt, whereas the corresponding shoot values were 88.50mg/kg dry wt, 62.40mg/kg dry wt, 35.60mg/kg dry wt for Pb, Ni and Cd respectively. The BCFs of metals obtained in the studied plants are presented in Figure 9.15.

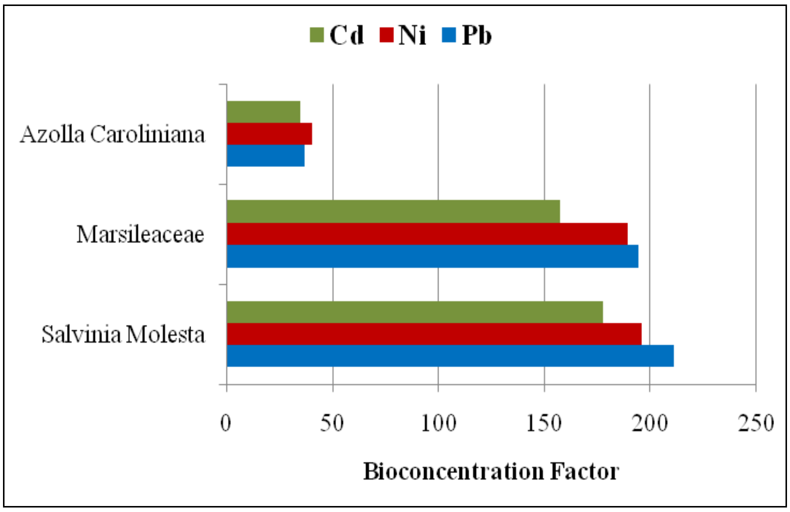


Figure 9.15: Bioconcentration factor of heavy metals in different aquatic plants

The BCFs value obtained for *Salvinia Molesta* were 210.86, 195.73 and 17.38 respectively for Pb, Ni and Cd; whereas the BCFs value of *Marsileaceae* were 194.08, 189.30 and 157.32 respectively for Pb, Ni and Cd. Low BCF value was obtained (36.93, 40.41 and 34.73 for PB, Ni and Cd) for *Azolla Caroliniana*. Maximum BCF values were obtained for *Salvinia Molesta* and *Marsileaceae* compared to *Azolla Caroliniana*.

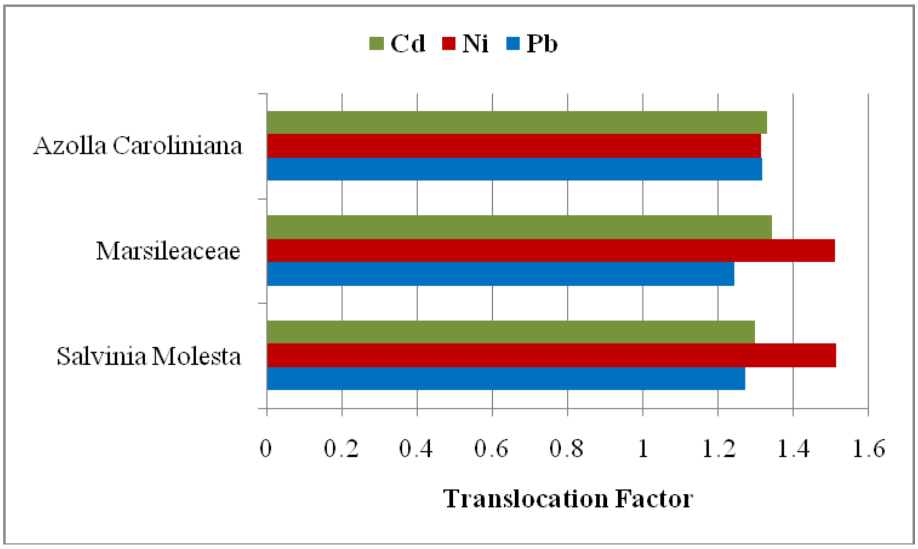


Figure 9.16: Translocation ability of heavy metals in different aquatic plants

Figure 9.16 shows the TF of metals in the studied plants. The results indicated that all the three studied plants showed a root to shoot translocation factor of greater than 1 for all the metals. Among the studied plants, translocation factor ranged between 1.31-1.27, 1.51-1.33 and 1.34-1.29 for Pb, Ni and Cd, respectively. TF>1 indicates, the efficient ability to transport metals from root to shoot; hence these plants are effectively transported metals from root to shoot.

9.4 Summary

Developing cost effective and environmental friendly technologies for the remediation of wastewaters polluted with toxic substances is a topic of global interest. The treatment of wastewater using horizontal flow constructed wetlands vegetated with *Eichhornia crassipes* and *Marsileaceae* were investigated. The monitoring of constructed wetlands showed that the performance of the system was good and it was effectively removed high concentration of pollutants such as COD, TDS, TSS, oil and grease, nitrate, phosphate, sulphate, bacteria and heavy metals within a few days under local conditions. The percentage removal of heavy metals by constructed wetland in synthetic wastewater was 94%, 86.80% and 80.36% for Pb, Ni and Cd respectively within 12 days. The experiment also showed that the maximum accumulation of heavy metals were observed in *Eichhornia Crassipes* than in *Marsileaceae.* It is due to the extensive adventitious root system *of Eichhornia Crassipes*, which absorbs toxic substances from wastewaters. The advantage of constructed wetlands is easy and cheap to construct. They are a suitable alternative for wastewater purification.

The phytoremediation using aquatic plant species such as *Salvinia molesta, Azolla Caroliniana* and *Marsileaceae* were used to remediate heavy metal contaminated water. The study revealed that the *Salvania molesta* and

Marsileaceae could remove Pb, Ni and Cd efficiently (>90.0%) within 21 days of treatment. Results from analysis confirmed the accumulation of different metals within the plants and a corresponding decrease of metals in the water. Maximum bioconcentration factor was obtained for *Salvinia Molesta* and *Marsileaceae* compared to *Azolla Caroliniana*. TF of metals in the studied plants showed a root to shoot translocation factor of greater than 1 for all the metals; hence these plants are effectively transported metals from root to shoot. Thus, these plant species can be used for the phytoremediation of aquatic water bodies contaminated with heavy metals. These plant species have a wide range of tolerance to all of the selected metals; and therefore it can be used for large scale removal of heavy metals from wastewater.

JASEELA C.”A STUDY ON THE SOIL AND WATER QUALITY OF SELECTED SITES AROUND SOLID WASTE DUMPING AREAS IN KERALA STATE”. THESIS. CWRDM (CENTRE FOR WATER RESOURCES DEVELOPMENT AND MANAGEMENT), UNIVERSITY OF CALICUT, 2018.

Chapter **10**

DECONTAMINATION OF HEAVY METALS IN SOIL BY PHYTOREMEDIATION AND ENHANCED PHYTOREMEDIATION TECHNIQUES

10.1 Introduction

Phytoremediation is a cost-effective, eco-friendly and in-situ method that has been used to remediate environmental media contaminated with organic and inorganic contaminants. Plants possess genetic potential to remove pollutants or convert pollutants into harmless products by degrading, bioaccumulating, immobilizing or extracting the pollutants. Phytoextraction is the use of higher plants to remove inorganic contaminants (mainly metals) from polluted soil (Lasat, 2002). Typical plant species used in for phytoextraction are hyperaccumulators, but plants from this group are not good biomass producers and grow more slowly than most species. Because of their slow growth, an alternative approach is to improve the phytoextraction potential of non-hyperaccumulator plant species. So there is a need to modify this method using modern chemical methods. Chemically enhanced phytoextraction (mostly chelating agents and nanoparticles) has been proposed as an alternative for the cleaning up of metal polluted soils.

Chelate-enhanced phytoextraction is based on the fact that the application of metal-chelating agents to a contaminated soil significantly enhances metal accumulation by plants (Garbisu & Alkorta, 2001; Tahmasbian & Sinegani, 2014; Singh & Prasad, 2015). The chelating agents have a property to desorb toxic metals from soil by forming strong water-soluble complexes. After complex formation, it can be removed from the soil by plants through enhanced phytoextraction or by using soil washing techniques. In the process of chelate enhanced phytoextraction, chelant can desorb metals from the soil matrix, and the mobilized metals move to rhizosphere for uptake by plant roots (Tahmasbian & Sinegani, 2014). The amounts of bio-available metals in soil solution are mainly determined by the properties of the soil and applied chelants (Tandy et al., 2004). In order to reduce discharge of metal chelants into groundwater and for reducing impact of chelant on soil micro-organisms, its selection, its amount and process of their application are important (Singh & Prasad, 2015). The most frequently-used solutions for extracting also have deficiencies: EDTA is toxic and expensive, and presents a low level of biodegradability (Finzgar et al., 2006); NTA is also the toxicant as a class II carcinogen (Peters, 1999); HNO_3 is lethal to soil micro-flora and destructive to the physic-chemical properties of soil; HCl can alter soil properties (Neilson et al., 2003) and citric acid is easily biodegradable, nontoxic acid that forms comparatively strong complexes (Qu et al., 2011).

Nano-phytoremediation is a combined technology between nanotechnology and phytotechnology for remediation of contaminated environments (Jiamjitrpanich et al., 2012). Nano-phytotechnology is an advantage technology which decreases the retention time of phytotechnology and decreases cost of nanotechnology. Nanoparticles are very reactive because of their many properties such as surface area, mobility, and can be modified in nano scale (Tasharrofi et al., 2018). The successful application of nZVI has been applied to decontaminate toxic metals in wastewater and soil (Alidokht et al., 2011; Li & Zhang, 2006; Kanel et al., 2006; Kanel et al., 2005). The objective of the work was to remediate heavy metal contaminated soils by phytoremediation and enhanced phytoremediation (nano-phytoremediation and chelate enhanced phytoremediation) techniques and to compare and understand the effectiveness of each method.

10.2 Materials and Methods

10.2.1 Plant used for phytoremediation

The five commonly available terrestrial plant species such as *Catharanthus roseus* (Periwinkle)*, Coleus aromaticus* (Panikoorka) and *Erva Laneta jus* (Cheroola), *Tradescantia spathacea* (boat lily) and *Alternanthera dentate* (Joy Weed) were selected and screened for the study (plate 10.4)**.** The study was continued after the screening period using *Catharanthus roseus, Tradescantia spathacea* and *Alternanthera dentate* which grew well in the heavy metal contaminated soil (plates 10.1-10.3).

10.2.1.1 Catharanthus roseus

Catharanthus roseus (Periwinkle) is a species of *Apocynaceae* family native to Madagascar. This ornamental plant is non-edible, evergreen sub-shrub or herbaceous plant most popular in subtropical gardens and its pleasant hardiness in dry and nutritionally deficient conditions. The species has long been cultivated for herbal medicine and as an ornamental plant. In traditional Chinese medicine, extracts from it have been used to treat numerous diseases, including diabetes, malaria, and Hodgkin’s disease. The vinblastine and vincristine are alkaloids extracted from this plant are used in the treatment of leukemia (Subhashini & Swamy, 2016).

10.2.1.2 Tradescantia spathacea

Tradescantia spathacea, commonly called boat lily or Moses-in-the-Cradle is a herb in the *Commelinaceae* family native to Belize, Guatemala, and southern Mexico. It is a short-stemmed tender foliage plant having small, dense, spreading clumps. It has fleshy rhizomes and rosettes of waxy lance-shaped leaves. Leaves are dark to metallic green above, with glossy purple underneath. It forms a solid groundcover of upright leaves. The six to eight-inch long, sword-shaped leaves are green above and purplish below. The plant is known to have an antioxidant and chemo protective anti mutagen (Arriaga-Alba et al., 2011), antimicrobial properties (Tan et al., 2015) and antitumor property (Rosales-Reyes et al., 2008).

10.2.1.3 Alternanthera dentate

Alternanthera dentate is a genus of flowering plants in the amaranth family, Amaranthaceae. It is a widespread genus with most species occurring in the tropical Americas and others in Asia, Africa, and Australia. Plants of the genus may be known generally as joy weeds. Several species are notorious noxious weeds. These are annual or perennial herbs or sub-shrubs. While some of the better-known species are aquatic plants, most are terrestrial. They take many forms, from prostrate to erect to floating. The inflorescence is a spike or a rounded head occurring in the leaf axils or the ends of branches.

10.2.2 Experimental design

The 0-30 cm surface layer of soil was collected in pots and used for this investigation. Soil used for the experiment was artificially contaminated with heavy metals (Cd, Pb, and Ni) in the form of Cd as $CdSO_4$, Pb as $Pb(NO_3)_2$, and Ni as $NiSO_4$. Medium growing plants with extensive rooting system (the tested plants included *Catharanthus roseus, Tradescantia spathacea* and

Alternanthera dentate) were selected for the study. Seedling of these plants was grown in non-contaminated soil and healthy plants were selected and were transplanted into the pots, which were then placed in a temperature controlled greenhouse. Plate10.1 shows the plot for the conduct of phytoremediation experiment

The experiment consists of 9 treatments as follows and control with three replications of each treatment.

T1 : Heavy metals contaminated soils + *Catharanthus roseus*
T2 : Heavy metals contaminated soils + nZVIs+ *Catharanthus roseus*
T3 : Heavy metals contaminated soils + citric acid+ *Catharanthus roseus*
T4 : Heavy metals contaminated soils + *Tradescantia spathacea*
T5 : Heavy metals contaminated soils + nZVIs+ *Tradescantia spathacea*
T6 : Heavy metals contaminated soils + citric acid+ *Tradescantia spathacea*
T7 : Heavy metals contaminated soils + *Alternanthera dentate*
T8 : Heavy metals contaminated soils + nZVIs+ *Alternanthera dentate*
T9 : Heavy metals contaminated soils + citric acid+ *Alternanthera dentate*

An amount of 6.50kg of soil was taken in each experimental pot and was spiked with 100mg/kg of lead, 55.0mg/kg of Ni and 50mg/kg of Cd. The same amount 1000mg/kg of nZVIs was applied to one set of each plant pot and 1000mg/kg of citric acid was added to another set of each plant pot. All the experimental pots were placed in a temperature controlled greenhouse. Plants were watered and natural light was used for the green house study. After 45 days, the plants were harvested and thoroughly washed with drinking water, separated into the shoots and roots and checked for dry biomass (at 45°C).

Plate 10.1: Plot for the conduct of phytoremediation experiment

10.2.3 Extraction and analysis of heavy metals in soil and plants

The soils were mixed homogeneously after being air-dried, and sieved to <2 mm (for physicochemical properties of soils) and 0.15 mm (for contents of heavy metals) (Qu et al., 2011). The soil and plants used in the experiment were extracted and analyzed for heavy metals to confirm their roles in phytoremediation and enhanced phytoremediation experiments. The procedure for the extraction and analysis of heavy metals from soil samples is explained in chapter 3.

The plants were harvested after 45days.The roots and shoots were separated and washed with distilled water to remove soil and dust. The plant parts were dried in an oven at 70°C for 72 hr and the dry weight were recorded by electronic balance. 0.2 g of plant parts were digested at 150°C for 200 min with 10 ml mixtures of $HNO_3/HClO_4$ (4:1) (Qu et al., 2008). After complete digestion, the volume of digested samples was adjusted to 20 ml with distilled water and the contents of metals were determined by inductively coupled plasma optical emission spectrometer (Thermo Scientific iCAP 7000 Seies ICP OES). Shoot and root of *Catharanthus roseus, Tradescantia spathacea and Alternanthera dentata* under different treatments are shown in plates 10.2 to 10.9.

	
Plate 10.2: Root of *Catharanthus roseus*	**Plate 10.3:Shoot of *Catharanthus roseus***

		
Plate 10.4*:* *Tradescantia spathacea + only* phytoremediation	**Plate 10.5*:*** *Tradescantia spathacea+* nano-phytoremediation (nZVIFe)	**Plate 10.6*:*** *Tradescantia spathacea+*chelate enhanced phytoremediation (citric acid)

		
Plate 10.7: *Alternanthera dentata + only* phytoremediation	**Plate 10.8:** *Alternanthera dentata +* nano-phytoremediation (nZVIFe)	**Plate 10.9***: Alternanthera dentate*+ chelate enhanced phytoremediation (citric acid)

10.2.4 Synthesis of nanozerovalent iron particles

The nZVIs were synthesized by the reductive precipitation process by mixing 1:1 volume ratio of $FeCl_3.6H_2O$ (0.18M) and sodium borohydride (0.8M) (Prabu & Parthiban, 2013; Giasuddin et al., 2007). The reaction is taking place as per the following mechanism:

$$4Fe^{3+} + 3BH_4 + 9H_2O \longrightarrow 4Fe^{0}_{(s)} + 3H_2BO_3 + 12H^{+}_{(aq)} + 6H_{2(g)} \quad (10.1)$$

The borohydride solution was added drop by drop into iron chloride solution with vigorous strring (400rpm) (Poursaberi et al., 2012; Rahmani et al., 2011).The formed black solid iron nano particles were filtered through whatman No 41. The synthesized iron nano particles were then washed several times with distilled water and absolute ethanol. The synthesized nanoparticles were finally dried in an oven at 50^0C overnight. For storage, a thin layer of ethanol was added to preserve the nano iron particles from oxidation. Then the mixture was agitated for 5-6 hours so that the nano particles became homogenously adsorbed on the surface (Madhavi et al., 2013).

The sizes and shapes of the nano- and submicron-particles were determined using a SU-6600 field emission SEM instrument equipped with a Horiba EDX analyzer (Hitachi High-Technologies, Tokyo, Japan). The size distribution of the nZVIs was further examined using a H07600 transmission electron microscope (Hitachi High-Technologies).

10.2.5 Phytoextraction efficiency

Plant biomass, bioconcentration factor, and soil mass are the three key variables that define the phytoremediation potential of a given plant species (Zhuang et al., 2007). Two indices were calculated to evaluate plants for phytoextraction purposes- bioconcentration factors (BCF) and translocation factors (TF).

10.2.5.1 Accumulation and translocation of metals in plants

Both BCF and TF can be used to estimate a plant's potential for phytoremediation purpose. BCF indicates the efficiency of a plant in up-taking heavy metals from soil and accumulating them into its tissues. It is a ratio of the heavy metal concentration in the plant tissue (root, stem or leaves) to that in soil. The higher BCF value the more suitable for phytoextraction [BCF values>2 were regarded as high values] (Blaylock, 1997; Mellem, 2009). It is calculated as follows (Zhuang et al., 2007).

Bioconcentration factor = metal concentration in the plant tissue/
metal concentration in the soil

TF indicates the efficiency of the plant in translocating the accumulated heavy metals from roots to shoots. It is a ratio of the concentration of the heavy metal in shoots (stem or leaves) to that in its roots. Metals that are accumulated by plants and largely stored in the roots of plants are indicated by TF values<1, with values greater indicating translocation to the aerial part of the plant (Mellem, 2009). It is calculated as follows (Padmavathiamma, 2007; Adesodun et al., 2010).

Translocation factor = metal concentration in aerial parts/
metal concentration in roots

10.2.6 Statistical analysis

All analytical results were performed as the average of three replicates. Descriptive statistics were made using SPSS 13.0 and Excel (Microsoft Inc.) software packages. The experimental data were expressed as mean± standard deviation (SD).

10.3 Results and Discussion

10.3.1 Soil characteristics

The physico-chemical parameters of contaminated soil before and after treatments are presented in Table 10.1 and Table 10.2.

Table 10.1: Physico-chemical characteristics of contaminated soil (mean ± SD, n=3)

Parameters	value
pH (1:2.5)	4.85 ±0.05
EC, (µS/m)	71.1 ±0.05
Chloride, (mg/kg)	356.0±0.52
Sulphate, (mg/kg)	317.2±0.60
Exchangeable calcium, (mg/kg)	1034.0±1.6 0
Exchangeable magnesium, (mg/kg)	560.0±1.30
Exchangeable sodium, (mg/kg)	235.0±0.60
Exchangeable potassium, (mg/kg)	92.4±0.42
Inorganic phosphorous, (mg/kg)	8.20±1.6 0
Organic carbon, (%)	1.2±0.50
Sand, (%)	83.75±1.0
Clay, (%)	13.75±0.60
Silt, (%)	2.50±0.20
Cation Exchange Capacity, (meq/100g)	7.10 ±1.30
Lead, (mg/kg)	100.50±4.50
Nickel, (mg/kg)	55.67±1.60
Cadmium, (mg/kg)	50.25±0.92

Table 10.2: Heavy metal concentration in soil after treatment (mean ± SD, n=3)

Treatments	Days	Pb(mg/kg)	Ni(mg/kg)	Cd (mg/kg)
Control	20	98.10±3.40	53.50±4.50	50.20±2.0
	45	97.0±4.0	53.0±4.50	50.0±3.10
T_1	20	53.0±4.06	42.50±3.10	38.30±2.50
	45	36.5±2.50	28.60±2.50	30.83±1.44
T_2	20	25.50±1.0	30.25±1.60	36.20±2.0
	45	12.30±0.80	22.50±1.0	22.45±1.50
T_3	20	18.90±1.8	22.3±2.0	25.60±3.50
	45	2.10±0.50	12.50±1.0	14.25±1.50
T_4	20	58.80±4.0	46.50±3.50	30.50±2.80
	45	38.70±2.60	30.45±3.10	32.80±3.50
T_5	20	27.50±3.0	32.25±2.50	38.20±1.50
	45	17.50±1.50	25.60±2.0	21.30±1.80
T_6	20	20.50±2.50	25.60±2.0	27.65±3.50
	45	6.80±0.80	14.20±1.0	13.20±1.50
T_7	20	50.20±4.0	40.50±3.80	35.60±3.0
	45	35.60±1.80	27.50±1.60	20.15±1.50
T_8	20	23.50±1.50	28.50±2.50	33.20±3.50
	45	16.50±1.80	20.25±2.0	21.50±2.50
T_9	20	17.0±3.0	20.50±3.0	21.55±2.50
	45	7.30±1.0	10.80±1.50	11.60±2.0

10.3.2 Effect of biomass production on metal uptake

After 45 days, the dry weights of *Catharathus rosaseus, Tradescantia spathacea* and *Alternanthera dentate* plants (shoots and roots) were recorded and the result of the average biomass production of three plants is shown in

Figure 10.1. The great differences in biomass were observed between the three tested plants by treating with phytoremediation and enhanced phytoremediation system. The biomass production (dry weight) was increased from 9.87 to 20.48mg/pot for *Catharathus rosaseus*, 6.9 to 18.2mg/pot for *Tradescantia spathacea* and 8.5 to 23.5mg/pot for *Alternanthera dentata*. The results showed that chemically enhanced phytoremediation could promote three tested plants to produce more biomass than only phytoremediation system. Hence, phytoremediation with metal mobilizing agents (nano-phytoremediation and chelated enhanced phytoremediation) can be applied to remediate toxic metals in contaminated soils.

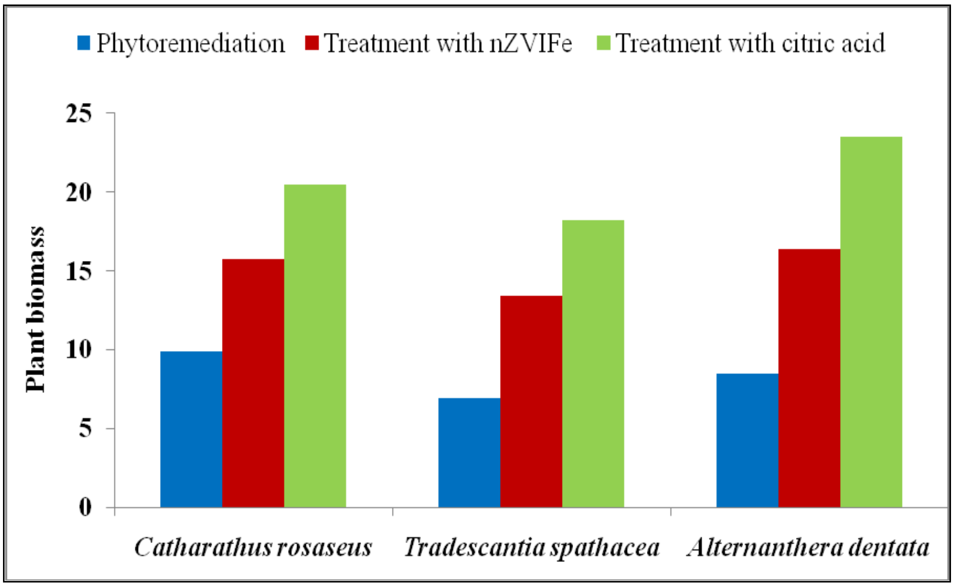


Figure 10.1: The total biomass production of *Catharathus rosaseus, Tradescantia spathacea* and *Alternanthera dentate*

10.3.3 Metal accumulation in plant tissues

The concentrations of Pb, Ni, and Cd in shoots and roots of *Catharathus rosaseus, Tradescantia spathacea* and *Alternanthera dentata* grown in the contaminated pots with and without enhanced phytoremediation treatments are presented in Table 10.3. Lead accumulation in shoots varied between 18.47 and 37.20mg/kg, with chelate assisted *Tradescantia spathacea* having the highest concentration and *Alternanthera dentata* (phytoremediation only) the lowest. Concentrations of Ni in the shoots ranged from 5.6 mg/kg in *Catharathus rosaseus* (phytoremediation only) to 18.95mg/kg in the chelate enhanced *Catharathus rosaseus*. Shoot concentrations of Cd varied between 5.13 and 16.8 mg/kg, with the lowest accumulation observed in *Tradescantia spathacea* (phytoremediation only) and the highest observed for the chelate enhanced *Catharathus rosaseus*.

The concentrations of Pb, Ni and Cd in the root of the three tested plants varied between 11.08 to 65.50 mg/kg, 14.50 to 22.0mg/kg and 7.40 to 17.90mg/kg, respectively. The maximum accumulation of PB, Ni and Cd in the root was obtained in acetic acid enhanced phytoremediation system. The results also found that chelate enhanced phytoremediation of the three tested plants exhibited excellent potential for lead accumulation, more than Ni and Cd accumulation.

The results of the study indicated that the application of chelates to soils significantly enhanced heavy metals removal especially lead by the tested plants, which was consistent with the findings of Zhuang et al. (2007) and Qu et al. (2011). Citric acid and nZVIs enhanced phytoremediation increases the phytoextraction rates and uptake amounts for metals in shoots of the tested plants. In all the three treatments, the heavy metal concentration was found to be greater in roots than in shoots.

Table 10.3: Concentrations of Pb, Zn, and Cd in shoots and roots of selected plant species after phytoremediation and enhanced phytoremediation treatments (mean, mg/kg ± SD, n=3)

Species	Plant parts	Pb	Ni	Cd
	Shoot	19.50±4.30	5.60±0.40	10.5±0.80
Catharathus rosaseus	Root	30.60±4.50	15.50±1.4	7.4±0.52
	Shoot	29.75±3.70	10.40±1.4	15.6±1.20
Catharathus rosaseus+ nZVIs	Root	51.50±5.60	19.60±1.7	7.65±1.50
	Shoot	32.50±4.0	18.95±3.0	16.8±1.50
Catharathus rosaseus+ Citric acid	Root	65.50±6.0	20.65±3.0	9.95±1.0
	Shoot	36.89±4.80	6.90±0.42	5.13±0.30
Tradescantia spathacea	Root	11.08±1.0	15.60±1.50	9.50±1.0
	Shoot	35.06±4.50	10.20±0.85	8.87±0.50
Tradescantia spathacea+ nZVIs	Root	49.50±4.90	22.0±3.50	11.50±0.80
	Shoot	37.20±4.50	14.10±1.0	7.73±0.50
Tradescantia spathacea+Citric acid	Root	52.0±5.10	20.50±3.20	17.90±3.0
	Shoot	18.47±1.50	6.60±0.40	5.63±1.0
Alternanthera dentate	Root	32.0±4.50	14.50±1.20	8.50±0.52
	Shoot	25.17±3.10	11.05±1.0	9.06±0.92
Alternanthera dentate+ nZVIs	Root	48.50±4.0	20.20±3.0	13.60±1.0
	Shoot	35.47±4.80	15.17±1.30	8.60±0.80
Alternanthera dentate +Citric acid	Root	51.50±5.10	20.80±3.50	16.50±1.40

10.3.4 Bioconcentration factor (BCF) and translocation factors (TF)

Both BCF and TF can be used to estimate a plant‘s potential for phytoremediation purpose. By comparing BCF and TF, we can compare the ability of different plants in taking up metals from soil and translocating them to shoots. Tolerant plants tend to restrict soil-root and root-shoot transfers, and therefore have much less accumulation in their biomass, while hyperaccumulators actively take up and translocate metals into their above ground biomass. Plants exhibiting TF and particularly BCF values less than one are unsuitable for phytoextraction (Fitz & Wenzel, 2002). Table 10.4 shows the BCF and TF values of the selected plant species which were studied in each treatment.

Table 10.4: Bio-concentration factor (BCF=C_{shoot}/C_{soil}) and TF of Pb, Ni, and Cd of tested plant species

Treatments BCF of shoot	Pb	Ni	Cd
T1	0.53	0.20	0.34
T2	2.42	0.46	0.69
T3	15.48	1.52	1.18
T4	0.29	0.23	0.16
T5	2.00	0.32	0.42
T6	5.47	0.99	0.59
T7	0.52	0.24	0.28
T8	1.53	0.55	0.42
T9	4.86	1.40	0.74
BCF of root			
T1	0.84	0.54	0.24
T2	4.19	0.87	0.34
T3	31.19	1.65	0.70
T4	0.95	0.51	0.29
T5	2.83	0.86	0.54
T6	7.65	1.44	1.36
T7	0.90	0.53	0.42
T8	2.94	1.00	0.63
T9	7.05	1.93	1.42
TF			
T1	0.64	0.36	1.42
T2	0.58	0.53	2.04
T3	0.50	0.92	1.69
T4	0.36	0.44	0.54
T5	0.71	0.37	0.77
T6	0.72	0.69	0.43
T7	0.58	0.46	0.66
T8	0.52	0.55	0.67
T9	0.69	0.73	0.52

The average BCF values of all the three tested plants treated with acetic acid and nZVIs were higher than Phytoremediation, which means that the plants had higher ability to uptake toxic metals with metal mobilizing agents. BCF values depend on the heavy metals, the accumulation ability, physiological factors of plants, and environmental conditions (Qu et al., 2011). The shoot BCFs of all the three tested plants varied from 0.52 to 15.48 Pb, 0.19 to 1.52 Ni and 0.16 to 1.18 Cd. The root BCFs varied between 0.29 to 31.19 Pb, 0.51 to 1.93 Ni and 0.24 to 1.42 Cd. The average BCF values of shoots were 3.75, 0.65, 0.53 in Pb, Ni and Cd, respectively; the average BCF values of roots were 6.43, 1.04, and 0.66, in Pb, Ni and Cd, respectively.

In the experiment, TF values of all the tested plants were lower than 1 except for Cd in *Catharathus rosaseus*. The lower TF value indicates that a small amount of toxic metals had moved into shoots. High values of TF indicate that plants could move and distribute more toxic metals (Qu et al., 2011). The results revealed that the Cd absorbed by roots of *Catharathus rosaseus* was translocated to shoot. Out of the total accumulated 26.475mg/kg of cadmium in chelate assisted phytoremediation, roots retained only 9.95mg/kg and the remaining was translocated to shoot (16.8mg/kg).

10.3.5 Removal efficiency

Figure 10.2 shows the percentage removal efficiency of *Catharathus rosaseus, Tradescantia spathacea* and *Alternanthera dentate* during phytoremediation and enhanced phytoremediation. The results of the study indicated that the application of citric acid and nZVIFe to soils significantly enhanced Pb, Ni and Cd removal by the three tested plants. This can be explained by the fact that application of metal mobilizing agents to soils has been proposed as a way of chemically enhancing root uptake and translocation of metal contaminants from soil to plants, thereby improving phytoextraction.

The removal efficiency of the tested plants was observed in the following order, treatment with Citric acid > treatment with nZVIFe > phytoremediation only. The citric acid enhanced phytoextraction rates of Pb, Ni and Cd were 97.90%, 77.27% and 71.50%, respectively for *Catharathus rosaseus*, 93.20%, 74.18% and 73.60%, respectively for *Tradescantia spathacea* and 92.70%, 80.36% and 76.80%, respectively for *Alternanthera dentate*.

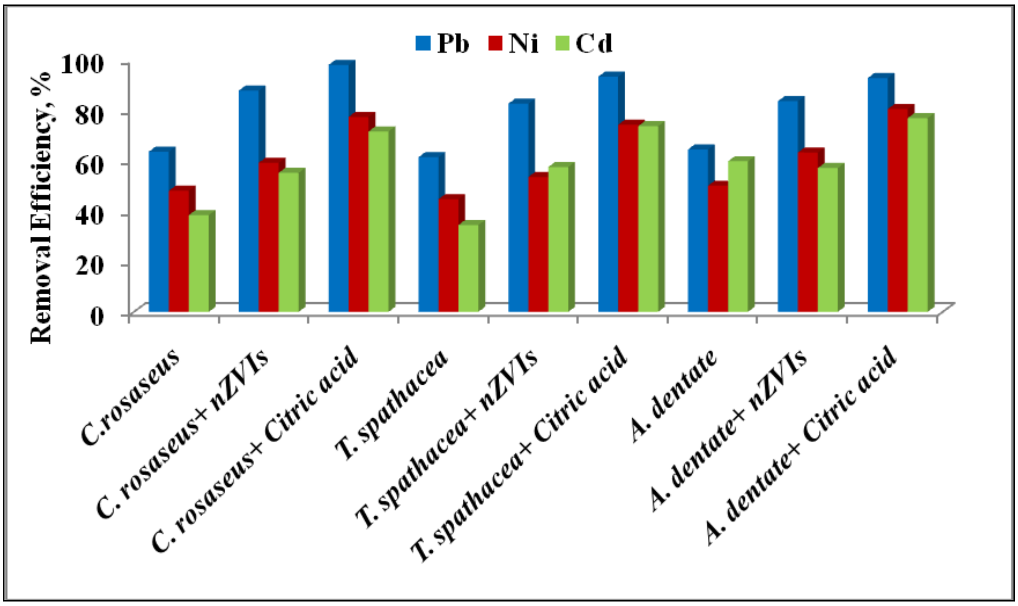


Figure 10.2: Removal Efficiency of Pb, Ni and Cd in the contaminated soil using phytoremediation and enhanced phytoremediation

10.3.6 Characterization of nZVI particles by Scanning Electron Microscopy and Transmission Electron Microscopy

The results of the characterization of the zerovalent iron nanoparticles performed by scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) are shown in the Figure 10.3.

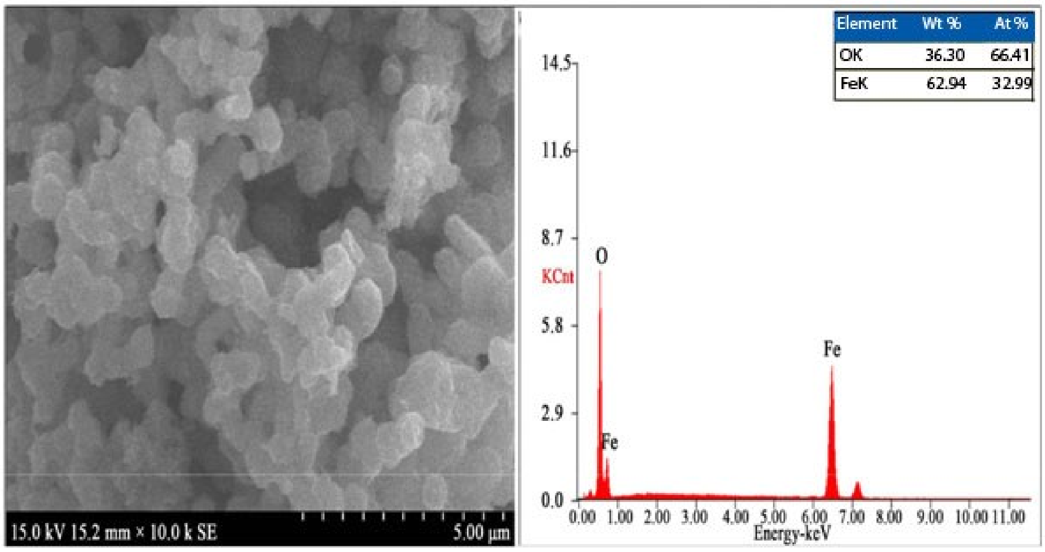


Figure 10.3: Scanning electron microscopy-energy dispersive X-ray spectroscopy image of the zero valent iron nanoparticles

Results indicated that the synthesized nZVI particles are in nano scale (can be seen on the scale bar at the bottom of the SEM image) and the nanoparticles are spherical in shape and exist as chain like aggregates. Aggregation of the nanoparticles is reported to be caused by the large surface area and magnetic dipole–dipole interactions of the individual particles (Uzum, 2008).

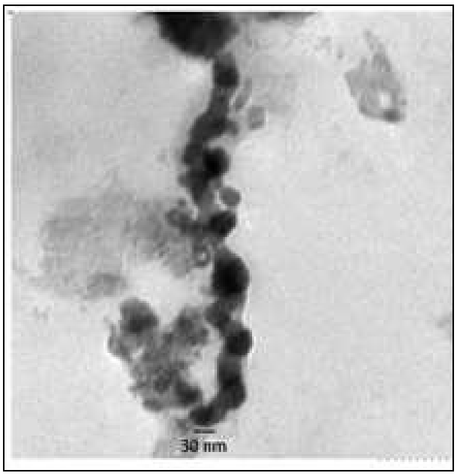


Figure 10.4: Transmission electron microscopy images of the zerovalent iron nanoparticles

Figure 10.4 represent the TEM images of iron nanoparticles synthesized using the sodium borohydride method. The nanoparticles were mostly spherical in shape and exist as chain-like aggregates (Tratnyek et al., 2001; Prabu & Parthiban, 2013). TEM images of NZVI nanoparticles indicated that, iron nanoparticles possess a core–shell structure, in which the shell represents the oxidised part that surrounds the Fe^0 core and preserves it against further oxidation. It appears that many primary nanoparticles are interconnected with one another to form larger nanoclusters, and single nanoparticle sizes are around 5–40 nm. The size distribution survey from TEM images of over 400 nanoparticles suggests that over 80% of the nanoparticles had diameters of less than 100 nm whereas 50% were less than 60 nm. The synthesized nanoparticles are formed chain-like as aggregated structures because of nanomaterial have a natural tendency to remain in a more thermodynamically stable state. The absence of high-resolution fringes in the shell image indicates that the shell is amorphous.

10.4 Summary

Phytoremediation or plant-based environmental remediation technology has been widely pursued in recent years as an in-situ, cost-effective potential strategy for the cleanup of heavy metals from contaminated sites. The terrestrial plant species such as *Catherathus rosaseus, Tradescantia spathacea* and *Alternanthera dentate* were selected to decontaminate the soil using phytoremediation and enhanced phytoremediation techniques (using nZVIFe and citric acid). The results of the study indicated that the application of chelates and nano-particle to soils significantly enhanced Pb, Ni and Cd removal using the selected plant species. This can be explained by the fact that application of metal mobilizing agents to soils has been proposed as a way of chemically enhancing root uptake and translocation of metal contaminants from soil to plants, thereby improving phytoextraction. The results of the study also revealed that, the enhanced phytoremediation could promote the selected plants species to produce more biomass than only phytoremediation system. We have observed that the removal efficiency of the tested plants followed the order: treatment with citric acid > treatment with nZVIFe > phytoremediation only. Within 45 days of citric acid enhanced phytoremediation study, removal efficiency of Pb, Ni and Cd (with an initial concentration of 100mg/kg of Pb, 55.0mg/kg of Ni & 50.0mg/kg of Cd) were 97.90%, 77.27% and 71.50%, respectively for *Catharathus rosaseus,* 93.20%, 74.18% and 73.60%, respectively for *Tradescantia spathacea* and 92.70%, 80.36% and 76.80%, respectively for *Alternanthera dentate*. Thus phytoremediation and enhanced phytoremediation techniques using selected plant species proved to be an efficient, environmental friendly method for the removal of heavy metals.

JASEELA C.”A STUDY ON THE SOIL AND WATER QUALITY OF SELECTED SITES AROUND SOLID WASTE DUMPING AREAS IN KERALA STATE”. THESIS. CWRDM (CENTRE FOR WATER RESOURCES DEVELOPMENT AND MANAGEMENT), UNIVERSITY OF CALICUT, 2018.

Chapter 11

CONCLUSIONS AND RECOMMENDATIONS

Disposal of municipal solid waste is one of the global environmental challenges faced by today's world particularly in developing countries. The main environmental problem associated with MSW dumping site is the potential risk posed by leachate migration and subsequent deterioration of the soil and water quality.

We had carried out a study on the deterioration of groundwater quality in the vicinity MSW dumping sites by monitoring the various physico-chemical and biological parameters. A total of 59 groundwater samples were collected from the four selected MSW dumping sites (Njeliamparamba, Laloor, Pettipalam and Vellaramkunnu) in Kerala and the results of analysis indicated that Njeliamparamba was found to be the area of most contaminated. Results obtained in Njeliamparamba revealed that, the quality of the groundwater samples collected within 300 meter from the dumping site were determined to be highly polluted. High amounts of TDS, Cl^-, HCO_3^-, Ca^{2+}, Mg^{2+}, NO_3^-, COD, BOD, lead, total coliform and *E.coli* in groundwater samples is more prominent at that site which deteriorates its quality for drinking and other domestic purposes. The result of the groundwater quality of Laloor indicated that, most of the physico-chemical parameters lie within BIS specification limits for drinking purpose. However, effect of leachate migration in proximity to the Laloor dumping site might have caused higher concentrations of nitrate and coliform bacteria. In Pettipalam dumping site, a pond sample was found to be highly contaminated which is 20 meter from the dumping site. Presence of coliforms bacteria in the Pettipalam and Vellaramkunnu dumping site indicated the presence of microbial pollution of the groundwater. With the help of Piper diagram, the interpretation of hydrochemical facies of groundwater samples in Njeliamparamba, Laloor and Pettipalam indicated that, dominant ions comprised of $(Na^{+}+K^{+})$ Cl^{-} type, and the type of water that predominates in Vellaramkunnu is calcium chloride type.

The impact of leachate on the groundwater quality of the surrounding area in Njeliamparamba is a major environmental concern. To evaluate the water quality issues associated with MSW, leachate and groundwater samples within 500 meter from the dumping site were collected and analyzed. The results of the physico-chemical and bacteriological analyses of the confirmed the presence of various contaminants such as organics, inorganics and heavy metals. The BOD_5/COD ratio (0.30) of the leachate indicated that the landfill is of intermediate nature. The water quality satus of groundwater samples indicated that, the samples collected within 300m distance from the dumping site were affected by leachate percolation. Since there is no natural or other possible reason for high concentration of the pollutants, it can be concluded that leachate has significant impact on groundwater quality in the area.

Spatial distribution of groundwater quality parameters was measured by Geographic Information System. Leachate Pollution Index and Water Quality Index in the study were applied to assess the overall quality of the leachate and groundwater. The LPI value at Njeliamparamba for both the seasons exceeded the standard LPI of 7.4 proposed for leachate disposal. The Canadian Council of Ministers of the Environment WQI map indicted that majority of the study area had poor and marginal water quality. However, the quality improved with increase in distance of the well from the pollution source. Quality assessments for irrigation suitability of the groundwater samples were assessed using soluble sodium percentage, sodium adsorption ratio, Kelly's ratio and magnesium hazard and the results showed that majority of the groundwater samples were found to be suitable for agriculture purposes.

Deteriorating soil quality is a grave consequence of MSW dumping which have resulted in growing public concern. To evaluate the soil quality and assessment of soil contamination at Njeliamparamba, a total of 50 soil samples were collected at the depth of 0-30cm and 30-60cm from 25 sites.The physicochemical characteristics of most of the samples revealed acidic nature and obtained mainly three types of texture (sandy loam, loam and clay loam). The mean value of the major ions (cations and anions) in soil samples follows the order: exchangeable calcium> sodium> potassium> magnesium > inorganic phosphorous and sulphate> chloride> alkalinity. The results revealed that the concentrations of all the physico-chemical parameters decreased from surface to sub-surface soil in all the stations, which confirmed the increased anthropogenic activities with time. The monitoring of pesticide residues indicated that out of twenty five sampling sites, only one sample showed the presence of lindane and three samples reported the presence of aldrin. The heavy metals such as Fe, Cu, Ni, Pb and Zn were detected in all the analysed soil samples and were found to be within the CCME soil quality limit except Pb. The results of the enrichment factor for surface soils revealed that most of the soils samples could be considered as deficiency or minimal enrichment for all the studied metals, while the values of Pb found to have significant enrichment. The results of the contamination factor also found to have low contamination levels for Cu, Ni, Zn, Cd and moderate contamination levels for Pb. The pollution load index calculated for each sampling sites were found to be low in all the studied samples except one sampling site indicates low pollution considering the total of the studied metals. The principal component analysis and correlation study revealed that, anthropogenic inputs derived from leachate are the contamination sources. The concentrations of available metals in the soils of Njeliamparamba were found to be above the critical limit for micronutrients. The results of the study indicated that the samples collected within the buffer zone had more contamination than those collected outside the zone.

The DRASTIC model in a Geograhic Information System environment was used to determine the groundwater vulnerability to contamination in the vicinity of a two solid waste disposal sites, Njeliamparamba and Laloor, municipal dumping sites in Kozhikode and Thrissure district. DRASTIC is an index model composed of several hydrogeological parameters. The ArcMap 10.1 was used to prepare a vulnerability map for the study area. According to the vulnerability map in the Njeliamparamba, the study area was divided into three vulnerability classes ranging between a minimum value of 120 and a maximum value of 243. The vulnerability classes are moderate vulnerable, high vulnerable and very high vulnerable. It can be concluded from the vulnerability map, that, the eastern and south eastern portion of Njeliamparamba dump site was very highly vulnerable to groundwater contamination. This is probably due to the lower sloped terrains towards the eastern portion which allows percolation of contaminants into the groundwater. The resulting vulnerability map was then validated using a chemical and bacteriological parameter analysed from nearby wells of the dumping site to assess the area which is of more potential risk to pollution. From the results of the study, it is clear that the concentrations of total dissolved solids and *E.coli* were correlated in different vulnerable zones; which validated the results obtained. The vulnerability index map in the Laloor dumping site were identified into three categories of groundwater vulnerable zones of contamination : 184 to 253, 253 to 320 and 320 to 398 corresponding to low, medium and high vulnerability zones respectively. At Laloor, high vulnerable zone is dominant near the dump site, so that dumping of any type of waste in this area will directly accelerate the pollution potential of groundwater at that area regardless of the amount of waste. The results revealed that the vulnerability index value was found to be higher in Laloor compared to Njeliamparamba; but more groundwater contamination was observed in Njeliamparamba due to high leachate percolation. The characteristics of groundwater samples from Laloor indicated that, the nitrate is the major contaminant; therefore the DRASTIC model was validated using the nitrate concentrations. The vulnerability map indicates that 80% of the nitrate contaminated samples were coming under the region of high vulnerable zone. The results provided a preliminary tool to identify potential areas or vulnerability zones with high risks of groundwater contamination due to the leachate percolation from solid waste dumping sites. The vulnerability map obtained from the DRASTIC method provides information about the locations that should be avoided waste dumping and also highlight the importance of showing high priority in terms of protection and contamination prevention.

Electro-coagulation technology was employed for the removal of organic and inorganic contaminants in MSW landfill leachate. This study investigated the removal of nitrate, COD and heavy metals such as Pb^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Cr^{3+} and Mn^{2+} from MSW landfill leachate. Experiments were conducted in a 1 L reactor using aluminum and iron electrodes. Effects of different parameters including pH (3, 7, 9 and 12), electro-coagulation time (20, 40, 60, 80 and 100min), applied voltage (2, 4, 6 and 8V), supporting electrolyte, NaCl (0.20, 0.40, 0.60, 0.80 and 1.0g/L), electrode material (Fe and Al) and initial concentration of different parameters were studied in order to evaluate the efficiency of electro-coagulation. The highest removal efficiency of nitrate (75.1± 0.2%) was observed under the following conditions: pH: 9, voltage: 8V, electrolysis time: 80 minutes, NaCl concentration of 0.60g/L, initial nitrate concentration of 101.0±1.5mg/L and Al as sacrificial anode. For higher removal of COD, the optimal conditions are pH : 7, voltage: 8V, electrolysis time : 80 minutes, NaCl concentration of 0.60g/L, initial COD concentration of 3.40g/L, and Al as sacrificial anode. The highest removal efficiency for heavy metals was observed at pH 6, 8V, 30 minutes of EC time, NaCl concentration of 0.60g/L, initial heavy metals concentration of 5.0mg/L and Fe as sacrificial anode. In order to minimize the energy consumption while maintaining higher removal efficiency, the current density must not be higher than 1.8mA/cm^{2}, with EC time in the range of 15 to 30 minutes for heavy metals and 60 to 80 min for nitrate and COD. This process consumes low amount of energy, making the process economically feasible technique and possible to scale up. The results also demonstrated that the electro-coagulation is a feasible technique for treatment of multi-pollutants (organic, inorganic and heavy metals) removal from the landfill leachate.

Developing cost effective and environmental friendly technologies for the remediation of wastewaters polluted with toxic substances is a topic of global interest. The treatment of wastewater using horizontal flow constructed wetlands vegetated with *Eichhornia crassipes* and *Marsileaceae* were investigated. The monitoring of CW shows that the performance of the system was good and it effectively removed high concentration of pollutants such as COD, TDS, TSS, oil and grease, nitrate, phosphate, sulphate, bacteria and heavy metals within a few days under local conditions. The percentage removal of heavy metals by constructed wetland in synthetic wastewater was 94.0%, 86.80% and 80.36% for Pb, Ni and Cd respectively within 12 days. The experiment also showed that the maximum accumulation of heavy metals were observed in *Eichhornia Crassipes* than in *Marsileaceae.* It is due to the extensive adventitious root system *of Eichhornia Crassipes*, which absorbs toxic substances from wastewaters. The advantage of constructed wetlands is that it is easy and cheap to construct and operate which suggests that they are a suitable alternative for wastewater purification.

Phytoremediation technology uses plants to clean up contaminated environments. The phytoremediation using aquatic plant species such as *Salvinia molesta, Azolla Caroliniana* and *Marsileaceae* were used to remediate heavy metal contaminated water. The study revealed that the *Salvania molesta* and *Marsileaceae* could remove Pb, Ni and Cd efficiently (>90.0%) within 21 days of treatment. Results from analysis confirmed the accumulation of different metals within the plants and a corresponding decrease of metals in the water. Maximum bioconcentration factor were obtained for *Salvinia Molesta* and *Marsileaceae* compared to *Azolla Caroliniana*. TF of metals in the studied plants showed a root to shoot translocation factor of greater than one for all the metals*;* hence these plants are effectively transported metals from root to shoot. Thus, these plant species can be used for the phytoremediation of aquatic water bodies contaminated with heavy metals. These plant species have a wide range of tolerance to all of the selected metals; and therefore it can be used for large scale removal of heavy metals from wastewater.

Phytoremediation and enhanced phytoremediation are emerging as effective innovative technologies for the removal of heavy metals in contaminated soil. The terrestrial plant species such as *Catherathus rosaseus, Tradescantia spathacea* and *Alternanthera dentate* were selected to decontaminate the soil using phytoremediation and enhanced phytoremediation techniques (using nano-particle and chelates). The results of the study indicated that the application of citric acid and nZVIFe to soils significantly enhanced Pb, Ni and Cd removal using the selected plant species. This can be explained by the fact that application of metal mobilizing agents to soils has been proposed as a way of chemically enhancing root uptake and translocation of metal contaminants from soil to plants, thereby improving phytoextraction. The results of the study also revealed that the enhanced phytoremediation could promote the selected plants species to produce more biomass than only phytoremediation system. In this experiment, removal efficiency of the tested plants was observed in the following order: treatment with citric acid > treatment with nZVIFe > phytoremediation. Within 45 days of citric acid enhanced phytoremediation study, removal efficiency of Pb, Ni and Cd (with an initial concentration of 100mg/kg of Pb, 55.0mg/kg of Ni & 50.0mg/kg of Cd) were 97.90%, 77.27% and 71.50%, respectively for *Catharathus rosaseus,* 93.20%, 74.18% and 73.60%, respectively for *Tradescantia spathacea* and 92.70%, 80.36% and 76.80%, respectively for *Alternanthera dentate*. Thus phytoremediation and enhanced phytoremediation techniques using selected plant species proved to be an efficient, environmental friendly method for the removal of heavy metals.

The following are some of the suggestions / recommendations drawn from the study:

- The impact of municipal solid waste landfill leachate on the surrounding soil and groundwater quality in Njeliamparamba is a major environmental concern. In this context, it is suggested to design properly engineered waste disposal facilities as well as the guidelines and standards should be followed to avoid the detrimental effects of leachate in to the soil and groundwater.

- The DRASTIC model can be a preliminary tool for identifying potential areas or vulnerability zones using basic hydrogeological variables that influence contaminant transport from surface sources to groundwater. The vulnerability map obtained from the study provides information about the locations that should be avoided for waste dumping and also highlight the importance of showing high priority in terms of protection and contamination prevention. Further studies are required to develop a three dimensional solute transport model to asses and predict the future condition of leachate concentration in groundwater system.

- Phytoremediation and constructed wetland technologies proved to be an economical option for the treatment of contaminated water, soil and leachate. The field application and utilization of this method with different plant species is encouraged. Economic viability of the enhanced phytoremediation technologies (chelate assisted and nano-phytoremediation) and also proper disposal of biomass produced needs to be studied. The technologies developed can be utilized for the complete removal of many other hazardous contaminants from a contaminated area.

- Electro-coagulation helped in the remediation of contaminants in wastewater within a short period of time. The technologies developed can be extended to large scale using the best experimental conditions obtained at laboratory scale. Sludge generated during electro-coagulation study can be scaled up (sludge management and reuse), mainly when the sludge contains economic compounds like metallic hydroxides as in the present study.

- Combined applications of different treatment technologies (physico-chemical and biological) for the treatment of leachate can be developed. Application study of this technique for the removal of young, medium and old landfill leachate needs to be carried out.

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REFERENCES

Abd El-Salam, M.M., & Abu-Zuid, G.I. (2014). Impact of landfill leachate on the groundwater quality: A case study in Egypt. *Journal of Advanced Research*, 6, 579–586.

Abdelwahab, O., Amin, N.K., & El-Ashtoukhy, E.S.Z. (2009). Electrochemical removal of phenol from oil refinery wastewater. *Journal of Hazardous Materials*, 163, 711–716.

Abood, A. R., Bao, J., Abudi, Z. N., Zheng, D., & Gao, C. (2013). Pretreatment of non-biodegradable landfill leachate by air stripping coupled with agitation as ammonia stripping and coagulation–flocculation processes. *Clean Technologies and Environmental Policy*, doi: 10.1007/s10098-012-0575-1.

Adamcová, D., Vaverková, M. D., Barton, S., Havlícek, Z., & Broušková, E. (2016). Soil contamination in landfills: a case study of a landfill in Czech Republic. *Solid Earth*, 7, 239–247.

Adamczyk-Szabela, D., Markiewicz, J., & Wolf, W. M. (2015). Heavy metal uptake by herbs. iv. influence of soil ph on the content of heavy metals in valeriana officinalis L.*Water. Air and Soil Pollution,* 226, 106. doi: 10.1007/s11270-015-2360-3

Adeolu, A.O., Ada, O. V., Gbenga, A.A., & Adebayo, O. A. (2011). Assessment of groundwater contamination by leachate near a municipal solid waste landfill. *African Journal of Environmental Science and Technology*, 5(11), 933-940.

Adesodun, J. K., Atayese, M. O., Agbaje, T. A., Osadiaye, B. A., Mafe, O. F., & Soretire, A.A. (2010). Phytoremediation potentials of sunflowers (*Tithonia diversifolia* and *Helianthus annus*) for metals in soils contaminated with zinc and lead nitrates. *Water, Air and Soil Pollution*, 207, 195-201.

Adriano, D. C. (2001). Trace elements in terrestrial environments. Biogeochemistry, bioavailability and risks of metals. New York: Springer-Verlag, 867

Agridiotis, V., Forster, C.F., & Carliell-Marquet, C. (2007). Addition of Al and Fe salts during treatment of paper mill effluents to improve activated sludge settlement characteristics. *Bioresource Technology,* 98, 2926–2934.

Akinbile, C. O. & Yusoff, M.S. (2011). Environmental impact of leachate pollution on groundwater supplies in Akure, Nigeria. *International Journal of Environmental Science and Development*, 2(1), 2010-0264.

Akinbile, C.O. (2012). Environmental impact of landfill on groundwater quality and agricultural soils in Nigeria. *Soil and Water Research*. 7, 18–26.

Aksu, Z. (2002). Determination of the equilibrium, kinetic and thermodynamic parameters of the batch biosorption of nickel (II) ions onto Chlorella vulgaris. *Process Biochemistry*, 38, 89–99.

Akyol, A. (2012). Treatment of paint manufacturing wastewater by electro-coagulation. *Desalination*, 285, 91–99.

Alam, S. M., Naqvi, S. S., & Ansari, M. R. (1999). Impact of soil pH on nutrient uptake by crop plants. In M. Pessarakli (Ed.), Handbook of plant and crop stress. New York: Marcel Dekker, 51–60.

Al-Hanbali, A., & Kondoh, A. (2008). Groundwater vulnerability assessment and evaluation of human activity impact (HAI) within the Dead Sea groundwater basin, Jordan. *Hydrogeology Journal*, 16(3), 499–510.

Ali, H., Khan, E., & Sajad, M.A. (2013). Phytoremediation of heavy metals-concepts and applications. *Chemosphere,* 9, 869–881.

Ali, S.M., Pervaiz, A., Afzal, B., Hamid, N., & Yasmin, A. (2014). Open dumping of municipal solid waste and its hazardous impacts on soil and vegetation diversity at waste dumping sites of Islamabad city. *Journal of King Saud University – Science*, 26, 59–65.

Alidokht, L.A., Khataee, R., Reyhanitabar, A., & Oustan, S. (2011). Cr (VI) Immobilization process in a Cr-spiked soil by zerovalent iron nanoparticles: optimization using response surface methodology. *Clean-Soil, Air, Water*, 39(7), 633–640.

Aller, L., Bennet, T., Lehr, J.H., Petty, R.J. & Hacket, G. (1987). DRASTIC: A standardized system for evaluating groundwater pollution using hydrological settings. Prepared by the National Water Well Association for the USEPA office of research and development, Ada, OK, USA.

Al-Maliky, J. H. A., Al-Adhub, A. H.Y., & Hussain, N. A. (2018). Removal efficiency of fecal coliform at different type of constructed wetland systems namely VSSF, HSSF and SF. *Journal of Pharmaceutical and Biological Sciences*, 6(1), 7-10. doi: 10.18231/2320-1924.2018.0002

Al-Shannag, M., Al-Qodah, Z., Alananbeh, K., Bouqellah, N., Assirey, E., & Bani-Melhem, K. (2014). Reduction of baker's yeast wastewater using batch electro-coagulation. *Environmental Engineering and Management Journal*, 13(12), 3153-3160.

Al-Shannag, M., Al-Qodah, Z., Bani-Melhem, K., Qtaishat, M. R., & Alkasrawi, M. (2015). Heavy metal ions removal from metal plating wastewater using electro-coagulation: Kinetic study and process performance. *Chemical Engineering Journal*, 260, 749–756.

Alvarado-Esquivel, C. (2013). Toxocariasis in waste pickers: a case control seroprevalence study. *PLoS ONE*, 8(1), 54897

Andreo-Martínez, P., García-Martínez, N., & Almela, L. (2016). Domestic wastewater depuration using a horizontal subsurface flow constructed wetland and theoretical surface optimization: a case study under dry mediterranean climate. *Water,* 8, 434. doi:10.3390/w8100434

Anikwe, K.C.A., & Nwobodo. (2002). Long term effect of municipal waste disposal on soil properties and productivity of sites used for urban agriculture in Abakaliki, Nigeria. *Bioresource Technology*, 83, 241–250.

Annepu, R.K. (2012). Sustainable solid waste management in India. Proceedings of international conference on waste, wealth and health, IIWM, Bhopal, India, 15–17, 171

Antropov, L. (1977). *Theoretical Electrochemistry*. 2nd Edition, Moscow: Mir Publishers.

APHA. (2012). Standard methods for examination of water and waste water. (22nd ed). APHA, AWWA, WPCF, Washington, DC.USA

Arriaga-Alba, M., Blasco, J.L., Ruíz-Pérez, N.J., Sánchez-Navarrete, J., Rivera-Sánchez, R., & González-Avila, M. (2011). Antimutagenicity mechanisms of the Rhoeo discolor ethanolic extract. *Experimental and toxicologic pathology*, 63(3), 243-248.

Asselin, M., Drogui, P., Brar, S.K., Benmoussa, H., & Blais, J.F. (2008). Organics removal in oily bilgewater by electro-coagulation process. *Journal of Hazardous Materials*, 151, 446–455.

Awawdeh, M. M., & Jaradat, R. A. (2010). Evaluation of aquifers vulnerability to contamination in the Yarmouk River basin, Jordan based on DRASTIC method. *Arabian Journal of Geosciences*. 3, 273–282. doi: 10.1007/s 12517-009-0074-9

Aydi, A. (2015). Assessment of heavy metal contamination risk in soils of landfill of Bizerte (Tunisia) with a focus on application of pollution indicators. *Environmental Earth Sciences*, 74, 3019–3027, doi: 10.1007/s12665-015-4332-8

Ayers, R. S., & Westcot, D. W. (1985). Water quality for agriculture, irrigation and drainage, 29, FAO, Rome.

Azims, M.D., Mahabubur, R.M., & Riaz, H.K. (2011). Characteristics of leachate generated at landfill sites and probable risks of surface and groundwater pollution in the surrounding areas: a case study of Matuail landfill site, Dhaka. *Journal of Bangladesh Academy of Sciences*, 35, 153–160.

Babiker, I., Mohammed, M., Hiyama, T., & Kato, K. (2005). A GIS-based DRASTIC model for assessing aquifer vulnerability in kakmigahara heights, Gifu Prefecture, central Japan. *Science of the Total Environment,* 345, 127–140.

Back, W., &Hanshaw, B. B. (1965). Advances in hydroscience. In chemical Geohydrology, *Academic Press, New York, 11*, 49.

Banu, S., & Berrin, T. (2015). Parametric fate and transport profiling for selective groundwater monitoring at closed landfills: a case study. *Waste Management*, 38, 263–270.

Baruah, T.C., & Barthakur, H.P. (1997). A Text Book of Soil Analysis. UBS Publishers Ltd., New Delhi.

Bashir, M.J.K., Isa, M.H., Kutty, S.R.M., Awang, Z.B., Aziz, A. H., & Mohajeri, S. (2009). Landfill leachate treatment by electrochemical oxidation. *Waste Management,* 29, 2534–2541.

Bauddh, K., Singh, K., Singh, B., & Singh, R.P. (2015). Ricinus communis: a robust plant for bio-energy and phytoremediation of toxic metals from contaminated soil. *Ecological engineering,* 84, 640–652.

Baun, A., Jensen, S.D., Bjerg, P., Christensen, T.H., Nyholm, N., 2000. Toxicity of organic chemical pollution in groundwater down gradient of a landfill (Grindsted, Denmark). *Environmental Science & Technology*, 34, 1647–1652.

Berry, W., Ketterings, Q., Antes, S., Page, S., Russell-Anelli, J., Rao, R. & DeGloria, S. (2007). Soil Texture. Agronomy Fact Sheet Series, 29, New York, 1-2.

Beyene, H., & Banerjee, S. (2011). Assessment of the pollution status of the solid waste disposal site of addis ababa city with some selected trace elements, Ethiopia. *World Applied Sciences Journal,* 14 (7), 1048-1057.

Bhargava, A., Carmona, F.F., Bhargava, M., & Srivastava, S. (2012). Approaches for enhanced phytoextraction of heavy metals. *Journal of Environmental Management*, 105, 103–120

Bhat, Z.A., Padder, S.A., Ganaie, A.Q., Dar, N. A., Rehman, H.U., & Wani, M.Y. (2017). Correlation of available nutrients with physico-chemical properties and nutrient content of grape orchards of Kashmir. *Journal of Pharmacognosy and Phytochemistry*, 6(2), 181-185.

Bhatia, M., & Goyal, D. (2014). Analyzing remediation potential of wastewater through wetland plants: a review, *Environmental Progress and Sustainable Energy,* 33, 9–27.

Bhuiyan, M.A.H., Parvez, L., Islam, M.A., Dampare, S.B., & Suzuki, S. (2010). Heavy metal pollution of coal mine-affected agricultural soils in the northern part of Bangladesh. *Journal of Hazardous Materials*, 173, 384–392.

BIS. (2012). Indian standard drinking water specification (second revision). Bureau of Indian Standards, New Delhi.

Blaylock, M. J., Salt, D. E, Dushenkov, S., Zakharova, O., Gussman, C., Kapulnik, Y., Ensley, B. D., & Raskin, I. (1997). Enhanced accumulation of Pb in Indian mustard by soil applied chelating agents. *Environmental Science & Technology*, 31 (3), 860-865.

Boughriba, M., Barkaoui, A.-E., Zarhloule, Y., Lahmer, Z., Houadi, B., & Verdoya, M. (2010). Groundwater vulnerability and risk mapping of the Angad transboundary aquifer using DRASTIC index method in GIS environment. *Arabian Journal of Geosciences*, 3, 207–220.

Bretzel, F.C., & Calderisi, M. (2011). Contribution of a municipal solid waste incinerator to the trace metals in the surrounding soil. *Environmental Monitoring and Assessment*, 182, 523–533.

Buat-Menard, P., & Cherselet, R. (1979). Variable influence of the atmospheric flux on the trace metal chemistry of oceanic suspended matter. *Earth and Planetary Science Letters*, 42, 398–411.

Cacador, I., & Duarte, B. (2015). Chromium phyto-transformation in sat marshes: the role of halophytes, in: Phytoremediation. *Springer International Publishing*, 211–217.

Calli, B., Mertoglu, N., Roest, K., & Inanc, B. (2006). Comparison of long-term performances and final microbial compositions of anaerobic reactors treating landfill leachate. *Bioresource Technology*, 97, 641-647.

Cañizares. P., Martínez, F., Jiménez, C., Lobato, J., & Rodrigo, M. A. (2006). Coagulation and electrocoagulation of wastes polluted with dyes**.** *Environmental Science & Technology*, 40(20), 6418-6424.

CCME. (2001). Canadian water quality guidelines for the protection of aquatic life: CCME Water Quality Index 1.0. Technical report. Canadian Council of Ministers of the environment, Winnipeg. http://www.ccme.ca/sourcetotap/wqi.html. Accessed 12 April 2013.

CCME. (2007). Canadian Soil Quality Guidelines for the Protection of Environmental and Human Health. Canadian Council of Ministers of the Environment, Winnipeg.

Census of India. (2011). Main sources of drinking water 2001-2011. Department of Census Kerala, Ministry of Home Affairs, India.

Central Ground Water Board (CGWB). (2013). Ground Water Information Booklet of Kannur District, Kerala State. Ministry of Water Resources, Government of India.

Central Ground Water Board (CGWB). (2013). Ground Water Information Booklet of Thrissur District, Kerala State. Ministry of Water Resources, Government of India.

Central Ground Water Board (CGWB). (2009). Groundwater information booklet of Kozhikode district, Kerala State. Ministry of Water Resources, Government of India.

Central Pollution Control Board (CPCB) (2000) Management of municipal solid waste. Ministry of Environment and Forests (MoEF), New Delhi, Indi

Central Pollution Control Board (CPCB). (2008). Guideline for water quality management. Central Pollution Control Board, Ministry of Environment and Forests, Government of India.

Central Soil Analytical Laboratory. (2007). Manual on soil analysis. A compilation of soil analytical works followed at Central Soil Analytical Laboratory, Thiruvananthapuram

Chakchouk, N., Elloumi, C., Belaid, S., Mseddi, L., Chaari, & Kallel, M. (2017). A combined electro-coagulation–electrooxidation treatment for dairy wastewater. *Brazilian Journal of Chemical Engineering*, 34(1), 109-117.

Chatterjee, R. (2010). Municipal solid waste management in Kohima city-India. *Iranian Journal of Environmental Health Science and Engineering*, 7(2), 173–180.

Chen, X. W., Tsz-Fung Wong, J., Mo, W. Y., Man, Y. B., Wang-Wai Ng, C., & Wong, M. H. (2015). Ecological performance of the restored south east new territories (sent) landfill in Hong Kong (2000–2012), *Land Degradation and Development*, 1, 1–13.

Chen, X., Chen, G., & Yue, P.L. (2000). Separation of pollutants from restaurant wastewater by electro-coagulation. *Separation and Purification Technology*, 19(1-2), 65-76.

Cheng, S. (2003). Effect of heavy metals on plants and resistance mechanisms. *Environmental Science and Pollution Research*, 10(4), 256–264.

Chimuka, L & Manungufala, T. E., (2009). Sources, bioavailability and fate of heavy metals and organic contaminants in compost manure. *Dynamic Soil, Dynamic Plant,* 3 (1), 32-38.

Chithra, K., Thilakavathi, R., Murugan, A. A., & Marimuthu, C. (2008). Treatment of textile effluent using sacrificial electrode. *Modern Applied Science*, 23(4), 38-43.

Christensen, T.H., Gentil, E., Boldrin, A., Larsen, A., Weidema, B.P., & Hauschild, M. (2009). C balance, carbon dioxide emissions and global warming potentials in LCA-modelling of waste management systems. *Waste Management and Research*, 27(8), 707–15.

Christensen, T.H., Kjeldsen, P., Bjerg, P.L., Jensen, D.L., Christensen, J.B., Baun, A., Albrechtsen, H.J., & Heron, G. (2001). Biogeochemistry of landfill leachate plumes, *Applied Geochemistry*, 16, 659–718.

Clark, T., & Stephenson, T. (1998). Effects of chemical addition on aerobic biological treatment of municipal wastewater. *Environmental Technology*, 19, 579–590.

Clayton, L.R. (2007). Phytoremediation. Encyclopedia of plant and crop science. Taylor & Francis, London, UK

Collivignarelli, C., Sorlini, S., & Vaccari, M. (2004). Solid wastes management in developing countries. CD-ROM of ISWA World Congress, Rome

Cristaldi, A., Gea, O. C., Jho, E. H., Zuccarello, P., Grasso, A., Copat, C., & Ferrante, M. (2017). Phytoremediation of contaminated soils by heavy metals and PAHs. *Environmental Technology & Innovation*. 8, 309-326.

Cui, L., Ouyang, Y., Lou, Q., Yang, F., Chen, Y., Zhu, W., & Luo, S. (2010). Removal of nutrients from wastewater with Canna indica L. under different vertical-flow constructed wetland conditions. *Ecological Engineering,* 36, 1083–1088.

D’Souza, P. & Somashekar, R. K. (2013). Assessment of stabilization, temporal variation and leachate contamination potential of municipal solid waste dumpsites in Bangalore. *International Journal of Environmental Protection*, 3(1), 28-35.

Daly, D., & Drew, D. (1999). Irish methodologies for karst aquifer protection. In: Beek B (ed) Hydrogeology and engineering geology of sinkholes and karst. Balkema, Rotterdam, 267– 327.

Daneshvar, N., Oladegaragoze, A., & Djafarzadeh, N. (2006). Decolorization of basic dye solutions by electro-coagulation: an investigation of the effect of operational parameters. *Journal of Hazardous Materials,* 129, 116–122.

Dang, Z., Liu, C., & Haigh, M. J. (2002). Mobility of heavy metals associated with the natural weathering of coal mine spoils. *Environmental Pollution*, 118, 419–426.

Davis., & De Viest. (1966). Hydrogeology. New York, John Wiley & Sons, 453.

De Baere, L. (2006). Will anaerobic digestion of solid waste survive in the future? *Water Science and Technology*, 53(8), 187–94.

De Morais, J.L., Zamora, P.P. (2005). Use of advanced oxidation processes to improve the biodegradability of mature landfill leachates. *Journal of Hazardous Materials*, 123(1-3), 181-187.

De, S., & Debnath, B. (2016). Prevalence of Health Hazards Associated with Solid Waste Disposal- A Case Study of Kolkata, India. *Environmental Science-Processes*, 35, 201–209. doi: 10.1016/j. proenv.2016.07.081

Department for Environment, Food and Rural Affairs (DEFRA) (2007). Incineration of municipal solid waste, waste management technology brief, the new technologies work steam of the defra Waste Implementation Programme.

Dharmarathne, N., & Jagath, G. (2013). Leachate characterization and surface - groundwater pollution at municipal solid waste landfill of Gohagoda, Sri Lanka. *International Journal of Scientific Research*, 3, 1-7.

District Survey Report of Wayanad District, Kerala State. (2016). Environment Impact Assessment (EIA) Notification under Environment (Protection) Act 1986, Department of mining and geology.

Dixit. R., Wasiullah., Malaviya, D., Pandiyan, K., Singh, U.B., Sahu, A., Shukla, R., Singh, B.P., Rai, J.P., Sharma, P. K., Lade, H., & Paul, D. (2015). Bioremediation of heavy metals from soil and aquatic environment: an overview of principles and criteria of fundamental processes. *Sustainability*, 7, 2189-2212.

Dong, J., Yang, Q.W., Sun, L.N., Zeng, Q., Liu, S.J., Pan, J., &Liu, X.L. (2011). Assessing the concentration and potential dietary risk of heavy metals in vegetables at a Pb/Zn mine site, China. *Environmental Earth Science,* 64, 1317-1321.

Ducic, T., & Polle, A. (2005). Transport and detoxification of manganese and copper in plants. *Brazilian Journal of Plant Physiology*, 17, 103–112.

Edward, P. J. (1997). Soil science and management. 3rd ed. Albany: Delmar Publishers, c1997. ISBN: 0827372930

El-Naas, M.H., Al-Zuhair, S., Al-Lobaney, A., & Makhlouf, S. (2009). Assessment of electro-coagulation for the treatment of petroleum refinery wastewater. *Journal of Environmental Management*, 91, 180–185.

El-Naqa, A., Hammouri, N. & Kuisi, M. (2006). GIS-based evaluation of groundwater vulnerability in the Russeifa area, Jordan. *Revista Mexicana de Ciencias Geológicas*, 23, 277-287.

El-Shazly. A.H., Al-Zahrani, A.A., & Al-Shahrani, S.S. (2011). Improvement of NO_3^- removal from wastewater by using batch electro-coagulation unit with vertical monopolar aluminum electrodes, *International Journal of Electrochemical Science*, 6, 4141- 4149.

El-Taweel, Y. A., Nassef, E. M., Elkheriany, I., & Sayed, D. (2015). Removal of Cr(VI) ions from wastewater by electro-coagulation using iron electrode. *Egyptian Journal of Petroleum*, 24, 183–192.

Erabeea, I. K., Ahsan, A., Josed, B., Arunkumare, T., Sathyamurthy, R., Idrusa, S., & Dauda, N. N. N. (2017). Effects of electric potential, NaCl, pH and distance between electrodes on efficiency of electrolysis in landfill leachate treatment. *Journal of Environmental Science and Health Part A*, 1–7.doi: 10.1080/10934529.2017.1303309

Erses, A.S., & Onay, T. T. (2003). In situ heavy metal attenuation in landfills under methanogenic conditions. *Journal of Hazardous Materials*, 25, 99(2), 159-75.

Evangelou, M.W.H., Ebel, M., & Schaeffer, A. (2007). Chelate assisted phytoextraction of heavy metals from soil: Effect, mechanism, toxicity, and fate of chelating agents. *Chemosphere*, 68, 989–1003.

Fabiyi, I.P. (2008). Depth of hand-dug wells and water chemistry. Example from IBNE local Government Area, Oyo state, Nigeria, *Journal of Social Sciences*, 17(3), 261–266.

Fageria, N., Baligar,V., & Clark, R. (2002). Micronutrients in crop production. *Advances in Agronomy*, 77, 185 –268.

Fatta, D., Papadopoulos, A., & Loizidou, M. (1999). A study on the landfill leachate and its impact on the groundwater quality of the greater area. *Environmental Geochemistry and Health*, 21, 175–190.

Finzgar, N., Zumer, A., & Lestan, D. (2006). Heap leaching of Cu contaminated soil with [S, S]-EDDS in a closed process loop. *Journal of Hazardous Materials*, 135, 418–422.

Fitz, W.J., & Wenzel, W.W. (2002). Arsenic transformations in the soil rhizosphere plant system: fundamentals and potential applicationto phytoremediation. *Journal of Biotechnology*, 99, 259-278.

Foo, K. Y., Lee, L. K., & Hameed, B. H. (2013). Batch adsorption of semi-aerobic landfill leachate by granular activated carbon prepared by microwave heating. *Chemical Engineering Journal*, 222, 259-264.

Foo, K.Y., & Hameed, B. H. (2009). An overview of landfill leachate treatment via activated carbon adsorption process. *Journal of Hazardous Materials*, 171, 54-60.

Foster, S.S. (1987). Fundamental concepts in aquifer vulnerability, pollution risk and protection strategy. In: Duijvenbooden Wvan, Waegeningh HG van (eds). TNO Committee on Hydrological Research, The Hague vulnerability of soil and groundwater to pollutants. *Proceedings and Information*, 38, 69–86.

Fowles, M. (2007). Black carbon sequestration as an alternative to bio-energy. *Biomass Bioenergy*, 31(6), 426– 32

Franco, D. V., Silva, L. M. D., & Jardim, W. F. (2009). Reduction of hexavalent chromium in soil and ground water using zerovalent iron under batch and semi-batch conditions. *Water, Air, and Soil Pollution*, 197 (1–4), 49–60.

Gajski, G., Oreščanin, V. & Garaj-Vrhovac, V. (2011). Cytogeno toxicity of sewage sludge leachate before and after calcium oxide-based solidification in human lymphocytes. *Ecotoxicology and Environmental Safety*, 74, 1408-1415.

Ganiyu, S. A., Badmus, B. S., Oladunjoye, M. A., Aizebeokhai, A. P., Ozebo, V. C., Idowu, O. A., & Olurin, O. T. (2016). Assessment of groundwater contamination around active dumpsite in Ibadan south western Nigeria using integrated electrical resistivity and hydrochemical methods. *Environmental Earth Sciences*, 75, 643, doi: 10.1007/s12665-016-5463-2

Gao, J., Oloibiri, V., Chys, M., Audenaert, W., Decostere, B., He, Y., Langenhove, H.V., Demeestere, K., & Hulle, S. W. H. V. (2015). The present status of landfill leachate treatment and its development trend from a technological point of view. *Reviews in Environmental Science and Bio/Technology*, 14, 93–122.

Garbisu, C., & Alkorta, I. (2011). Phytoextraction: a cost-effective plant-based technology for the removal of metals from the environment. *Bioresource Technology*, 77(3), 229-36

Gengec, E., Kobya, M., Demirbas, E., Akyol, A., & Oktor, K. (2012). Optimization of baker's yeast wastewater using response surface methodology by electro-coagulation. *Desalination*, 286, 200–209.

Ghosh, N. C & Sharma, K. D. (2006). Groundwater modeling and management. Capital publishing company, New Delhi.

Giasuddin, A. B. M., Kanel, S.R., & Choi, H. (2007). Adsorption of humic acid onto nano scale zero valent iron and its effect on arsenic removal. *Environmental Science Technology,* 41, 2022–2027.

Ginocchio, R., Rodríguez, P. H., Badilla-Ohlbaum, R., Allen, H. E., & Lagos, G. E. (2002). Effect of soil copper content and pH on copper uptake of selected vegetables grown under controlled conditions. *Environmental Toxicology and Chemistry*, 21(8), 1736–44.

Giripunje, M. D., Abhay,F., & Pravin, U.M. (2015). Remediation techniques for heavy-metalcontaminatio in lakes: a review. *Clean - Soil Air Water,* 43(9), doi: 10.1002/clen.2014 0419

Giusti, L. (2009). A review of waste management practices and their impact on human health. *Waste management*, 29(8), 2227–2239.

Gogu, R.C., & Dassargues, A. (2000). Sensitivity analysis for the EPIK method of vulnerability asessment in a small karstic aquifer, southern Belgium. *Hydrogeology Journal*, 8, 337–345.

Guerrero, L.A., Maas, G., & Hogland, W. (2013). Solid waste management challenges for cities in developing countries. *Waste Management*, 33(1), 220–232.

Gunjan, B., Swamee, P.K., & Arvind, K. (2012). Assessment of groundwater quality near municipal solid waste landfill by an Aggregate Index Method. *International Journal of Environmental Science*, 2, 1492–1503.

Guo, J. S., Abbas, A. A., Chen, Y. P., Liu, Z. P., Fang, F., & Chen, P. (2010). Treatment of landfill leachate using a combined stripping, Fenton, SBR, and coagulation process. *Journal of Hazardous Materials*, 178 (1-3), 699-705

Guo, Z. R., Zhang, G., Fang, J., & Dou, X. (2006). Enhanced chromium recovery from tanning wastewater. *Journal of Cleaner Production*, 14 (1), 75-79.

Gupta, N. (2014). Groundwater vulnerability assessment using DRASTIC method in Jabalpur district of Madhya Pradesh. *International Journal of Recent Technology and Engineering*, 3, 36-43.

Gupta, N., Yadav K. K., & Kumar, Y. (2015). A review on current status of municipal solid waste management in India. *Journal of Environmental Sciences*, 37, 206 – 217.

Gurses, A., Yalcin, M., & Dogan, C. (2002). Electro-coagulation of some reactive dyes: a statistical investigation of some electrochemical variables. *Waste Management,* 22, 491–499.

Hakanson, L. (1980). An ecological risk index for aquatic pollution control. A sedimentological approach. *Water Research*, 14(8), 975–1001.

Hallaq,A., & Elaish, B. (2012). Assessment of aquifer vulnerability to contamination in Khanyounis Governorate, Gaza Strip – Palestine, using the DRASTIC model within GIS environment. *Arabian Journal of Geosciences*, 5, 833– 847.

Han, Z., Ma, H., Shi, G., He, L., Wei, L., & Shi, Q. (2016). A review of groundwater contamination near municipal solid waste landfill sites in China. *Science of the Total Environment,* 569–570, 1255–1264.

Harbaugh, A.W., Banta, E.R., Hill, M.C., & Mcdonald, M.G. (2000). MODFLOW- 2000, The US Geological Survey Modular Ground-water Model- users guide to modularization concepts and the groundwater flow process. US Geological Survey Open-File Report 00-92, 121

Harikumar, P.S. (2010). Treatment of wastewater using artificial wetlands. *Everything about Water,* 77.

Harikumar, P.S., & Jesitha, K. (2016). Nano-phytotechnological remediation of endosulfan using zero valent iron nanoparticles. *Journal of Environmental Protection*, 7, 734-744.

Harikumar, P.S., & Megha, T. (2017). Treatment of cadmium, lead and copper using phytoremediation enhanced by titanium dioxide nanoparticles. *Eco Chronicle*, 12(2), 25 – 34.

Harikumar, P.S., Nasir, U. P., & Rahman, M. P. M (2009). Distribution of heavy metals in the core sediments of a tropical wetland system. *International Journal of Environmental Science and Technology*, 6, 225-232. doi: org/10.1007/BF03327626

Harmsen, K. (1983). Theories of cation adsorption by soil constitutes: discrete-site models, in: Bolt, 1894 G.H. (Ed.), *Soil Chemistry B*, Physico-chemical models. Elsevier, Amsterdam, 77-139.

Hegde, U., Chang, T.C., & Yang, S.S. (2003). Methane and carbon dioxide emissions from Shan-chu-ku landfill site in northern Taiwan. *Chemosphere,* 52, 1275–1285.

Herath, I., & Vithanage, M. (2015). Phytoremediation in Constructed Wetlands. doi: 10.1007/978-3-319-10969-5_21

Hesse, P.R. (1971). *Textbook of soil chemical analysis*. CBS Publishers, New Delhi

Hong, K.J., Tokunaga, S., & Kajiuchi, T. (2002). Evaluation of remediation process with plant-derived biosurfactant for recovery of heavy metals from contaminated soils. *Chemosphere*, 49, 379–387.

Hooda, V. (2007). Phytoremediation of toxic metals from soil and waste water. *Journal of Environmental Biology*, 28(2), 367-376.

Hopps, H.C., & Feder, G.L. (1986). Chemical qualities of water that contribute to human health in a positive way. *Science of the Total Environment*. 54, 207-216.

Hua C.Y., Loa S.L., & Kuan W.H. (2003). Effects of co-existing anions on fluoride removal in electro coagulation (EC) process using aluminum electrodes. *Water Research*, 37 (18), 4513–4523.

Huan-jung, F., Shu, H.Y., Yang, H.S., & Chen, W.C. (2006). Characteristics of landfill leachates in central Taiwan. *Science of the Total Environment*, 361, 25–37.

Hurley, T., Sadiq, R., & Mazumder, A. (2012). Adaptation and evaluation of the Canadian Council of Ministers of the Environment Water Quality Index (CCME WQI) for use as an effective tool to characterize drinking source water quality. *Water Research*, 46(11), 3544-3552.

Imfeld, G., Braeckevelt, M., Kuschk, P., & Richnow, H.H. (2009). Monitoring and assessing processes of organic chemicals removal in constructed wetlands. *Chemosphere,* 74, 349–362.

Inan, H., Dimoglo, A., Simsek, H., & Karpuzcu, M. (2004). Olive oil mill wastewater treatment by means of electro-coagulation. *Separation and Purification Technology*, 36, 23–31.

Inanç, B., Çallı, B., & Saatçi, M. (2000). Characterization and anaerobic treatment of the sanitary landfill leachate in Istanbul. *Water Science and Technology*, 41, 223–230.

Indian Meteorological Department (IMD). (2013). Normal south west monsoon rainfall data, Kozhikode district, Kerala, India.

IPCC (2007). Climate change: the physical science basis. In: contribution of working group I to the fourth assessment report of the intergovernmental panel on climate. Cambridge University Press, Cambridge, UK and New York, NY, USA

Iwegbue, C.M.A., Nwajei, G.E., Ogala, J.E., & Overah, C.L. (2010). Determination of trace metal concentrations in soil profiles of municipal waste dumps in Nigeria. *Environmental Geochemistry and Health*, 32, 415–430.

Jalali, M. (2005). Nitrate pollution of groundwater in Toyserkan, *Western Iran Environmental Earth Science*, 62(5), 907 – 913.

Janpoor, F., Torabian, A., & Khatibikamal, V. (2011). Treatment of laundry waste-water by electro-coagulation. *Journal of Chemical Technology and Biotechnology,* doi: 10.1002/jctb.2625

Jasmin, I., & Mallikarjuna, P. (2015). Delineation of groundwater potential zones in Araniar River basin, Tamil Nadu, India: an integrated remote sensing and geographical information system approach. *Environmental Earth Sciences*, 73, 3833–3847.

Jeyapriya, S.P. & Saseetharan, M. K. (2010). Effect of municipal solid waste on the characteristics of soil. *Pollution Research Paper***,** 29 (1), 37-41.

Jhamnani, B., & Singh, S.K. (2009). Groundwater contamination due to Bhalaswa landfill site in New Delhi. *International Journal of Civil and Environmental Engineering*, 1(3), 121-125.

Jiamjitrpanich, W., Parkpian, P., Polprasert, C. & Kosanlavit, R. (2013). Trinitrotoluene and its metabolites in shoots and roots of *Panicum*

Maximum in nano-phytoremediation. *International Journal of Environmental Science and Development*, 4, 7-10.

Jomjun, N., Siripen, T., Maliwan, S., Jintapat, N., Prasak, T., Somporn, C., & Petch, P. (2010). Phytoremediation of arsenic in submerged soil by wetland plants. *International Journal of Phytoremediation*, 13, 35–46.

Jones-Lee, A., & Lee, G.F. (1993). Groundwater pollution by municipal landfills:leachate composition, detection and water quality significance. Proc. Sardinia '93 IV International Landfill Symposium, Sardinia, Italy, 109–1103.

Kale, S.S., Kadam, A. K., Kumar, S., & Pawar, N.J. (2010). Evaluating pollution potential of leachate from landfill site from the Pune metropolitan city and its impact on shallow basaltic aquifers. *Environmental Monitoring* Assessment, 162, 327–346.

Kalogo, Y., Habibi, S., MacLean, H.L., & Joshi, S.V. (2006). Environmental implications of municipal solid waste-derived ethanol. *Environmental Science & Technology*, 41(1), 35–41.

Kanel, S. R., Greneche, J. M., & Choi, H. (2006). Arsenic (V) removal from groundwater using nano scale zero-valent iron as a colloidal reactive barrier material. *Environmental Scienceand Technology*, 40(6), 2045–2050.

Kanel, S. R., Manning, B., Charlet, L., & Choi, H. (2005). Removal of arsenic (III) from groundwater by nanoscale zero-valent iron. *Environmental Science and Technology*, 39(5), 1291–1298.

Kanmani, S., & Gandhimathi, R. (2013). Assessment of heavy metal contamination in soil due to leachate migration from an open dumping site. *Applied Water Science,* 3, 193–205, doi: 10.1007/s13201-012-0072-z

Karak, T., Bhagat, R.M. & Bhattacharyya, P. (2012) Municipal solid waste generation, composition and management: The world scenario. *Critical Reviews in Environmental Science and Technology,* 42(15), 1509–1630.

Kasassi, A., Rakimbei, P., Karagiannidis, A., Zabanitou, A., Tsiouvaras, K., Nastis, A., & Tzafeirpoulou, K. (2008). Soil contamination by heavy metals: measurement from a closed unlined landfill. *Bioresource Technology*, 99, 8578–8584.

Kathale, N. (2012). Physico-chemical status of the groundwater of southeastern area - Chandrapur, Maharashtra, India. *International Journal of Interdisciplinary Research*, 2, 165-172.

Kathiravale, S., Muhd Yunus, M.N. (2008). Waste to wealth. *Asia Europe Journal,* 6(2), 359–371.

Kaushal, R., Kumar, V. G. K., Chabukdhara, M. (2012). Municipal solid waste management in India-current state and future challenges: a review. *International Journal of Engineering Science and Technology,* 4 (4), 1473-1489.

Kelley, W.E. (1976). Groundwater pollution near a landfill. *Journal of Environmental Engineering*, ASCE 102(EE6), 1189–1199.

Kelly, W.P. (1940). Permissible composition and concentration of irrigated waters. In: Proceedings of the A.S.C.F 607.

Kelly, W.R., & Wilson, S.D. (2002). Temporal changes in shallow groundwater quality in northeastern Illinois. Proc. 12th annual Illinois groundwater consortium (IGC) conference, www.siu.edu/orda/ igc/proceedings/02/ kelly.pdf.

Kerala State Planning Board. (2013). Soil fertility assessment and information management for enhancing crop productivity in Kerala, Government of Kerala. 133

Kermet-Said, H., & Moulai-Mostefa, N. (2015). Optimization of turbidity and cod removalfrom pharmaceutical wastewater by electro-coagulation: isotherm modeling and cost analysis. *Polish Journal of Environmental Studies*, 24 (3), 1049-1061.

Khan, A., Khan, H.H., Umar, R., & Khan, M.H. (2014). An integrated approach for aquifer vulnerability mapping using GIS and rough sets: study from an alluvial aquifer in north India. *Hydrogeology Journal*, 22, 1561-1572.

Khodapanah, L., Sulaiman, W. N. A., & Khodapanah, D. N. (2009). Groundwater quality assessment for different purposes in Eshtehard District, Tehran, Iran. *European Journal of Scientific Research*, 36 (4), 543-553.

Khoufi, S., Feki, F., &Sayadi, S. (2007). Detoxification of olive mill wastewater by electro-coagulation and sedimentation processes. *Journal of Hazardous Materials,* 142(1-2), 58-67.

Kim, H., & Tan. (2005). Principal of soil chemistry, 3rd ed., Brijbasi Art Press Ltd, U.P, India. 6062.

Kjeldsen, P., Barlaz, M.A., Rooker, A.P., Baun, A., Ledin, A., & Christensen, T.H. (2002). Present and long-term composition of MSW landfill leachate: a review. *Critical Reviews in Environmental Science and Technology*, 32, 297–336.

Kobya, M., Can, O.T., & Bayramoglu, M. (2003). Treatment of textile wastewaters by electro-coagulation using iron and aluminum electrodes. *Journal of Hazardous Materials*, B100, 163–178.

Kobya, M., Hiz, H., Senturk, E., Aydiner, C., & Demirbas, E. (2006). Treatment of potato chips manufacturing wastewater by electro-coagulation. *Desalination*, 190, 201–211.

Koda, E., Wiencław, E., & Martelli, L. (2009). Transport modelling and monitoring research use for efficiency assessment of vertical barrier surrounding old sanitary landfill. Annals of warsaw university of life sciences – SGGW land reclamation, 41, 41–48.

Komárek, M., Tlustoš, P., Száková, J., Chrastný, J., & Ettler, V. (2007). The use of maize and poplar in chelant enhanced phytoextraction of lead from contaminated agricultural soil. *Chemosphere*, 67, 640–651.

Kulikowska, D., & Klimiuk, E. (2008). The effect of landfill age on municipal leachate composition. Bioresource Technology, 99(13), 5981–5985.

Kumar, D., & Alappat, B. J. (2005). Evaluating leachate contamination potential of landfill sites using Leachate Pollution Index. *Clean Technology and Environment*, 7, 190–197.

Kumar, D., & Alappat, B.J. (2003). A technique to quantify landfill leachate pollution. Proceedings of the ninth international landfill symposium, Italy.

Kumar, M., & Babel, A. L. (2011). Available micronutrient status and their relationship with soil properties of Jhunjhunu Tehsil, Rajasthan, India. *Journal of Agricultural Science*. 3(2), 97-106.

Kumar, N., Bauddh, K., Dwivedi, N., Barman, S. C., & Singh, D. P., (2011). Accumulation of metals in selected macrophytes grown in mixture of drain water and tannery effluent and their phytoremediation potential. *Journal of Environmental Biology,* 33, 923-927.

Kumar, S. V., Amarender, B., Dhakate, R., Sankaran, S., & Kumar, R. K. (2014). Assessment of groundwater quality for drinking and irrigation use in shallow hard rock aquifer of Pudunagaram, Palakkad district Kerala. *Applied Water science*, doi: 10.1007/s13201-014-0214-6.

Kumar, S., Smith, S. R., Fowler, G., Velis, C., Kumar, S. J., Arya, S., Rena, Kumar, R., & Cheeseman, C. (2017). Challenges and opportunities associated with waste management in India. *Royal Society Open Science,* 4, 160764.http://dx.doi.org/10.1098/rsos.160764

Kumari, P., Gupta, N.C., & Kaur, A. (2017). A review of groundwater pollution potential threats from municipal solid waste landfill sites: assessing the impact on human health. *Journal of Environmental Health Engineering*, 4(1), 11525.doi: 10.5812/ajehe.11525.

Lasat, M. M. (2002). Phytoextraction of toxic metals: a review of biological mechanisms. *Journal of Environmental Quality*, 31, 109–120.

Lasat, M.M. (2000). Phytoextraction of metals from contaminated soil: a review of plant/soil/metal interaction and assessment of pertinent agronomic issues. *Journal for Hazardous Substance Research*, 2(5), 1–25.

Latrach, L., Masunaga, T., Ouazzani, N., Hejjaj, A., Mahi, M., & Mandi, L. (2015). Removal of bacterial indicators and pathogens from domestic wastewater by the multi-soil-layering (MSL) system. *Soil Science and Plant Nutrition*, 61, 337–346.

Li, X. Q., & Zhang, W. X. (2006). Iron nanoparticles: the core-shell structure and unique properties for Ni (II) sequestration. *Langmuir*, 22(10), 4638–4642.

Li, X. Q., & Zhang, W. X. (2007). Sequestration of metal cations with zerovalent iron nanoparticles - A study with high resolution X-ray photoelectron spectroscopy (HR-XPS). *Journal of Physical Chemistry C*, 111, 6939–6946

Liao, S.W., & Chang, W. L. (2004). Heavy metal phytoremediation by water hyacinth at constructed wetlands in Taiwan.*Journal of Aquatic Plant Management,* 42, 60-68.

Liu, H. J., Zhao, X., & Qu, J. H. (2010). Electro-coagulation in water treatment. Electrochemistry for the environment. *Springer-Verlag*, New York, 247. doi: 10.1007/978-0-387-68318-8 10.

Liu, R., & Lal, R. (2012). Nanoenhanced materials for reclamation of mine lands and other degraded soils: a review. *Journal of Nanotechnology*, doi:10.1155/2012/461468

Lorah, M. M., Cozzarelli, I. M. & Böhlke, J. K. (2009). Biogeochemistry at a wetland sediment– alluvial aquifer interface in a landfill leachate plume. *Journal of Contaminant Hydrology*, 105, 99- 117.

Lu, X., Kruatrachue, M., Pokethitiyookb, P., & Homyokb, K. (2004). Removal of cadmium and zinc by water hyacinth, Eichhornia crassipes. *Scienceasia,* 30, 93–103.

Machender, G., Dhakate, R., Prasanna, L., & Govil, P. K. (2010). Assessment of heavy metal contamination in soils around Balanagar industrial area, Hyderabad, India. *Environmental Earth Sciences*, doi: 10.1007/s12665-010-0763-4

Mackova, M., Prouzova, P., Stursa, P., Ryslava, E., Uhlik, O., Beranova, K., Rezek, J., Kurzawova, V., Demnerova, K., & Macek, T. (2009). Phytorhizoremediation studies using long-term PCB-contaminated soil. *Environmental Science and Pollution Research,* 16, 817-829.

Madhavi, V., Prasad, T.N.V.K.V., & Madhavi, G. (2013). Synthesis and spectral characterization of iron based micro and nanoparticles. *International Journal of Nanomaterials and Biostructures*, 3(2), 31–34.

Mahar, A., Wang, P., Ali, A., Awasthi, M. K., Lahori, A. H, Wang, Q., Li, R., & Zhang, Z. (2016). Challenges and opportunities in the phytoremediation of heavy metals contaminated soils: A review, *Ecotoxicology and Environmental Safety*, 126, 111–121.

Mahmood, Q., Zheng, P., Islam, E., Hayat, Y., Hassan, M.J., Jilani, G., & Jin, R.C. (2005). Lab scale studies on Water hyacinth (Eichhornia crassipes marts solms) for biotreatment of textile wastewater. *Caspian Journal of Environmental Sciences*, 3(2), 83–88.

Mandal, A., & Sengupta, D. (2006). An assessment of soil contamination due to heavy metals around a coal-fired thermal power plant in India. *Environmental Geology*, 51, 409–420.

Manimekalai, B., & Vijayalakshmi, P. (2012). Analysis of leachate contamination potential of a municipal landfill using leachate pollution index. *IOSR Journal of Environmental Science, Toxicology and Food Technology,* 2 (1), 16-39.

Mapanda, F., Mangawayana, E. N., Nyamangara, J., & Giller, K. E. (2005). The effect of longterm irrigation using wastewater on heavy-metal contents of soils under vegetables in Harare, Zimbabwe. *Agriculture Ecosystems Environment*, 107, 151–165.

Martınez-Huitle, C.A., & Brillas, E. (2009). Decontamination of wastewaters containing synthetic organic dyes by electrochemical methods: a general review. *Applied Catalysis B*, 87, 105–145.

Marzougui, A., & Mammou, A.B. (2006). Impacts of the dumping site on the environment: case of the Henchir El Yahoudia Site, Tunis, Tunisia. *Comptes Rendus Geoscience*, 338, 1176–1183.

Mellem, J., Baijanth, H., & Odhav, B. (2009). Translocation and accumulation of Cr, Hg, As, Pb, Cu and Ni by Amaranthus dubius (Amaranthaceae) from contaminated sites. *Journal of Environmental Science and Health*, 44, 568-575.

Miehr, R., Tratnyek P.G., Bandstra J.Z., Scherer M.M., Alowitz, M.J., & Bylaska, E.J. (2004) The diversity of contaminant reduction reactions by zero-valent iron: role of the reductate. *Environmental Science and Technology*, 38(1), 139-147.

Milosevic, N., Thomsen, N.I., & Juhler, R.K. (2012). Identification of discharge zones and quantification of contaminant mass discharges into a local stream from a landfill in a heterogeneous geologic setting. *Journal of Hydrology*, 446-447, 13–23.

Miretzky, P., Saralegu,i A., & Cirelli, F. A. (2004). Aquatic macrophytes potential for the simultaneous removal of heavy metals (Buenos Aires, Argentina). *Chemosphere*, 57(8), 997-1005.

Mishra, V.K., & Tripathi, B.D. (2008). Concurrent removal and accumulation of heavy metals by the three aquatic macrophytes. *Bioresource Technology*, 99, 7091–7097.

Mishra, V.K., Tripathi, B.D., & Kim, K.H. (2009). Removal and accumulation of mercury by aquatic macrophytes from an open cast coal mine effluent. *Journal of Hazardous Materials*, 172, 749–754.

Mollah, M.Y.A., Schennach, R., Parga, J.R., & Cocke, D.L. (2001). Electro-coagulation (EC) –science and applications. *Journal of Hazardous Materials*, 84, 29–41.

Mor. S., Ravindra, K., Dahiyaa, R. P., & Chandra, A. (2006). Leachate characterization and assessment of groundwater pollution near municipal solid waste landfill site. *Environmental Monitoring Assessment*, 118, 435-456.

Morteza, E., Moaveni, P., Aliabadi, F.H & Kiyani, M. (2013). Study of photosynthetic pigments changes of maize (Zea mays L.) under nano TiO_2 spraying at various growth stages. *Springer Plus*, 2, 247.

Mukherjee, S., Mukhopadhyay, S., Hashim, M. A., & Gupta, B. S. (2015). Contemporary environmental issues of landfill leachate: assessment & remedies. *Critical Reviews in Environmental Science and Technology*, 45(5), 472-590.

Nagarajan, R., Subramani, T., & Elango, L. (2012). Impact of leachate on groundwater pollution due to non-engineered municipal solid waste landfill sites of erode city, Tamil Nadu, India. *Iranian Journal of Environmental Health Sciences & Engineering*, 9(1), 35-47.

Narayana, T. (2009). Municipal solid waste management in India: from waste disposal to recovery of resources. *Waste Management*, 29, 1163–1166.

Neill, M. (2004). Microbiological Indices for total coliform and E. coli bacteria in estuarine waters. *Marine Pollution Bulletin*, 49(9–10), 752–760.

Neilson, J.W., Artiola, J.F., & Maier, R.M. (2003). Characterization of lead removal from contaminated soils by non-toxic soil-washing agents. *Journal of Environmental Quality*, 32, 899-908.

Neshat, A., Pradhan, B., Pirasteh, S., & Shafri, H. Z. M. (2013). Estimating groundwater vulnerability to pollution using a modified DRASTIC model in the Kerman agricultural area, Iran. *Environmental Earth Science*, doi: 10.1007/s12665-013-2690-7

Ngo, H.H., Guo, W.S., & Xing, W. (2008). Applied technologies in municipal solid waste landfill leachate treatment. Encyclopedia of life support systems (EOLSS), pp 17

Nhari, F., Sbaa, M., Vasel, J.L., Fekhaoui, M., & El Morhit, M. (2014). Soil contamination of the landfill uncontrolled by heavy metals: case of the landfill of Ahfir-Saidia (Eastern Morocco). *Journal of Materials and Environmental Science*, 5(5), 1477–1484.

Ni'am, M.F., Othman, F., Sohaili, J., & Fauzia, Z. (2007). Electro-coagulation technique in enhancing COD and suspended solids removal to improve wastewater quality. *Water Science & Technology*, 56(7), 47–53.

Nowak, R., Włodarczyk-Makuła, M., Wiśniowska, E., & Grabczak, K. (2016). The comparison of the effectiveness of pre-treatment processes of landfill leachate. *Annual Set the Environment Protection*, 18, 122–133.

NSCA (2002) Comparison of emissions from waste management options. National society for clean air and environmental protection bridgwater AV (1994) Catalysis in thermal biomass conversion. *Applied Catalysis A*, 116(1–2), 5–47

Nyquist, J., & Greger, M. (2007). Uptake of Zn, Cu, and Cd in metal loaded Elodea Canadensis. *Environmental and Experimental Botany,* 60(2), 219-226.doi: 10.1016/j.envexpbot.2006.10.009

Obiajunwa, E.I., Pelemo, D.A., Owalabi, S.A., Fasai, M.K., & Johnson-Fatokun, F.O. (2002). Characterisation of heavy metal pollutants of soils and sediments around a crude oil production terminal using EDXRF. *Nuclear Instruments and Methods in Physics Research Section B*, 194 (1), 61–64.

Ogundiran, O. O., & Afolabi, T. A. (2008). Assessment of the physicochemical parameters and heavy metals toxicity of leachates from municipal solid waste open dumpsite. *International Journal of Environmental Science and Technology*, 5 (2), 243-250.

Olorunfemi, I. E., Fasinmirin, J. T., & Ojo, A. S. (2016). Modeling cation exchange capacity and soil water holding capacity from basic soil properties. *Eurasian Journal of Soil Science*, 5 (4), 266 – 274.

Pacheco, F.A.L., & Fernandes, L.F. S. (2012). The multivariate structure of DRASTIC model. *Journal of Hydrology*, doi: 10.1016/jhydrol.2012.11.20

Padmavathiamma, P. K., & Li, L.Y. (2007). Phytoremediation technology: hyperaccumulation metals in plants. *Water, Air and Soil Pollution*, 184, 105-126.

Pak, K. S. (2005). Factors influencing treatment of nitrate contaminated water using batch electro-coagulation process. *International Journal of Current Engineering and Technology*, 5 (2), 714-718.

Panwar, S. P., Nagpal, S., & Sharma, M. (2017). A review on present practices, issues and challenges of municipal solid waste management in India. *International Journal on Emerging Technologies*, 8(1), 647-651.

Pappu, A., Saxena, M., & Asokar, S.R. (2007). Solid waste generation in India and their recycling potential in building materials. *Journal of Building and Environment,* 42 (6), 2311–2324.

Patil, S.S., Shedbalkar, U.U., Truskewycz, A., Chopade, B.A., & Ball, A.S. (2016). Nanoparticles for environmental clean-up: a review of potential risks and emerging solutions. *Environmental Technology & Innovation,* 5, 10–21.

Pawels, R., & Tom, A. P. (2013). Assessment of technological options for solid waste treatment in Kerala. *International Journal of Scientific and Research Publications*, 3 (8), 1-9.

Peters, R.W. (1999). Chelant extraction of heavy metals from contaminated soils. *Journal of Hazardous Materials*, 66, 151–210.

Piper, A. M. (1944). A graphical procedure in the geochemical interpretation of water analysis. *Transactions. American Geophysical Union*, 25, 914–928.

Piscopo, G. (2001). Groundwater vulnerability map, explanatory notes, Castlereagh Catchment. NSW Department of Land and Water Conservation, New South Wales, Australia.

Ponder, S. M., Darab, J. G., & Mallouk, T. E. (2000). Remediation of Cr(VI) and Pb(II) aqueous solutions using supported, nanoscale zero-valent iron. *Environmental Science and Technology*, 34 (12), 2564–2569.

Poursaberi, T., Hassanisadi, M., & Nourmohammadian, F. (2012). Application ofsynthesized nanoscale zero-valent iron in the treatment of dye solution containing basicyellow 28. *Progress Color Colorants Coat*, 5, 35-40.

Prabu, D., & Parthiban, R. (2013). Synthesis and characterization of nanoscale zero valent iron (NZVI) nano particles for environmental remediation. *Asian Journal of Pharmacy and Technology,* 3 (4), 181-184.

Prasad, K., & Shukla, J.P. (2014) Assessment of groundwater vulnerability using gis-based drastic technology for the basaltic aquifer of Burhner watershed, Mohgaon Block, Mandla (India). *Current Science*, 107, 1649-1656.

Priya, E. S., & Selvan,P. S. (2017). Water hyacinth (Eichhornia crassipes) – An efficient and economic adsorbent for textile effluent treatment – a review. *Arabian Journal of Chemistry*, 10, S3548–S3558.

Qu, J., Wang, L., Yuan, X.,Cong, Q., & Sha, S. (2011). Guan Effects of ammonium molybdate on phytoremediation by alfalfa plants and (im) mobilization of toxic metals in soils. *Environmental Earth Sciences*, 64, 2175–2182.

Qu, J., Yuan, X., Cong, Q., & Wang, S. (2008). Determination of total mass and morphology analysis of heavy metal in soil with potassium biphthalatesodium hydroxide by ICP-AES. *Spectroscopy and Spectral Analysis*, 28, 2674–2678.

Quartacci M.F., Baker A.J.M., & Navari-Izzo F. (2005). Nitrilotriacetate- and citric acid-assisted phytoextraction of cadmium by Indian mustard (Brassica juncea (L.) Czernj, Brassicaceae). *Chemosphere*, 59, 1249–1255.

Rafiei, B., Nejad, B. M., Hashemi, M., & Khodaei, A. S. (2010). Distribution of heavy metals around the Dashkasan Au Mine. *International Journal of Environmental Research***,** 4(4), 647-654

Rahim, B. E. A., Yusoff, I., Samsudin, A. R., Yaacob, W. Z. W., & Rafek, A. G. M. (2010). Deterioration of groundwater quality in the vicinity of an active open-tipping site in West Malaysia. *Hydrogeology Journal*, 18, 997–1006.

Rahmani, A.R., Ghaffari, H.R., & Samadi, M.T. (2011). A comparative study on arsenic (iii) removal from aqueous solution using nano and micro sized zero- valent iron. *Iranian Journal of Environmental Health Science & Engineering*, 8(2), 157-166.

Rai, P.K. (2008). Heavy metal pollution in aquatic ecosystems and its phytoremediation using wetland plants: an ecosustainable approach. *International Journal of Phytoremediation,* 10, 133–160.

Rana, R., Ganguly, R., & Gupta, A.K. (2015). An assessment of solid waste management system in Chandigarh City, India. *Electronic Journal of Geotechnical Engineering*, 20, 1547-1572.

Raskin, I., Smith, R. D., & Salt, D. E., (1997). Phytoremediation of metals using plants to remove pollutants from the environment. *Current Opinion in Biotechnology*. 8(2), 221-226.

Ray, M.R. (2009) Airway inflammation and upregulation of beta2 Mac-1 integrin expression on circulating leukocytes of female ragpickers in India. *Journal of Occupational Health*, 51(3), 232–238.

Ray, M.R., Roychoudhury, S., Mukherjee, G., Roy, S., & Lahiri, T. (2005). Respiratory and general health impairments of workers employed in a municipal solid waste disposal at an open landfill site in Delhi. *International Journal of Hygiene and Environmental Health,* 208(4), 255–262.

Regadío, M., Ruiz, A.I., & Soto, I.S. (2012). Pollution profiles and physicochemical parameters in old uncontrolled landfills. *Waste Management*, 32, 482–497.

Renou, S., Givaudan, J.G., Poulain, S., Dirassouyan, F., & Moulin, P. (2008). Landfill leachate treatment: review and opportunity. *Journal of Hazardous Materials*, 150, 468–498.

Reyes-López, J.A., Ramírez-Hernández, J., Lázaro-Mancilla, O., Carreón-Diazconti, C., & Garrido, M.M.L. (2008). Assessment of groundwater contamination by landfill leachate: a case in México. *Waste Management*, 28 (1), S33–S39.

Rizo, O.D., Merlo, M.H., Castillo, F.E., & Lopez, J.A.O. (2012). Assessment of metal pollution in soils from a former Havana (Cuba) solid waste open dump. *Bulletin of Environmental Contamination and Toxicology*, 88, 182–186.

Rizwan, R. & Gurdeep, S. (2010). Assessment of groundwater quality status by using water quality index method in Orissa, India. *World Applied Sciences Journal,* 9(12), 1392–1397.

Rodríguez, J., Castrillón, L., Marañón, E. Sastre H., & Fernández, E. (2004). Removal of non-biodegradable organic matter from landfill leachate by adsorption. *Water Research*, 38, 3297–3303.

Rosales-Reyes, T., de La Garza, M., Arias-Castro, C., Rodríguez-Mendiola, M., Fattel-Fazenda, S., Arce-Popoca, E., Hernández-García, S., & Villa-Treviño, S. (2008). Aqueous crude extract of *Rhoeo discolor*, a Mexican medicinal plant, decreases the formation of liver preneoplastic foci in rats. *Journal of Ethnopharmacology*, 115(3), 381- 386.

Saeed, T., & Sun, G., (2012). A review on nitrogen and organics removal mechanisms in subsurface flow constructed wetlands: dependency on environmental parameters, operating conditions and supporting media. *Journal of Environmental Management*, 112, 429–448.

Safari, S., Aghdam, M. A., & Kariminia, H.R. (2016). Electro-coagulation for COD and diesel removal from oily wastewater. *International Journal of Environmental Science and Technology*, 13, 231–242.

Sami Serti. (2000). Assessment of the long-term transport processes and chemical evaluation in waste deposits, Doctoral thesis, Royal Institute of Technology, Stockholm.

Sany, S.B.T., Salleh, A., Rezayi, M., Saadati, N., Narimany, L., & Tehrani, G. M. (2013). Distribution and contamination of heavy metal in the coastal sediments of Port Klang, Selangor, Malaysia. *Water Air Soil Pollution*, 224, 1476.

Sasmaz, A., Obek, E., & Hasar, H. (2008). The accumulation of heavy metals in Typha latifolia L. grown in a stream carrying secondary effluent. *Ecological engineering*, 33, 278-284.

Sawaittayothin, V., & Polprasert, C. (2007). Nitrogen mass balance and microbial analysis of constructed wetlands treating municipal landfill leachate. *Bioresource Technology*, 98, 565-570.

Sawyer, G.N., & McCarthy, D.L. (1967). Chemistry of sanitary engineers, 2nd edn. McGraw Hill, New York, 518.

Scholz, M., & Lee, B.H. (2005). Constructed wetlands: a review. *International Journal of Environmental Studies,* 62, 421–447

Selvam, S., Manimaran, G., Sivasubramanian, P., Balasubramanian, N., & Seshunarayana, T. (2013). GIS-based evaluation of water quality index of groundwater resources around Tuticorin coastal city, south India, *Environmental Earth Sciences*, 1-23.

Sengil, I.A., & Ozacar, M. (2006). Treatment of dairy wastewaters by electro-coagulation using mild steel electrodes. *Journal of Hazardous Materials*, 137, 1197–1205.

Sever, L.E. (1997). Environmental contamination and health effects: what is the evidence?. T*oxicology & Industrial Health*, 13(2–3), 145–161.

Shakery, A., Moor, F., & Razikordmahalleh, L. (2010). 19th world congress of soil science, Soil solutions for a changing world. Brisbane, Australi

Sharholy, M., Ahmed, K., Mahmood, G., & Trivedi, R.C. (2008). Municipal solid waste management in Indian cities: a review. *Waste Management*, 28, 459–476.

Sharma, A., Gupta, A.K., &Ganguly, R. (2018). Impact of open dumping of municipal solid waste on soil properties in mountainous region. *Journal of Rock Mechanics and Geotechnical Engineering*, 10, 725-739.

Sharma, S., & Shah, K.W. (2005). Generation and disposal of solid waste in Hoshangabad. In: Book of proceedings of the second International Congress of Chemistry and Environment, Indore, India, 749–751

Sharma, S., Singh, B., & Manchanda, V.K., (2015). Phytoremediation: role of terrestrial plants and aquatic macrophytes in the remediation of radionuclides and heavy metal contaminated soil and water. *Environmental Science and Pollution Research*, 22 946–962.

Sheoran, A.S., & Sheoran, V. (2006). Heavy metal removal mechanism of acid mine drainage in wetlands: a critical review. *Minerals Engineering*, 19, 105–116.

Sikder, A. H. F., Begum, K., Parveen, Zakia., & Md. Hossain, F. (2016). Assessment of macro and micro nutrients around brick kilns agricultural environment. *Information Processing in Agriculture*. http://dx. doi.org/10.1016/j.inpa.2016.02.001. 1-9

Singh, A., & Prasad, S. M. (2015). Remediation of heavy metal contaminated ecosystem: an overview on technology advancement. *International Journal of Environmental Science and Technology*, 12, 353–366.

Singh, B.R., Gupta, S.K., Azaizeh, H., Shilev, S., Sudre, D., Song, W.Y., Martinoia, E, & Mench, M. (2011). Safety of food crops on land contaminated with trace elements. *Journal of the Science of Food and Agriculture*, 91, 1349–1366.

Singh, S. K., & Tang, W. Z. (2013). Statistical analysis of optimum Fenton oxidation conditions for landfill leachate treatment, *Waste Management*, 33 (1), 81-88.

Singh, S., & Sinha, S. (2005). Accumulation of metals and its effects in Brassica juncea L.Czern.grown on various amendments of tannery wastes. *Ecotoxicology and Environmental Saftey*, 62 (1), 118 -127.

Smahi, D., Hammoumi, O.E., & Fekri, A. (2013). Assessment of the impact of the landfill on groundwater quality: a case study of the Mediounasite, Casablanca, Morocco. *Journal of Water Resources* and Protection, 5, 440–445.

Soupios, P., Papadopoulos, I., Kouli, M., Georgaki, I., Vallianatos, F. & Kokkinous, E. (2006). Investigation of waste disposal areas using electrical methods: a case study from Chania, Crete, Greece. *Environmental Geology*, doi:10.1007/S00254-006-0418-7

Souza, L. A., Piotto, F. A., Nogueirol, R. C., & Azevedo, R. A. (2013). Use of non-hyperaccumulator plant species for the phytoextraction of heavy metals using chelating agents. *Scientia Agricola*, 70 (4), 290-295.

Srivastava, V., Ismail, S. A., Singh, P., & Singh, R. P. (2014). Urban solid waste management in the developing world with emphasis on India:

challenges and opportunities. *Reviews in Environmental Science and Bio/Technology*, doi: 10.1007/s11157-014-9352-4

Subhashini, V., & Swamy, A.V.V.S. (2016). Phytoremediation of Heavy Metals Contaminated Soils by Catharanthus roseus. *International Journal of Science and Research*, 5 (2), 726-729.

Sudarsan, J. S., Roy, R. L., Baskar, G., Deeptha, V. T., & Nithiyanantham, S. (2015). Domestic wastewater treatment performance using constructed wetland. *Sustainable Water Resources Management*, 1(2), 89–96.

Sukumaran, D. (2013). Phytoremediation of heavy metals from industrial effluent using constructed wetland technology. *Applied Ecology and Environmental Sciences,* 1(5), 92-97.

Sutherland, R.A. (2000). Bed sediment associated trace metals in an urban stream, Oahu, Hawaii. *Environmental Geology*, 39, 611–627.

Szabolcs & Darab C. (1964). The influence of irrigation water of high sodium carbonate content of soils, Proceedings of 8th International Congress of ISSS, 2, 803-812.

Tahmasbian, I., & Sinegani, S. A. A. (2014). Chelate-assisted phytoextraction of cadmium from a mine soil by negatively charged sunflower, *International Journal of Environmental Science and Technology,* 11, 695–702.

Tan, J.B.L., Lim, Y.Y., & Lee, S.M. (2015). Antioxidant and antibacterial activity of Rhoeo spathacea (Swartz) Stearn leaves. *Journal of Food Science* and *Technology*, 52(4), 2394–2400.

Tandy, S., Bossart, K., Mueller, R., Ritschel, J., Hauser, L., Schulin, R., & Nowack, B. (2004). Extraction of heavy metals from soils using biodegradable chelating agents. *Environmental Science&Technology,* 38, 937–944.

Tasharrofi, S., Hassani, S. S., Taghdisian, H., & Sobat, Z. (2018). 24- environmentally friendly stabilized nzvi-composite for removal of heavy metals. *New Polymer Nanocomposites for Environmental Remediation*, 623-642.

Tesoriero, A. J., Inkpen, E.L, & Voss, F.D. (1998). Assessing ground-water vulnerability using logistic regression. Paper from proceedings for the Source Water Assessment and Protection 98 Conference, Dallas, TX, 157–165

Thakur, S., Singh, L., Wahid, Z.A., Siddiqui, M.F., Atnaw, S.M., & Din, M.F.M. (2016). Plant-driven removal of heavy metals from soil: uptake, translocation, tolerance mechanism, challenges, and future perspectives. *Environmental Monitoring and Assessment.* 188 1–11.

The Energy and Resources Institute (TERI) (2015). Urban waste management in Himachal Pradesh.

Thomaz, E. L. & Luiz, J. C. (2012). Soil loss, soil degradation and rehabilitation in a degraded land area in Guarapuava (Brazil). *Land Degradation and Development*, 23, 72–81.

Tomlinson, D.L., Wilson, J.G., Harris, C.R., & Jeffrey, D.W. (1980). Problemsin the assessment of heavy metal levels in estuaries and the formation of a pollution index. *Helgola¨nder Meeresuntersuchungen*, 33(1–4), 566–575.

Tratnyek, P.G., Scherer, M.M., Deng B., & Hu, S. (2001). Effects of natural organic matter, anthropogenic surfactants, and model quinones on the reduction of contaminants by zero-valent iron. *Water Resource*, (35), 4435-4441.

Truog, E. (1946). Soil reaction influence on availability of plant nutrients. Soil science society of America proceedings 11, 305-308.

U. S. Environmental Protection Agency (USEPA) (2000). Introduction to phytoremediation, national risk management research laboratory, EPA/600/R-99/107, http://www.clu-in.org/download/remed/introphyto.pdf.

Ujang, Z., Soedjono, E., Salim, M.R., & Shutes, R.B. (2005). Landfill leachate treatment by an experimental subsurface flow constructed wetland in tropical climate countries. *Water Science & Technology*, 52(12), 243–250.

Urase, T., Salequzzaman, M., Kobayashi, S., Matsuo, T., Yamamoto, K., & Suzuki, N. (1997). Effect of high concentration of organic and inorganic matter in landfill leachate on the treatment of heavy metals in very low concentration level. *Water Science & Technology*, 36 (12), 349–356

USDA. (1994). United State Department of Agriculture, Permeability Key. http://www.nrcs.usda.gov/mo10/mo10guides/permkey/

USDA-NRCS (U.S. Department of Agriculture, National Resources and Conservation Service). (1999). Guide to Texture by Feel. www.nrcs.usda.gov/wps/portal/nrcs/ detail/soils/edu/?cid=nrcs142p2_054311.

USEPA. (1999). SW-846, Reference Methodology. Standard opening procedure for the digestion of soil/sediment sample using a hot plate/beaker digestion technique, Chicago.

Uzum, C., Shahwan, T., Ero˘glu, A. E., Lieberwirth, Scott, T. B., & Hallam, K.R. (2008). Application of zero-valent iron nanoparticles for the removal of aqueous Co^{2+} ions under various experimental conditions. *Chemical Engineering Journal*, 144, 213–220.

Van Stemproot, D., Evert, L., & Wassenaar, L. (1993). Aquifer vulnerability index: a GIS compatible method for groundwater vulnerability mapping. *Canadian Water Resources Journal,* 18, 25–37.

Varma, A. (2013). Status of municipal solid waste generation in Kerala and their characteristics.

Vasanthi, P., Kaliappan, S., Srinivasaraghavan, R. (2008). Impact of poor solid waste management on groundwater. *Environmental Monitoring and Assessment*, 143, 227–238.

Venkatesan, G., & Swaminathan, G. (2009). Review of chloride andsulphate attenuation in groundwater nearby solid-wastelandfill sites. *Journal of Environmental Engineering and Landscape Management*, 17(1), 1–7.

Vrba, J, Zaporozec A. (1994). Guidebook on mapping groundwater vulnerability**.** *International Association of Hydrogeologists*, Heise, Hanover, Germany

Vymazal, J. (2010). Constructed wetlands for wastewater treatment. *Water,* 2, 530–549.

Vymazal, J., (2005). Removal of enteric bacteria in constructed treatment wetlands with emergent macrophytes: a review. *Journal of environmental science and health*, 40(6-7), 1355-1367.

Vymazal, J., (2013). Emergent plants used in free water surface constructed wetlands: a review. *Ecological engineering*, 61, 582–592.

Waheed, S., Siddique, N., Hamid, Q., & Chaudhry, M.M. (2010). Assessing soil pollution from a municipal waste dump in Islamabad, Pakistan: a study by INAA and AAS. *Journal of Radioanalytical and Nuclear Chemistry*, 285,723–732.

Wakley, A., & Black, I.A. (1934). Soil Science, 37, 29-38

Wang, A. S., Angle, J. S., Chaney, R. L., Delorme, T. A., & Reeves, R. D. (2006). Soil pH effects on uptake of Cd and Zn by Thlaspi caerulescens. *Plant and Soil*, 281, 325–337.

Watmough, S., Eimer, M., & Dillon, P. (2007). Manganese cycling in central Ontario forests: response to soil acidification. *Applied Geochemistry*, 22, 1241–1247.

Werz, H., & Hotzl, H. (2007). Groundwater risk intensity mapping in semiarid regions using optical remote sensing data as an additional tool. *Hydrogeology Journal*, 15(6), 1031–1049.

WHO (2007). Population health and waste management: scientific data and policy options. Report of a WHO Workshop, Rome, Italy, 29–30 March 2007. World Health Organisation (WHO), European Centre for Environment and Health.

Wijesekara, S. S. R. M. D. H. R., Mayakaduwa, S. S., Siriwardana, A. R., de Silva, N., Basnayake, B. F. A., Kawamoto, K., & Vithanage, M. (2014). Fate and transport of pollutants through a municipal solid waste landfill leachate in Sri Lanka. *Environmental Earth Sciences*, 72, 1707–1719, doi: 10.1007/s12665-014-3075-2

Wilcox, L.V. (1955). Classification and use of irrigation water, USDA, Circular, Washington, DC, USA, 969.

Wiszniowski, J., Robert, D., Surmacz-Gorska, J., Miksch, K., & Weber, J.V. (2006). Landfill leachate treatment methods: A review. *Environmental Chemistry Letters*, 4, 51–61.

World Bank (1999). What a waste: solid waste management in Asia. Urban Development Sector Unit East Asia and Pacific Region

World Bank (2012). What a waste: a global review of solid waste management. Urban development series knowledge papers World Development Indicator Database (2013). http://data.worldbank.org/data-catalog/world-development-indicato

World Bank (2018). What a Waste 2.0: A Global Snapshot of Solid Waste Management to 2050. Municipal Solid Waste Management: A Roadmap for Reform for Policy Makershttp://www.worldbank.org/en/topic/urbandevelopment/brief/solid-waste-management

Wu, F.Y., & Sun, E.J. (1998). Effects of copper, zinc, nickel, chromium and lead on the growth of water convolvulus in water culture, *Environmental Protection*, 21(1), 63-72.

Wu, H., Zhang, J., Ngo, H.H., Guo, W., Hub, Z., Liang, S., Fan, J., & Liu, H. (2015). A review on the sustainability of constructed wetlands for wastewater treatment: design and operation. *Bioresource Technology*, 175, 594–601.

Wysocka, M. E. (2015). Influence of location of landfills on groundwater quality. *Annual Set The Environment Protection*, 17, 1074–1093 (in Polish).

Xiaoli, C., Shimaoka, T., Xianyan, C., Qiang, G. & Youcai, Z. (2007). Characteristics and mobility of heavy metals in an MSW landfill: implication in risk assessment and reclamation. *Journal of Hazardous Materials*, 144(1–2), 485–491.

Xu, Y., & Zhao, D. (2007). Reductive immobilization of chromate in water and soil using stabilized iron nanoparticles. *Water Research*, 41 (10), 2101–2108.

Xu, Z. Y., Zeng, G. M., Yang, Z. H., Xiao, Y., Cao, M., Sun, H. S., Ji, L. L., & Chen, Y. (2010). Biological treatment of landfill leachate with the integration of partial nitrification, anaerobic ammonium oxidation and heterotrophic denitrification. *Bioresource Technology*, 101 (1), 79-86

Yalcuk, A., & Ugurlu,A. (2009). Comparison of horizontal and vertical constructed wetlandsystems for landfill leachate treatment. *Bioresource Technology*, 100, 2521–2526.

Yang, Y.L., Yang, T.Y., Yu, X.H., & Zhao, B. (2013). Reach on groundwater pollution caused by landfills in Karst region in Guangzhou. *Ground Water*, 35, 77–80.

Yao, P. (2017). Perspectives on technology for landfill leachate treatment, *Arabian Journal of Chemistry,* 10, S2567–S2574.

Zaidi, S., Chaabane, T., Sivasankar, V., Darchen, A., Maachi, R., & Msagati, T.A.M. (2015). Electro-coagulation coupled electro-flotation process: feasible choice in doxycycline removal from pharmaceutical effluents, *Arabian Journal of Chemistry*. doi: 10.1016/j.arabjc.2015.06.009

Zarei, I., Pourkhabbaz, A., & Khuzestani, R.B. (2014). An assessment ofmetal contamination risk in sediments of Hara BiosphereReserve, southern Iran with a focus on application of pollution indicators. *Environmental Monitoring and Assessment*. doi:10.1007/s10661-014-3839-x

Zaroual, Z., Azzi, M., Saib, N., & Chainet, E. (2006). Contribution to the study of electro-coagulation mechanism in basic textile effluent, *Journal of Hazardous Materials*. 131, 73–78.

Zawawia, M.H., Syafalnia, & Abustan, I. (2012). Assessment of hydrochemical and isotopic characteristics at Matang Landfill Site using multivariate analysis. *Procedia Engineering*, 50, 333–342.

Zayen, A., Manif, S., Aloui, F., Fki, F., Loukil, S., & Bouaziz, M. (2010). Anaerobic membrane bioreactor for the treatment of leachates from Jebel Chakir discharge in Tunisia. *Journal of Hazardous Material,* 177, 918-923.

Zeng, F., Ali, S., Zhang, H., Ouyang, Y., Qiu, B., Wu, F. & Zhang, G. (2011). The influence of pH and organic matter content in paddy soil on heavy metal availability and their uptake by rice plants. *Environmental Pollution*, 159, 84 –91.

Zhang, T., Ding, L., & Ren, H. (2009). Pre-treatment of ammonium removal from landfill leachate by chemical precipitation. *Journal of Hazardous Materials,* 166 (2-3), 911-915

Zhou, Q.X., & Song, Y.F. (2004). Remediation of contaminated soils: principles and methods. Science Press, Beijing

Zhuang, P., Yang, Q. W., Wang, H. B., & Shu, W. S. (2007). Phytoextraction of heavy metals by eight plant species in the field. *Water Air and Soil Pollution,* 184(1), 235-242.

Zorrig, W., Rabhi, M., Ferchichi, S., Smaoui, A., & Abdelly, C. (2012). Phytodesalination: a solution for salt-affected soils in arid and semi-arid regions, *Journal of Arid Land Studies,* 22 299–302.

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Application of GIS and DRASTIC Modeling for Evaluation of Groundwater Vulnerability near a Solid Waste Disposal Site

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Abstract

The study aims at evaluating the groundwater vulnerability to contamination in the vicinity of a solid waste disposal site, Njelianparamba, a municipal dumping site in Kozhikode, Kerala, India, using DRASTIC model using Geographic Information System environment. Vulnerability maps are intended to show areas of most potential to groundwater contamination on the basis of hydrogeological conditions and human impacts. The DRASTIC model consists of seven hydrogeological parameters that affect groundwater quality. The ESRI GIS software, Arc Map 10.1 was used to create the groundwater vulnerability map by overlaying the seven layers. The resulting vulnerability map was then validated using chemical and bacteriological analysis of samples collected from nearby wells of the dumping site to assess the area which is of more potential risk to pollution. According to the vulnerability map, the study area was divided into three vulnerability classes ranging between a minimum value of 120 and a maximum value of 243. The vulnerability classes are moderate vulnerable, high vulnerable and very high vulnerable. The vulnerability map revealed that the eastern and south eastern portion of Njelianparamba dump site was very highly vulnerable to groundwater contamination. This is probably due to the lower sloped terrains towards the eastern portion which allows percolation of contaminants into the groundwater.

Keywords

Groundwater Vulnerability, DRASTIC Model, Geographic Information System, Hydrogeological Parameters

1. Introduction

Conservation and monitoring of groundwater resources are crucial since deterioration of groundwater quality

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has been reported to be one of the major problems faced all over the world due to urbanization, industrialization, irrigation activities and municipal landfill leachate [1].

Landfill leachate is considered as the main cause of groundwater contamination in the nearby areas of the dumpsite [2]. Leachate consists of organic matter (biodegradable), ammonia-nitrogen, heavy metals, chlorinated organic and inorganic salts, which are a great threat to the surrounding soil, groundwater and even surface water [3] [4]. The composition of leachate does not vary and it differs with different sites and environmental conditions, depending on the nature of the waste deposited, rainfall, soil characteristics, and on age of the landfill [5] [6]. The groundwater vulnerability to contamination depends on intrinsic susceptibility and anthropogenic contamination. Many studies have been conducted related to groundwater vulnerability due to landfill leachate [2] [7]. There is a need for groundwater monitoring around the landfill sites to understand the degree of contamination.

Groundwater vulnerability to contamination was defined by International Association of Hydrogeologist as the "Vulnerability is an intrinsic property of a groundwater that depends on the sensitivity of that system to human and natural impacts" [8]. The groundwater vulnerability to contamination is based on the concept that physical environment can provide protection to groundwater against natural and human impacts with respect to contaminants in the groundwater [9]. Groundwater vulnerability deals with the hydrogeological parameters which affect different contaminants in various ways based on their interactions and chemical properties. Vulnerability assessment is a predictable tool to demarcate areas that are more likely to contamination as a result of anthropogenic activities.

DRASTIC model was introduced by the US Environmental Protection Agency to assess groundwater pollution potential [10] [11]. The DRASTIC model in a geographical information system environment was used in many vulnerability studies to evaluate the vulnerability of the study area [12]-[15]. The regions which are more vulnerable to contamination can be identified using groundwater vulnerability mapping based on the hydrogeological parameters that affect and control the movement of groundwater [10]. The output of the groundwater vulnerability studies can provide information that can be used to prevent further pollution of contaminated areas. The main objective of the present study is to assess the groundwater vulnerability in the vicinity of a municipal solid waste disposal site at Njelianparamba using a DRASTIC model and to validate the model using real time collected on water quality from the field.

2. Materials and Methods

2.1. Study Area

Njelianparamba, a solid waste dumping site of Kozhikode Corporation is situated in Cheruvannur Nallalam area, Kerala, India. An average of 200 tonnes of waste per day is dumped in 18 hectares. The area is located between latitude of 11˚13'30"N to 11˚11'N and longitude of 75˚48'E to 75˚50'30"E. The site is one of the primary industrial areas of the Kozhikode district. A number of small, medium and large industrial units on clay, agro-forestry, chemical and metals are located in and around the site. The height of the dump is about 3 to 4 m above ground level and average of 60 - 80 tonnes of organic waste (vegetable, meat and fish waste) from markets and households are deposited in to the dump daily. The landfill originally accepted only non-hazardous solid wastes but now receives both degradable and non-degradable waste including hazardous waste. Organic solid wastes are treated at the waste treatment plant at Njelianparamba. However, there is no leachate treatment facility in the dump yard. The leachate from the plant and trench yard is collected in a pond on the north east side of the site.

The study area is characterised by a humid tropical climate with high rainfall. The climate is divided in to four seasons—summer, south west tropical monsoon period (SW), north east tropical monsoon period (NE) and winter. The SW and NE monsoons are responsible for 82.77% of the total rainfall in the area. June to November is the rainy season in the study area (monsoon season) during which time about 70% of the rainfall is contributed by the SW monsoon. The average annual rainfall recorded in the area during the study period is 2777 mm [16]. The mean maximum temperature is 31.67˚C and the minimum is 22.97˚C. The relative humidity ranges from 74% to 92% during morning hours and 64 to 89% in evening hours. Physiographically the area lies in the middle portions of the Kozhikode district with an elevation ranging from 15 to 50 m above the mean sea level. **Figure 1** shows the location map of the study area.

2.2. Hydrogeology

The geological formations of Njelianparamba primarily consist of porous laterite and forms potential phreatic-

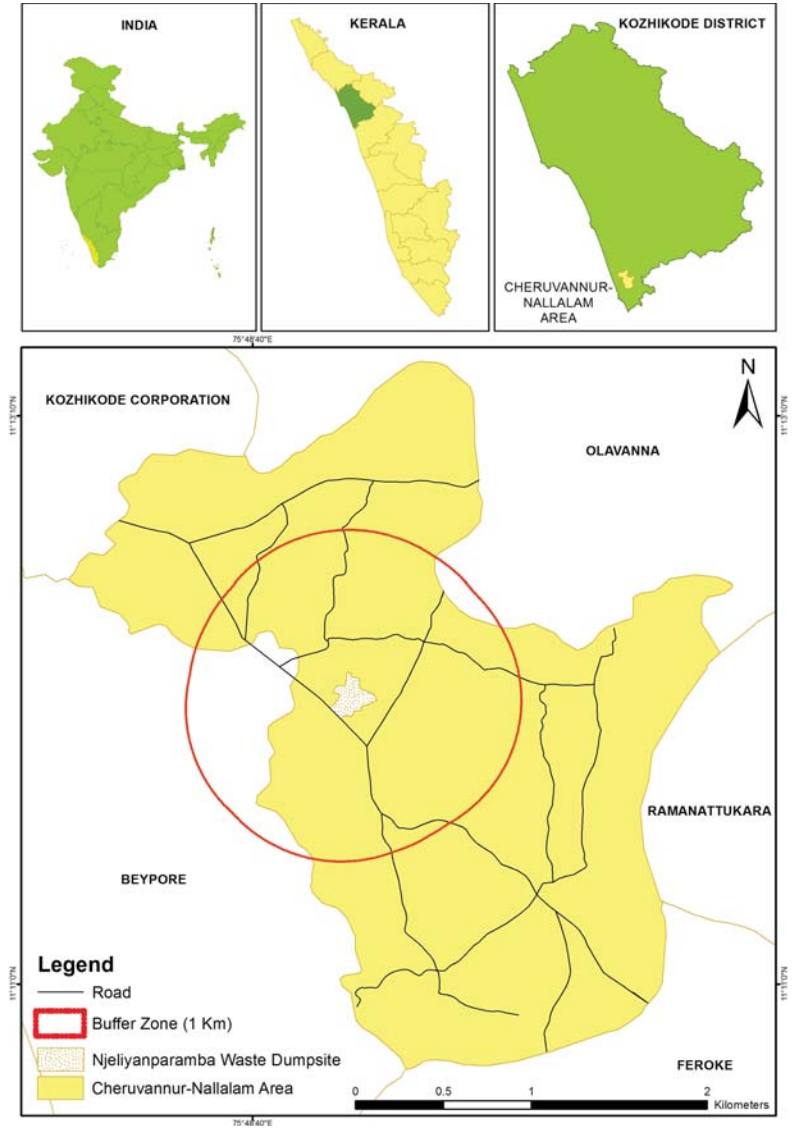

Figure 1. Location map of the study area.

aquifers; it comes under the midland terrain of Kozhikode district [17]. Lateritic soil is derived from laterite under a tropical climate with alternating wet and dry conditions. The soil is reddish in colour, moderately permeable with an infiltration rate that enables absorption of most of the rain. The pH of the soil ranges from 5.5 to 6.5 and the texture is sandy loam. Groundwater occurs under phreatic conditions in weathered crystalline rocks and under confined to semi-confined conditions in deeper crystalline formations. Dug wells are the principle water supply for drinking and other purposes in the study area. The average groundwater level during the pre-monsoon period is 2 to 16 mbgl (metres below ground level), whereas the water table level in post-monsoon is 0.38 to 9 mbgl. The effects of leachate percolation are observed in many nearby dug wells in the form of a brown oily appearance and unpleasant foul smell.

2.3. DRASTIC Model

A GARMIN GPS was used to record the latitude and longitude of sampling points which were imported into the GIS platform. The DRASTIC model is based on seven parameters, corresponding to seven layers to be used as input parameters for modelling. The **DRASTIC** model is considered for seven hydrogeological parameters which are **D**epth to water, net **R**echarge, **A**quifer media, **S**oil media, **T**opography, **I**mpact of vadose zone media, and hydraulic **C**onductivity of the aquifer [18]. The parameters would be weighted and rated according to their relative susceptibility to the pollutant according to their relative contribution to the potential contamination [10]. DRASTIC assigns the weights and ratings would be given to each of the seven parameters, each is classified in to classes on the scale of 1-10, in which 1 denotes least vulnerable while 10 is for the most vulnerable areas. This rating would be further scaled into weights based on the importance of the parameter in determining aquifer characteristics, these scaled on 1-5 where, 1 is least significant and 5 is most significant. The DRASTIC vulnerability index can be calculated by linear addition of the weights and rating. The equation for calculating the DI is

$$\text{DRASTIC Index} = \text{DrDw} + \text{RrRw} + \text{ArAw} + \text{SrSw} + \text{TrTw} + \text{IrIw} + \text{CrCw} \qquad (1)$$

where D the is depth to water table, R the net recharge, A the aquifer media, S the soil media, T the topography, I the impact of vadose zone, C the hydraulic conductivity, r is the rating value assigned to units of parameters and w is the weight assigned to each parameter.

The DRASTIC model was used to prepare a vulnerability map for the study area using ArcMap 10.1. Groundwater vulnerability map identifies the region, most potent to groundwater contamination on the basis of hydrogeologic and anthropogenic factors. The map was developed by using Geographic Information System to combine the seven data layers. It is determined by using the weighted sum overlay method under the spatial analyst tool in the ArcMap tool box. The seven hydrogeological raster inputs were compiled in the weighted sum overlay method specifying the weight for each input, which is then processed into the final vulnerability map. The flow chart of methodology for GW vulnerability analysis is given in **Figure 2**.

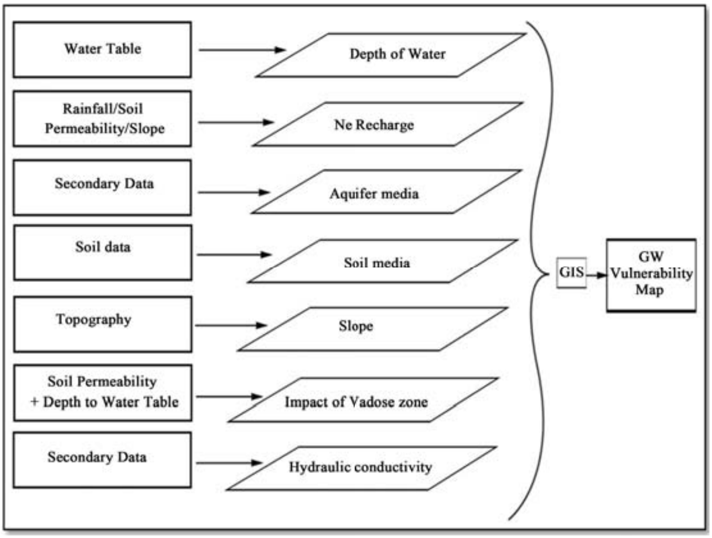

Figure 2. Methodology for groundwater vulnerability study.

2.4. Sampling and Analysis

Sampling and analysis of the groundwater samples were conducted according to the Standard Methods for Examination of Water and Wastewater [19]. A random sampling method was used followed to study the impact of solid waste leachate on groundwater quality. A total of 29 sampling sites were randomly chosen with a buffer zone of 1 Km radius from the landfill site. Out of these sites, 20 groundwater samples were collected within the buffer zone and 9 samples from outside of the zone. To validate the vulnerability map, a total of 29 groundwater samples were collected and analysed for total dissolved solids and *E. coli*. Pre-cleaned polyethylene bottle of 1 lire capacity were used for the analysis of total dissolved solids and sterilized bottle for bacteriological analysis. The total dissolved solids was analysed by gravimetric method and the bacteriological analysis was done by the Multiple Tube Dilution technique.

About 57 soil samples were collected, out of which, 49 samples were collected within the buffer zone and 8 samples from outside the buffer zone. These samples were analysed for texture analysis using hydrometer method to determine the soil media map [20]. All the chemicals used in this study were of analytical reagent grade. To ensure standard quality control/quality assurance procedures, replicates were analyzed for each sample.

3. Results and Discussion

3.1. Depth to Water Table

The depth to water determines the depth of material through which a contaminant must travel before reaching the aquifer, and it may help to determine the amount of time during which contact with the surrounding media is maintained. The deeper water table levels imply lesser chance for contamination to occur. A total number of 29 wells locations were selected from the study area to calculate the average depth to water table. Depth of groundwater ranged from 5 - 15 m. The depth to water table map was then classified into ranges defined by the DRASTIC model and assigned rates ranging from 1 (minimum impact on vulnerability) to 10 (maximum impact on the vulnerability) are shown in **Figure 3**.

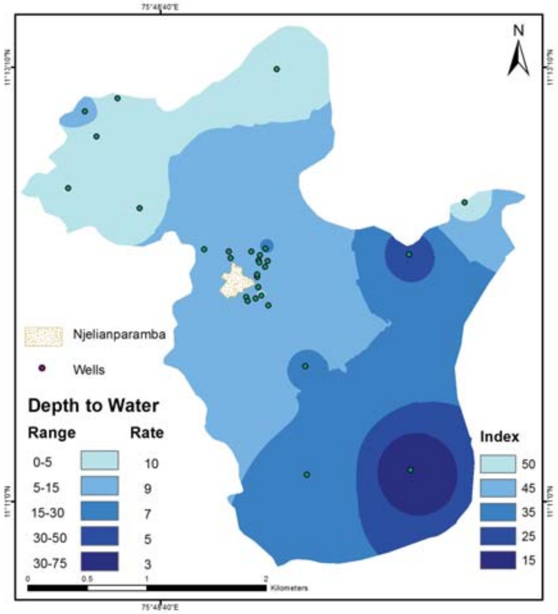

Figure 3. Depth to ground water range, rating and index map.

3.2. Net Recharge

Net recharge is the amount of water which penetrates the ground surface and reaches the water table, recharge water represents the medium for transporting pollutants. Recharge water is thus available to transport a contaminant vertically to the water table and horizontally within the aquifer. Rainfall is an important factor which transports surface pollutants and landfill leachate by infiltration. Recharge data were not available for the study area. Therefore, net recharge was calculated by a combination of ratings for slope, soil permeability and rainfall following the method given by [21].

$$\text{Recharge value} = \text{Slope } (\%) + \text{Rainfall} + \text{Soil permeability} \tag{2}$$

The range, rating and index of net recharge are given in **Figure 4**. The slope (%) in the study area was derived from the NASA SRTM (Shuttle Radar Topographic Mission) data that provides the digital elevation model (DEM) obtained from the USGS ftp site. The soil permeability map was generated from soil texture data. The CWRDM rainfall stations maintained by the meteorological observatory were used to measure the rain fall (3200 mm) in the study area. The net recharge map was generated by superimposing the net recharge parameters, according to the values given in **Table 1**.

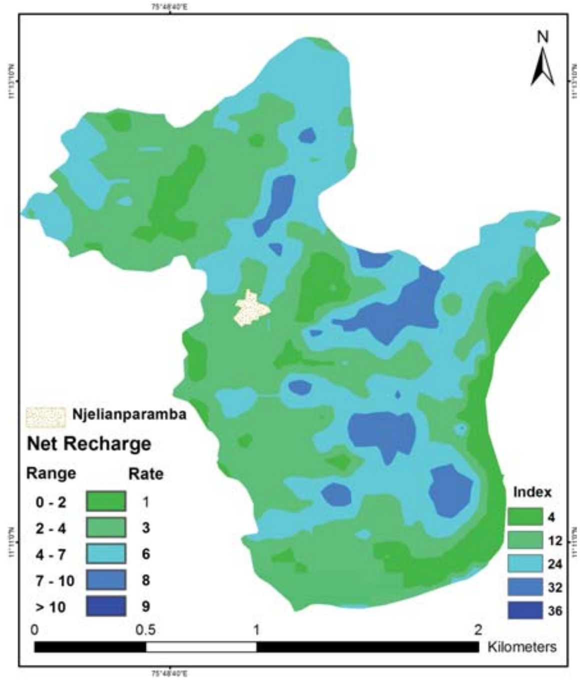

Figure 4. Net recharge range, rating and index map.

Table 1. Data used for measurement of net recharge in the study area.

Slope %	Rating	Rainfall (mm)	Rating	Soil Permeability	Rating	Net recharge	Rating
0 - 2	10					0 - 2	4
2 - 6	9					2 - 4	12
6 - 12	5	3200	4	1 - 100	1	7 - 7	24
12 - 18	3					7-10	32
>18	1					>10	36

3.3. Aquifer Media

Aquifer media refers to consolidated or unconsolidated rock which serves as an aquifer. It is the saturated zone material, which controls the pollutant attenuation processes which determine the flow rates and types of contamination. The sand and gravel are the basic rock formation in the study area. The assigned rating for aquifer media is found to be 8. The range, rating and index of aquifer media given in **Figure 5**.

3.4. Soil Media

Soil media refers to the weathered portion of the earth surface characterised by considerable biological activity. Soil acts as a transport media for contaminants to travel vertically into the groundwater because of its ability to infiltrate impurities through rainfall recharge. Soil pollution potential is mostly affected by the soil types. Soil types were analysed and identified from different sampling stations using soil texture analysis. Based on soil texture, the soil map was classified into three classes—sandy loam, loam and clay loam with ratings 6, 5 and 3 (**Figure 4**). The rating value of 6 was covering the greatest area of the study area. This result was then compiled in to a soil media map using the USEPA DRASIC system. The range, rating and index of soil media of the study area are shown in **Figure 6**.

3.5. Topography

Topography refers to the slope of the land surface. It indicates that plain surfaces will let the runoff water to remain on the surface and allow contaminant percolation to the saturated zone and also indicates that steeper slopes can be a sign of higher groundwater velocity. Slope classes with their range, rating and index of the study area are shown in **Figure 7**. A digital elevation model (DEM) was used to extract the slope of the study area.

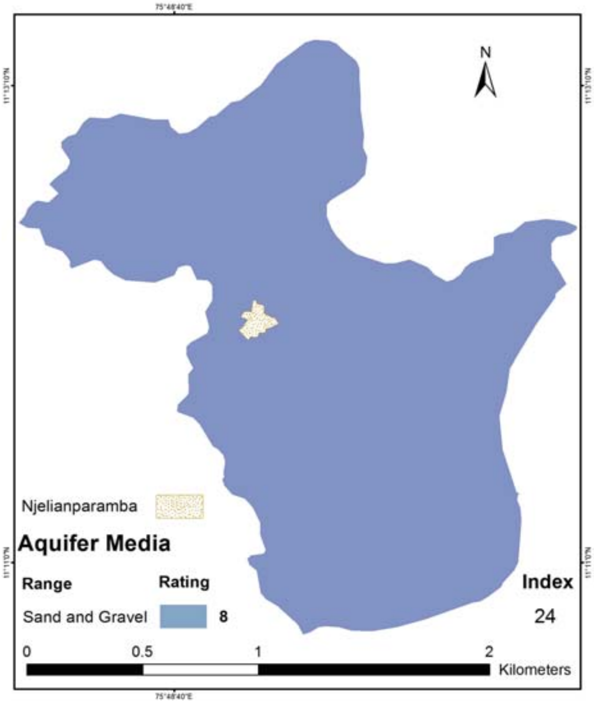

Figure 5. Aquifer media range, rating and index map.

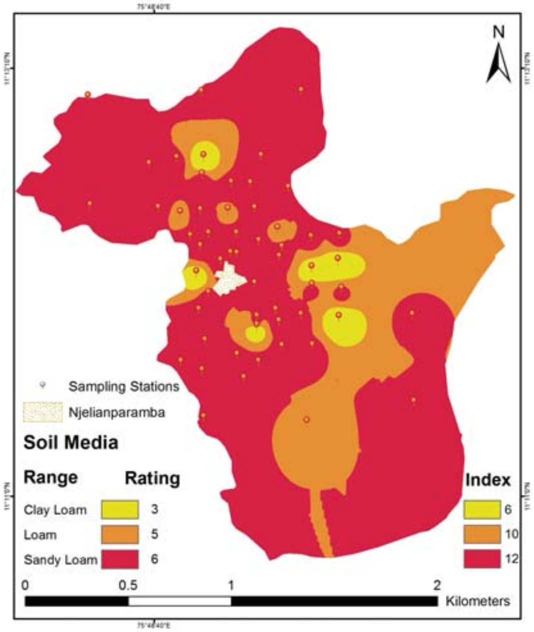

Figure 6. Soil media range, rating and index map.

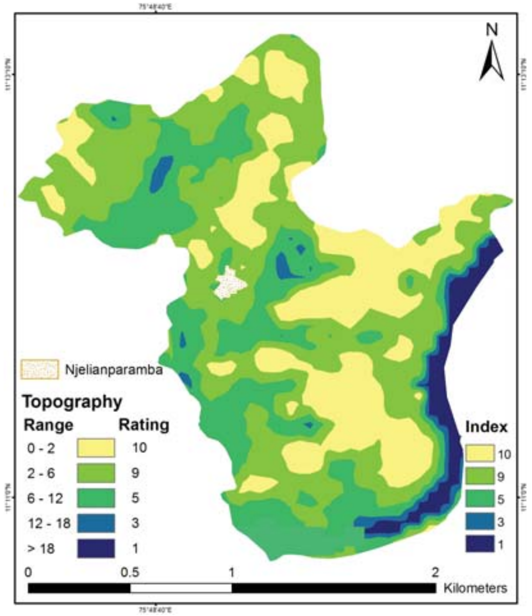

Figure 7. Topography range, rating and index map.

3.6. Impact of Vadose Zone

The vadose zone is mainly the unsaturated above the water table which controls the passage and filters the contaminants into the saturated zone. The vadose zone in the study area is mainly composed of sand and gravel. It is rated as 8 according to the USEPA-DRASTIC method. The vadose zone range, rating and index are shown in **Figure 8**.

3.7. Hydraulic Conductivity

Hydraulic conductivity is the ability of an aquifer to transport water and control the groundwater flow rate under a constant hydraulic gradient. It determines the rate of flow of contaminant material through groundwater, as it is controlled by the amount and void spaces, porosity**,** fracturing etc. A low conductivity means high resistance against contamination and high conductivity indicates high vulnerability while transportation [22]. Hydraulic conductivity value was obtained from the soil permeability class based on the United State Department of Agriculture [23] as shown in **Table 2**. The texture analysis data from the soil media layer was used to determine soil permeability for the study area. The indigenous value for hydraulic conductivity was found to be within the range of 1 - 100 gpd/ft^2 with a rating of 1 [10]. The range, rating and index for hydraulic conductivity of the study area are shown in **Figure 9**.

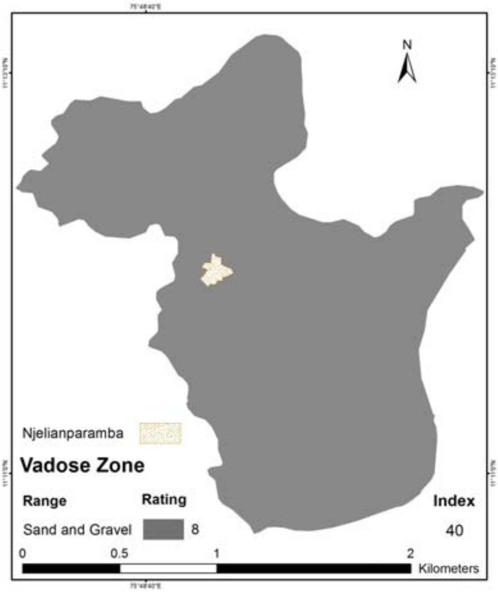

Figure 8. Vadose zone range, rating and index map.

Table 2. Soil permeability class [23].

Texture class	Texture	Permeability rate	Permeability class
Coarse	Gravel, coarse sand Sand, loamy sand	> 20 inches/h 6.20 inches/h	Very rapid Rapid
Moderately coarse	Coarse sandy loam, sandy loam, fine sandy loam	2 - 6 inches/h	Moderately rapid
Medium	Very fine sandy loam, loam, silt loam, silt	0.60 - 2 inches/h	Moderate
Moderately fine	Clay loam, sandy clay loam, silty clay loam	0.20 - 0.60 inches/h	Moderately slow
Fine	Sandy clay, silty clay, clay (<60%)	0.06 - 0.20 inches/h	Slow
Very fine	Clay (>60%), clay pan	<0.06 inches/h	Very slow

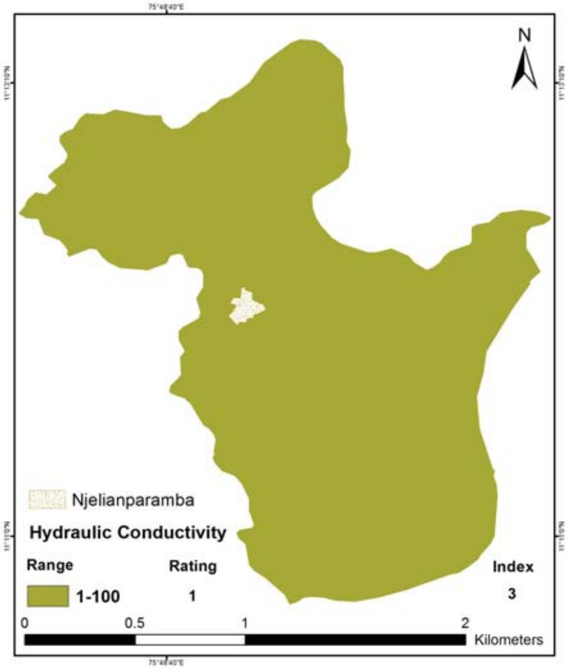

Figure 9. Hydraulic conductivity range, rating and index map.

3.8. Vulnerability Map

To create the vulnerability map, all the seven parameter index map layers were overlaid using the Geoprocessing tool, weighted sum overlay falling under the Spatial Analyst extension in the Arc toolbox. This method overlay the resultant map layers, multiplying each by their given weight with their corresponding rate (as per the USEPA), summing them together to get the index. The study area was divided into three vulnerability classes ranging between a minimum value of 120 and a maximum value of 243. These classes are moderate vulnerable, high vulnerable and very high vulnerable as shown in the vulnerability zone map in **Figure 10**. The vulnerability classes were categorized according to the USEPA DRASTIC Index and vulnerability class [10], as given in the **Table 3**.

According to vulnerability map of the study area, the eastern and south eastern portion of Njelianparamba dump site was very highly vulnerable to groundwater contamination. This is probably due to the lower slope terrains towards the eastern part that is mostly covered with loam and sandy loam which allows enhanced percolation of contaminants into the groundwater. About 75% of the study area falls under high vulnerability class including the areas close to Njelianparamba dump site.

3.9. Validation of DRASTIC Model

A total of 29 groundwater samples were collected from different vulnerability zones of the study area. A buffer zone of 1 km from the Njelianparamba dumping site was considered to assess the correlation between distance and the selected contamination detection factors. For validation of the vulnerability index map, a chemical and bacteriological parameter was considered to justify with the USEPA DRASTIC vulnerability index. The samples were analyzed for the estimation of total dissolved solids and *E. coli* as per the standard procedure [19] and the results were produced in the form of maps as shown in **Figure 11** and **Figure 12**. These maps along with the buffer zone were then correlated with the vulnerability map to interpret the problematic areas.

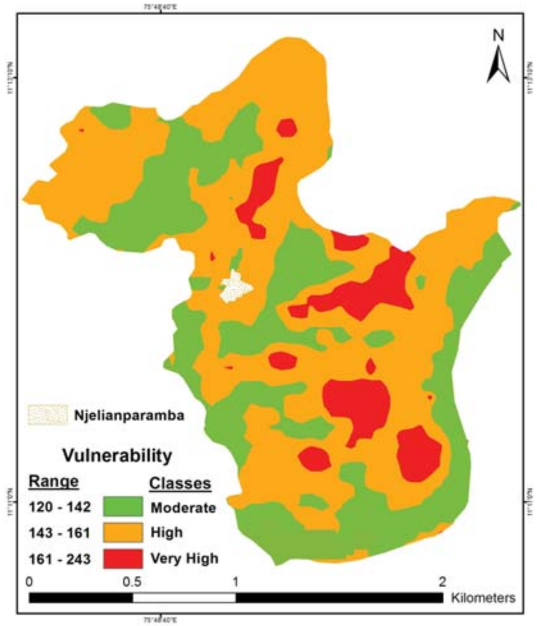

Figure 10. Groundwater vulnerability map of the study area.

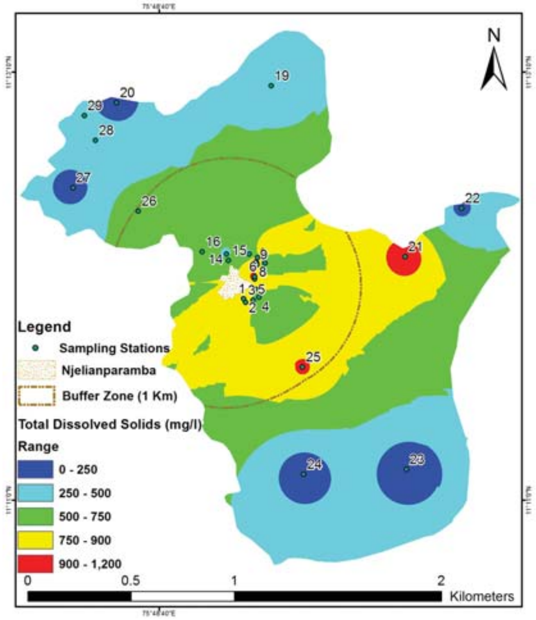

Figure 11. Concentration of total dissolved solids in different vulnerability zones.

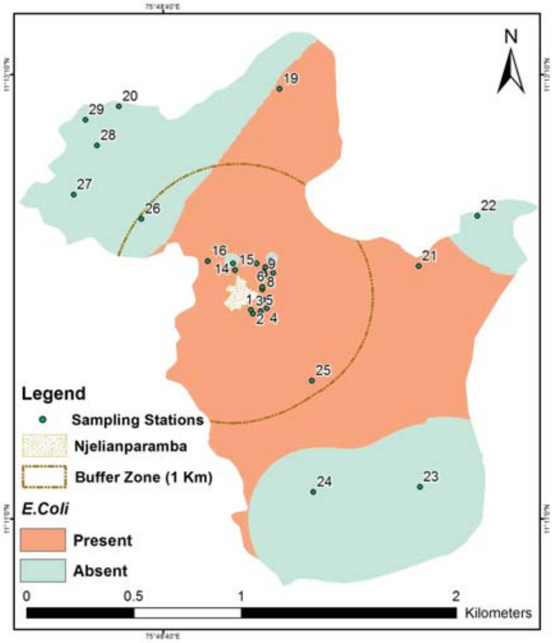

Figure 12. *E. coli* in different vulnerability zones.

Table 3. DRASTIC Index and vulnerability class.

DRASTIC index	Vulnerability class
1 - 100	Low
101 - 140	Moderate
140 - 200	High
>200	Very high

In the case of validation using total dissolved solids, a total of 20 groundwater samples were found to be within the buffer zone and 9 samples laid outside the buffer zone. The dissolved solids concentration in samples that laid inside the buffer zone, were detected between a range of 500 - 1200 mg/l which is above the permissible limit as prescribed by Bureau of Indian Standards [24]. This indicates that leachate percolation is maximum at 1 km distance from the dumping site. The samples collected from outer portion of buffer zone were within the permissible limit of 500 mg/l except the sample 21, which falls under very high vulnerable zone. The samples collected at greater distances from the dumping site had lower concentration of dissolved solids.

The *E. coli* bacteria were found to be present in samples in vicinity to the dumping site particularly within the buffer zone of 1 km. Most of the samples within the buffer zone had the presence of *E. coli*. This validates that the area surrounding the dumpsite is contaminated in correlation to the highly vulnerable area present in the vulnerability map. But an exception of 3 samples (26, 13 and 14) within the buffer zone did not have the presence of *E. coli* bacteria which can be due to the presence of residual chlorine detected in these samples; indicating the presence of regular chlorination of the wells. The samples outside the buffer zone were free from Ecoli except sample 21and 19 lying towards the eastern portion of the study area. Both of these samples fall under the very high vulnerable class in the vulnerability map which explains the presence of bacteria.

4. Conclusion

The DRASTIC model in a geographical information system environment was used to determine the groundwater vulnerability to contamination in the vicinity of a solid waste disposal site, Njelianparamba, a municipal dumping site in Kozhikode, Kerala, India. The ArcMap 10.1 was used to prepare a vulnerability map for the study area. According to the vulnerability map, the study area was divided into three vulnerability classes ranging between a minimum value of 120 and a maximum value of 243. The vulnerability classes are moderate vulnerable, high vulnerable and very high vulnerable. It can be concluded from the vulnerability map, that the eastern and south eastern portion of Njelianparamba dump site was very highly vulnerable to groundwater contamination. This is probably due to the lower sloped terrains towards the eastern portion which allows percolation of contaminants into the groundwater. The resulting vulnerability map was then validated using a chemical and bacteriological parameter analysed from nearby wells of the dumping site to assess the area which is of more potential risk to pollution. From the results of the study, it is clear that the concentrations of total dissolved solids and *E. coli* were correlated in different vulnerable zones; which validated the results obtained.

References

[1] Gupta, N. (2014) Groundwater Vulnerability Assessment Using DRASTIC Method in Jabalpur District of Madhya Pradesh. *International Journal of Recent Technology and Engineering*, **3**, 36-43.

[2] Kale, S.S., Kadam, A.K., Kumar, S. and Pawar, N.J. (2010) Evaluating Pollution Potential of Leachate from Landfill Site from the Pune Metropolitan City and Its Impact on Shallow Basaltic Aquifers. *Environmental Monitoring Assessment*, **162**, 327-346. http://dx.doi.org/10.1007/s10661-009-0799-7

[3] Renou, S., Givaudan, J.G., Poulain, S., Dirassouyan, F. and Moulin, P. (2008) Landfill Leachate Treatment-Review and Opportunity. *Journal of Hazardous Materials*, **150**, 468-493. http://dx.doi.org/10.1016/j.jhazmat.2007.09.077

[4] Robinson, A.H. (2005) Landfill Leachate Treatment. *Membrane Technology*, 6-12. http://dx.doi.org/10.1016/S0958-2118(05)70435-3

[5] Iaconi, C.D., Ramadori, R. and Lopez, A. (2006) Combined Biological and Chemical Degradation for Treating a Mature Municipal Landfill Leachate. *Biochemical Engineering Journal*, **31**, 118-124. http://dx.doi.org/10.1016/j.bej.2006.06.002

[6] Park, S., Choi, K.S., Joe, K.S., Kim, W.H. and Kim, H.S. (2001) Variations of Landfill Leachate's Properties in Conjunction with the Treatment Process. *Environmental Technology*, **22**, 639-645. http://dx.doi.org/10.1080/09593332208618244

[7] Mor, S., Ravindra, K., Dahiyaa, R.P. and Chandra, A. (2006) Leachate Characterization and Assessment of Groundwater Pollution Near Municipal Solid Waste Landfill Site. *Environmental Monitoring Assessment*, **118**, 435-456. http://dx.doi.org/10.1007/s10661-006-1505-7

[8] Jaroslav, V. and Zoporzec, A. (1994) Guidebook on Mapping Groundwater Vulnerability. *International Contributions to Hydrogeology*, Verlag Heise, Hannover, **16**, 129.

[9] Baalousha, H. (2006) Vulnerability Assessment for the Gaze Strip Palestine Using DRASTIC. *Environmental Geology*, **50**, 405-414. http://dx.doi.org/10.1007/s00254-006-0219-z

[10] Aller, L., Bennett, T., Lehr, J., Petty, R. and Hackett, G. (1987) DRASTIC: A Standardized System for Evaluating Groundwater Pollution Potential Using Hydrogeologic Setting. US Environmental Protection Agency Report EPA/600/2-87/035, 622.

[11] United States Environmental Protection Agency (1994) Handbook: Groundwater and Wellhead Protection. Report No. EPA/625/R-94/001, US EPA, Washington DC, 239.

[12] El-Naqa, A., Hammouri, N. and Kuisi, M. (2006) GIS-Based Evaluation of Groundwater Vulnerability in the Russeifa Area, Jordan. *Revista Mexicana de Ciencias Geológicas*, **23**, 277-287.

[13] Prasad, K. and Shukla, J.P. (2014) Assessment of Groundwater Vulnerability Using GIS-Based DRASTIC Technology for the Basaltic Aquifer of Burhner Watershed, Mohgaon Block, Mandla (India). *Current Science*, **107**, 1649-1656.

[14] Awawdeh, M., Obeidat, M. and Zaiter, G. (2015) Groundwater Vulnerability Assessment in the Vicinity of Ramtha Wastewater Treatment Plant, North Jordan. *Applied Water Science*, **5**, 321-334. http://dx.doi.org/10.1007/s13201-014-0194-6

[15] Khan, A., Khan, H.H., Umar, R. and Khan, M.H. (2014) An Integrated Approach for Aquifer Vulnerability Mapping Using GIS and Rough Sets: Study from an Alluvial Aquifer in North India. *Hydrogeology Journal*, **22**, 1561-1572. http://dx.doi.org/10.1007/s10040-014-1147-8

[16] IMD (2013) Normal South West Monsoon Rainfall Data. Indian Meteorological Department, Kozhikode District, Ke-

rala, India.

[17] CGWB (2009) Groundwater Information Booklet of Kozhikode District, Kerala State. Central Ground Water Board, Ministry of Water Resources, Government of India.

[18] Aller, L., Bennet, T., Lehr, J.H., Petty, R.J. and Hacket, G. (1985) DRASTIC: A Standardized System for Evaluating Ground Water Pollution Using Hydrological Settings. Prepared by the National Water Well Association for the USEPA Office of Research and Development, Ada, OK, USA.

[19] APHA, AWWA, WEF (2012) Standard Methods for Examination of Water and Waste Water. 22nd Edition, American Public Health Association, Washington DC.

[20] Baruah, T.C. and Barthakur, H.P. (1997) A Text Book of Soil Analysis. UBS Publishers Ltd., New Delhi.

[21] Piscopo, G. (2001) Groundwater Vulnerability Map, Explanatory Notes, Castlereagh Catchment. NSW Department of Land and Water Conservation, New South Wales, Australia. http://www.water.nsw.gov.au/__data/assets/pdf_file/0008/549377/quality_groundwater_castlereagh_map_notes.pdf

[22] Rahman, A. (2008) A GIS Based DRASTIC Model for Assessing Groundwater Vulnerability in Shallow Aquifer in Aligarh, India. *Applied Geography*, **28**, 32-53. http://dx.doi.org/10.1016/j.apgeog.2007.07.008

[23] USDA (1994) United State Department of Agriculture, Permeability Key. http://www.nrcs.usda.gov/mo10/mo10guides/permkey/

[24] BIS (2012) Indian Standard Drinking Water Specification. Bureau of Indian Standards, New Delhi, IS 10500:2012.

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Geospatial and Statistical Assessment of Groundwater Contamination Due to Landfill Leachate—A Case Study

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Abstract

This study was conducted to measure the impact of a municipal solid waste landfill on groundwater quality around Njelianparamba, a solid waste dumping site in Kozhikode district, Kerala state, India. One of the major problems associated with dumping of municipal solid waste landfill is the release of leachate and its impact on surrounding groundwater. In this study, physico-chemical and bacteriological parameters of groundwater samples collected from the region surrounding the leachate area during the pre- and post-monsoon seasons were analysed. The majority of the groundwater samples contained contaminants at a level beyond the permissible limit set by the Bureau of Indian Standards for drinking water quality. The Geographic Information System software of the Environmental Systems Research Institute, (USA) ArcMap 10.1 was used to prepare spatial distribution maps of different parameters and Leachate Pollution Index and Water Quality Index in the study area were applied to assess the overall quality of groundwater. Characterisation of leachate and groundwater samples revealed that, water in the domestic wells has been deteriorated in response to the percolation of leachate. Additionally spatial and correlation analysis revealed that contamination was present maximum within 300 m radius around the landfill site.

Keywords

Correlation Analysis, Geographic Information System, Leachate, Leachate Pollution Index, Percolation, Water Quality Index

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1. Introduction

Groundwater has long been considered as an important water source owing to its relatively low susceptibility to

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pollution and large storage capacity. Groundwater is comparatively safe and reliable when compared with surface water [1]. However, deterioration of groundwater quality has become a serious problem in recent years. Groundwater is not easily contaminated, but once this occurs it is difficult to remediate. Accordingly, the indiscriminate dumping of municipal solid wastes over vast areas that occurs in developing countries, poses a serious threat to the groundwater quality. In Kerala, groundwater or dug wells are the most reliable water sources and 63% of the populations depend on groundwater for their drinking, domestic, and agricultural needs [2].

Rapid industrialisation, growing population and changing life style are the root causes of increasing solid waste generation in developing countries. In India, about 0.15 million tones of solid waste are generated daily [3]. Landfills have been identified as one of the major threats to groundwater resources throughout the world [4]. Nevertheless, land filling is the most common method used to dispose municipal solid waste due to its favourable economics [5]. Areas near landfills have a greater possibility of groundwater contamination because of the potential for landfill leachate to infiltrate such system [6]. Therefore, it is important to consider this problem as one of the main environmental concerns in developing countries as it may lead to many adverse impacts in future.

Protection of groundwater is a major environmental issue since the importance of water quality on human health has attracted a great deal of interest in recent years [7]. After waste is disposed at landfills, it undergoes a number of physical, chemical and microbiological changes that leads to the release of a toxic liquid known as leachate, which contains innumerable organic and inorganic compounds. The leachate will continuously migrate through the soil strata, eventually contaminating the groundwater system if no action is taken to prevent this phenomenon [8]. The rate and characteristics of leachate produced depends on many factors such as solid waste composition, particle size, degree of compaction, hydrology of the site, landfill age, moisture and temperature conditions and available oxygen [9].

The pollution potential of a particular landfill can be assessed through various indices. Environmental indices such as the Water Quality Index (WQI) and Leachate Pollution Index (LPI) have been developed to determine the extent of pollution. The potential of leachate from different landfills to contaminate local systems can be evaluated using an index known as LPI [10]. This index values can also be used to determine if a landfill requires immediate remediation. Additionally, the CCME WQI is a very useful and efficient tool for summarization and monitoring data to understand the groundwater quality [11].

2. Materials and Methods

2.1. Study Area

Njelianparamba, a solid waste dumping site of Kozhikode City, India is situated 9 km from the city. An average of 200 tonnes of waste per day is dumped in to 18 hectare area. The dumping site is located at 11˚13′30″N to 11˚11′N and 75˚48′E to 75˚50′30″E. The area is one of the primary industrial areas of the Kozhikode district. A number of small, medium and large industrial units on clay, agro-forestry, chemical and metals are located in and around the site. The height of the dump is about 3 to 4 m above ground level and average of 60 - 80 tonnes of organic waste (vegetable, meat and fish waste) from markets and households are deposited in to the dump daily. The landfill originally accepted only non-hazardous solid wastes but now receives both degradable and non-degradable waste including hazardous waste. Organic solid wastes are treated at the waste treatment plant at Njelianparamba. However, there is no leachate treatment facility in the dump yard. The leachate from the plant and trench yard is collected in a pond on the north east side of the plant.

The study area is characterized by a humid tropical climate with high rainfall. The climate is divided in to four seasons—summer, south west tropical monsoon period (SW), north east tropical monsoon period (NE) and winter. The SW and NE monsoons are responsible for 82.77% of the total rainfall in the area. June to November is the rainy season in the study area (monsoon season) during which time about 70% of the rainfall is contributed by the SW monsoon. The average annual rainfall recorded in the area during the study period is 2777 mm [12]. The mean maximum temperature is 31.67˚C and the minimum is 22.97˚C. The relative humidity ranges from 74% to 92% during morning hours and 64% to 89% in evening hours. Physiographically the area lies in the middle portions of the Kozhikode district with an elevation ranging from 15 to 50 m above the mean sea level. **Figure 1** shows the details of Njelianparamba and the sampling locations.

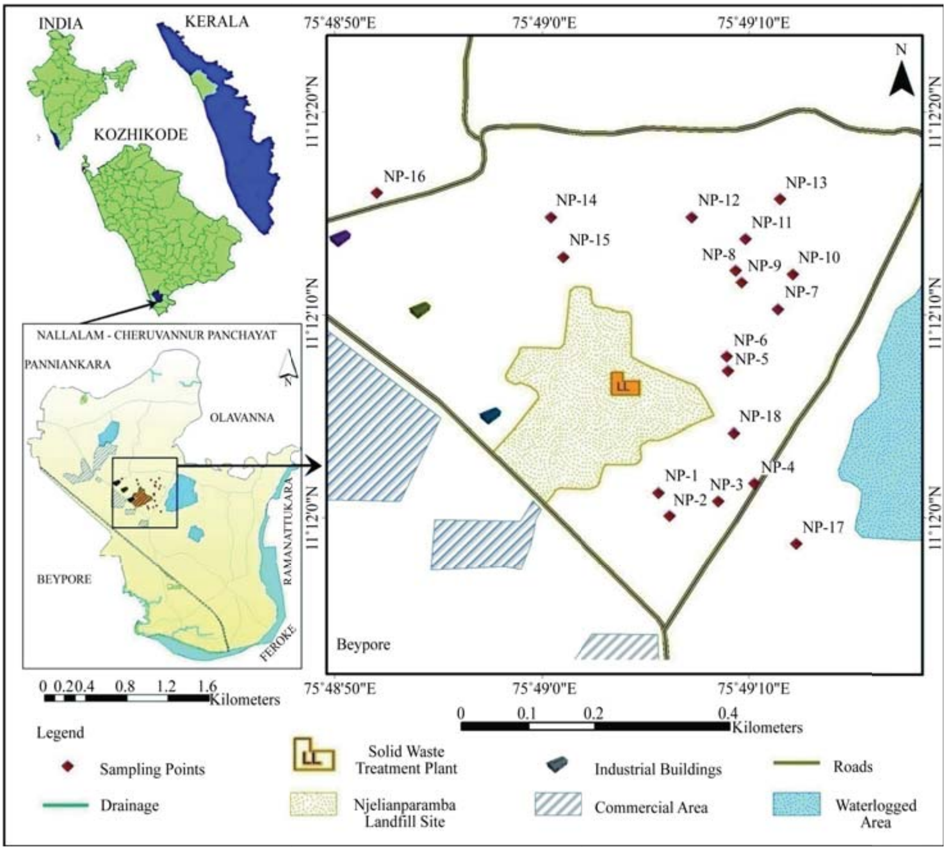

Figure 1. Map of Njelianparamba showing the sampling locations.

2.2. Hydrogeology

The geological formations of Njelianparamba primarily consist of porous laterite and forms potential phreatic aquifers; it comes under the midland terrain of Kozhikode district [13]. Lateritic soil is derived from laterite under a tropical climate with alternating wet and dry conditions. The soil is reddish in colour, moderately permeable with an infiltration rate that enables absorption of most of the rain. The pH of the soil ranges from 5.5 to 6.5 and the texture is sandy loam. Groundwater occurs under phreatic conditions in weathered crystalline rocks and under confined to semi-confined conditions in deeper crystalline formations. Dug wells are the principle water supply for drinking and other purposes in the study area. The average groundwater level during the pre-monsoon period is 2 to 16 mbgl (metres below ground level), whereas the water table level in post-monsoon is 0.38 to 9 mbgl. The effects of leachate percolation are observed in many nearby dug wells in the form of a brown oily appearance and unpleasant foul smell.

2.3. Sampling and Analysis

The sampling and analysis of a leachate sample and 18 groundwater samples were conducted during November 2013 (post-monsoon) and May 2014 (pre-monsoon). A random sampling method was used to collect groundwater samples within a 0.5 km radius of the landfill site and examine its impact on the groundwater quality. The samples were collected only from eastern side of the solid waste treatment plant; no well was identified in the western side of the plant. Pre-cleaned polyethylene bottle (1 L) were used to collect the leachate samples from the drains of the dumping site and groundwater samples from wells around the landfill site. The pH, electrical conductivity and dissolved solids were recorded on site at the time of sampling with a multi-parameter PCSTestr35. To analyze biological oxygen demand (BOD), samples were collected in 300 ml BOD bottles and dissolved oxygen was fixed onsite (Modified Winkler's method). The total hardness, Ca^{2+}, Mg^{2+}, Cl^{-} and total alkalinity were analyzed by titrimetric methods [14]. The Na^{+} and K^{+} concentrations were determined by the Flame Photometric Method while SO_4^{2-}, PO_4^{2-} and NO_3^{2-} were analyzed by UV-VIS Spectrophotometer (Thermo Evolution, USA). The chemical oxygen demand (COD) was measured by open reflux digestion method and BOD was estimated by Azide modification of the Winkler method. For heavy metal analyses (Fe, Zn, Ni, Cu, Pb and Cd), samples were separately collected in to a pre-washed polyethylene containers (100 mL) and acidified onsite to avoid precipitation of metals, after which they were analyzed using Thermo M5 Series Atomic Absorption Spectrophotometer. The bacteriological analysis (total coliform, faecal coliform and *E. coli*) was conducted by the Multiple Tube Dilution technique. All chemicals used in this study were of analytical reagent grade and glassware used for analysis was washed with acid solution followed by distilled water. To ensure standard quality control/quality assurance procedures, replicates were analyzed for each sample. Sampling and analysis were conducted according to the Standard Methods for Examination of Water and Wastewater [14].

2.4. Spatial Interpretation Using Geographic Information System

The base maps for generating the study maps were collected from the Soil Survey Department of the Kozhikode district. The map of Njelianparamba was digitized and various findings were spatially represented using the ArcMap 10.1 software. A GARMIN GPS was used to record the latitude and longitude of sampling points which were imported into the GIS platform. The interpolation technique, Inverse Distance Weighting (IDW) was used for the spatial modelling of the study results. IDW is an algorithm used to interpolate data spatially or estimate values between measurements. The distribution of total coliform, fecal coliform, *E. coli* and variations in the dissolved solids with distance from landfill site in groundwater samples of the study area are represented through interpolated GIS maps that were processed by the IDW method.

3. Results and Discussion

3.1. Leachate Characterisation

The results of physico-chemical analyses of the leachate samples are compared with the National standards set by Ministry of Environment and Forests, Government of India [15] in **Table 1**. The pH of leachate was 5.02 to

Table 1. Physico-chemical characteristics of leachate.

Parameters	Pre-monsoon	Post-monsoon	Leachate disposal Standard (MoEF 2000)
pH	5.02	4.54	5.5 - 9.0
TDS	16300	14300	2100
Chloride	8483	4954	1000
COD	36000	34012	250
BOD	11022	10230	30
SO_4^{2-}	792	532	-
NO_3^{-}	111	101	-
F^{-}	0.6	0.52	2
Na^{+}	2872	2042	-
K^{+}	3536	3399	-
Fe	30	29	-
Cu	0.35	0.29	3
Zn	1.6	1.4	5
Cd	0.1	0.12	2
Ni	1.12	1.0	3
Pb	0.23	0.22	0.1

All values are in mg/L, except pH, EC (in µS/cm).

4.54 in the pre- and post-monsoon seasons respectively, indicating the leachate is acidic in nature. The pre- and post-monsoon dissolved solids were 16300 mg/L and 14300 mg/L respectively which were considerably high than the concentration set by the Ministry of Environment and Forests, discharge standard for leachate disposal. The higher value of dissolved solids in the samples is probably due to the large concentration of cations and anions which indicated the presence of inorganic materials. The high BOD and COD indicate the high organic pollution. Leachate contained high levels of chloride that exceed the recommended standards for leachate disposal. Because chloride is inert and non-biodegradable, it can be used as an indicator of contamination [16].

High nitrate concentration is primarily due to domestic waste. The high concentration for sodium and potassium around the landfill indicate impact of leachate. While the high concentration of iron reflects dumping of metal scrap and tin. The color of leachate is dark brown which possibly originated during the oxidation of ferrous to ferric form leading to the formation of ferric hydroxide colloids and compounds with fulvic and humic substances [17]. The presence of Pb (0.23 mg/L) in the leachate sample indicate the disposal of lead batteries, chemicals for photograph processing and lead based paints at the landfill site [18]. Cu (0.35 mg/L), Zn (1.6 mg/L) and Ni (1.12 mg/L) were also present in the leachate sample. The pre-monsoon leachate samples showed higher concentration of pollutants than the post-monsoon samples which was attributed to the dilution effect of rain water.

3.1.1. Leachate Pollution Index

The LPI (Leachate Pollution Index) provides a proficient method for evaluating extent of leachate pollution from landfill sites. This index is a comparative and quantitative measure of leachate pollution potential that can be efficiently applied to areas prone to leachate migration and subsequent groundwater pollution. To determine the LPI, the sub-index values must be calculated based on the concentration of the leachate pollutants obtained from the sub-index curves for the pollutant variables. The weights for these parameters were calculated based on the significance levels of the individual pollutants. The p values obtained were multiplied by the respective weights assigned to each parameter to determine the LPI using the Equation (1) [19].

$$\mathrm{LPI} = \sum_{i=1}^{n} WiPi \tag{1}$$

where LPI = the weighted additive leachate pollution index, Wi = the weight for the i^{th} pollutant variable, Pi = the sub index value of the i^{th} leachate pollutant variable, n = number of leachate pollutant variables used in calculating LPI

$$\sum_{i=1}^{n} Wi = 1$$

However, if data for all leachate pollutant variables included in LPI is not available, the LPI can be calculated using the dataset of the available leachate pollutants. In such case, the LPI can be calculated by the Equation (2)

$$\mathrm{LPI} = \frac{\sum_{i=1}^{m} WiPi}{\sum Wi} \tag{2}$$

where m represents the number of leachate pollutant variables for available data, but in that case, $m < 18$ and $\sum Wi < 1$.

The contamination potential of leachate can be calculated in terms of LPI. The calculated LPI of Njelianparamba dumping sites were 28.81 and 25.09 in the pre-and post-monsoon seasons respectively, as given in **Table 2**. The LPI value at Njelianparamba was higher than its standard value of 7.4 which is the permissible limit for the leachate disposal set by the Municipal Solid Waste Management and Handling Rules, Government of India [15]. The LPI for the two seasons was calculated to determine the seasonal variation in the pollution. Pollution potential values reported during pre-monsoon season indicate that the leachate had polluting potential during pre-monsoon season than the post-monsoon season. Groundwater quality status was lower during the pre-monsoon season, confirming that the pre-monsoon season is more susceptible for pollution potential. The LPI values computed in this study were significantly higher than those reported for other metropolitan cities in India. The LPI value of Pune metropolitan landfill site was 24.67 in pre-monsoon and 19.04 in post-monsoon

Table 2. LPI in the pre-monsoon (May 2014) and post-monsoon (November 2013) seasons.

Leachate Constituents	Mean value		Individual pollution rating Pi		Weight Wi		Overall pollution rating PiWi	
	Pre-monsoon	Post-monsoon	Pre-monsoon	Post-monsoon	Pre-monsoon	Post-monsoon	Pre-monsoon	Post-monsoon
pH	5.02	4.54	8	8	0.055	0.055	0.44	0.44
TDS	16300	14300	38	35	0.050	0.050	1.9	1.75
Chloride	8483	4954	79	40	0.048	0.048	3.79	1.92
COD	36000	34012	82	81	0.062	0.062	5.08	5.02
BOD	11022	10230	66	64	0.061	0.061	4.03	3.90
Ammonia Nitrogen	111	101	10	10	0.051	0.051	0.51	0.51
Fe	30	29	5	5	0.045	0.045	0.23	0.23
Cu	0.35	0.29	5	5	0.050	0.050	0.25	0.25
Zn	1.6	1.4	5	5	0.056	0.056	0.28	0.28
Ni	1.12	1.0	5	5	0.052	0.052	0.26	0.26
Pb	0.23	0.22	5	5	0.063	0.063	0.32	0.32
Total					0.593	0.593	17.08	14.88
			LPI				**28.81**	**25.09**

All values are in mg/L except pH.

season [17] and unscientific landfill site in Banglore was 17.1 [20]. These studies concluded that LPI serves as a crucial tool for policy makers and public to identify the pollution threat from landfill. LPI of the leachate shall be treated prior to discharge to meet the leachate disposal standard.

3.1.2. Physico-Chemical Characteristics of Groundwater Samples

The physico-chemical composition of groundwater samples in the pre-monsoon and post-monsoon seasons was statistically analyzed and the results provided in **Table 3**. 40% of the samples were acidic in nature; and the pH of the water samples varied from 4.76 to 7.68 and 4.36 to 7.13 in the pre- and post-monsoon seasons respectively. The relatively high value of EC and dissolved solids in the samples indicated the presence of inorganic material in both the seasons. The highest dissolved solids were found in the samples collected near the landfill site, indicating that free ions leached from the waste into the groundwater [21]. Of the samples collected, 70% samples had high dissolved solid levels than the limit prescribed by the Bureau of Indian Standards for drinking water [22]. Temporal changes in dissolved solids during the pre- and post-monsoon seasons are shown in **Figure 2**. The higher concentration of dissolved solids during the pre-monsoon suggests that the leachate have more pollution potential during pre-monsoon season. COD is a measure of oxygen equivalent to the content of organic matter liable to oxidation with a strong chemical oxidant and thus an index of organic pollution. The concentration of COD ranged from 48 to 264 mg/L, 24 to 220 mg/L during the pre-and post-monsoon seasons respectively.

3.1.3. Major Anions in Groundwater

Groundwater contamination can be traced by considering excess chloride ions as an index of pollution [17] (Kale *et al*. 2010). Higher concentrations of chlorides were observed in wells close to the dumping site (NP-1, NP-5, NP-6, NP-8, NP-9 and NP-18). The highest value was recorded in well NP-8 which is 106 m away from the site. Pollution sources such as domestic effluents, fertilizers, and septic tanks, as well as natural source such as rainfall can lead to high Cl^- content in groundwater. Sulphate concentrations in the samples were found to range from 40 to 440 mg/L and 19 to 272 mg/L in the pre- and post-monsoon seasons respectively. The major sources of nitrate in groundwater include domestic sewage, runoff from agricultural fields and leachate from landfill sites. Drinking water containing more than 45 mg/L NO_3^- can cause methamoglobinemia in infants and

Table 3. Physico-chemical characteristics of groundwater samples: pre- and post-monsoon seasons.

Water quality Parameters	Pre-monsoon				Post-monsoon				Desirable Limit (BIS 2012)
	Max	Min	Mean	SD	Max	Min	Mean	SD	
pH	7.68	4.76	6.60	0.99	7.13	4.36	6.01	0.88	6.5 - 8.5
EC	1644	292	939.39	418.51	1487	181	621.11	305.8	-
TDS	1170	202	665.39	297.94	994	130	484.44	274.79	500
SO_4^{2-}	440	44	78.26	112.28	272	19	64.83	67.66	200
Cl^-	620	44	210.44	148.64	310	3.92	197.67	96.09	250
TA	357	3.40	160.18	127.02	503.23	42.58	118.50	115.17	200
TH	524	34.90	251.87	154.35	440	44	176.22	112.28	200
Ca^{2+}	116	9.31	55.71	34.48	164.16	6.8	47.91	44.01	75
Mg^{2+}	84.85	0.94	27.34	22.64	38.88	BDL	15.43	12.54	30
Na^+	294	26.0	128.56	71.74	112	11.20	69.30	32.20	-
K^+	364	3.63	68.92	91.62	38.88	3.3	42.36	12.54	-
COD	264	48	124.0	59.06	220	24	100.0	56.46	-
NO_3^-	95.63	1.35	27.42	23.06	83	BDL	21.50	0.88	45
Fe	0.67	BDL	0.15	0.42	0.52	BDL	0.08	0.23	0.30
Cu	0.04	BDL	0.011	0.02	0.59	BDL	0.12	0.19	0.05
Zn	0.22	BDL	0.06	0.04	0.03	BDL	0.0	0.01	5.0
Mn	0.23	0.03	0.07	0.06	0.18	BDL	0.05	0.07	0.10
Cd	0.02	BDL	0.01	0.003	0.004	BDL	0.001	0.003	0.003

All values are in (mg/L) except EC (μS/cm) and pH, BDL—Below Detection Limit.

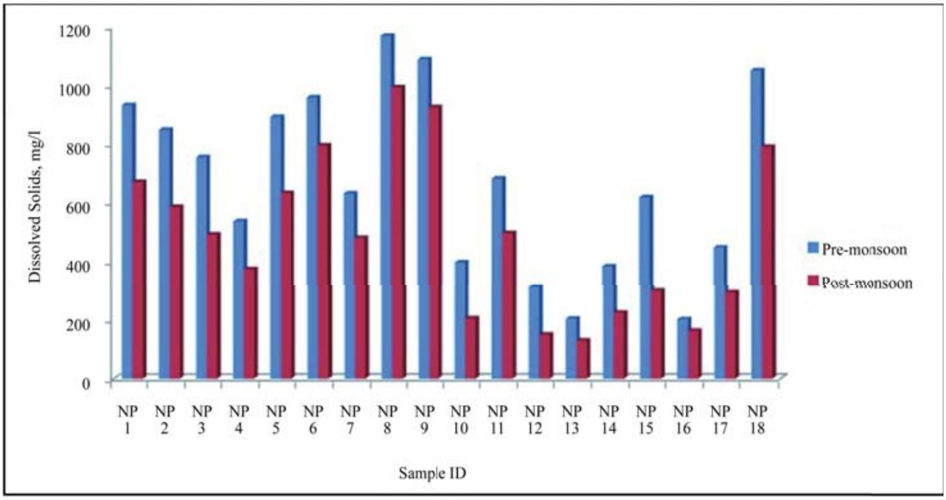

Figure 2. Variations in dissolved solids in pre-monsoon and post-monsoon seasons.

gastric carcinomas [23] [24]. The nitrate concentrations exceeded the desirable limit at three locations. Nitrate concentration in groundwater samples is attributed to dumping of organic waste at landfill site [25].

3.1.4. Major Cations in Groundwater

Almost all samples contained concentration of major cations exceeding their limits. The hardness of samples was found to range from 35 to 524 mg/L and 44 to 440 mg/L in the pre- and post-monsoons, respectively. Most of the sample stations reported hardness values exceeding the maximum desirable limit of 200 mg/L prescribed by BIS. High levels of hardness may affect water supply system resulting in excessive soap consumption, calcification of arteries and cause urinary concretions, diseases of kidney bladder and stomach disorder [26]. Ca^{2+} and Mg^{2+} are important ions influencing total hardness. Calcium ranged from 9 to 164 mg/L with an average value of 55.71 mg/L for pre-monsoon samples and 6.8 to 164 mg/L with an average value of 47.91 mg/L for post-monsoon samples. The permissible limit of calcium ion concentration in groundwater is 75 mg/L [22]. The concentration of Mg^{2+} ions ranged from 0.94 to 84 mg/L and BDL to 38.88 mg/L in the pre- and post-monsoon seasons, respectively. The permissible limit of magnesium ion in groundwater is 30 mg/L according to the BIS. Sodium ranged from 26 to 249 mg/L and 11.20 to 112 mg/L in the pre- and post-monsoon seasons, respectively. The occurrence of sodium above acceptance levels in wells closest to the landfill indicates possible leachate flow into groundwater [27]. Higher concentrations of potassium were found in well samples in the pre-monsoon than post-monsoon season.

3.1.5. Heavy Metals in Groundwater

The groundwater samples were analysed for Cu, Fe, Mn, Cd and Zn. Iron levels in the groundwater ranged from BDL to 0.67 mg/L and 0.52 to BDL in the pre- and post-monsoon seasons, respectively. The concentration of iron exceeded in 61% of the samples collected from the study area. Cu and Zn were found to be within the permissible limit prescribed by the BIS. The concentration of Mn exceeded the limit in the sample collected from NP-8, NP-9 and NP-18. The Cd concentrations of the sample were ranged from BDL to 0.02 mg/L and BDL to 0.004 mg/L in the pre- and post-monsoon seasons, respectively.

3.1.6. Spatial Distribution of Bacteria in the Groundwater Sources

The bacteriological analysis of the groundwater quality was spatially represented and analysed in the form of GIS maps. The distribution of bacteria and the distance between the well and landfill site were the two major criteria used to prepare the maps. The distribution of total coliform, fecal coliform and *E. coli* bacteria was represented through interpolated GIS maps that were processed by the Inverse Distance Weighting (IDW) method. As shown in **Figure 3**, 39% of the total samples analyzed were contaminated with a very high count of total coliform (≥2400). Similarly, 33% of the total samples analyzed were contaminated with fecal coliform (≥2400), (**Figure 4**). As shown in **Figure 5**, 44% of the samples were contaminated with *E. coli*. All well samples were grossly contaminated with bacteria with the highest concentration being observed in wells close to the dumping site. The results also demonstrate that large amounts of organic matter were present in groundwater samples caused by leachate percolation which provided nutrients for microbial growth.

3.1.7. CCME Water Quality Index

The Canadian Council of Ministers of the Environment introduced an index to determine water quality (CCME WQI). This index provides a suitable method to aggregate a complex water quality data that can be understood easily by the public, policy makers, planners and water distributors [28]. CCME WQI includes three elements: scope (F1), the number of water quality variables not meeting the water quality objective; frequency (F2), the number of times, objectives are not met and amplitude (F3), the degree to which objectives are not met. The CCME WQI is calculated using the Equation (3)

$$CCMEWQI = 100 - \frac{\sqrt{F_1^2 + F_2^2 + F_3^2}}{1.732} \tag{3}$$

The factor of 1.732 has been introduced to scale the index from 0 to 100, where zero signifies very poor water quality and values close to 100 signify excellent water quality. The water quality is ranked in the following five categories shown below. A WQI map was created using the CCME WQI classification to understand the groundwater quality.

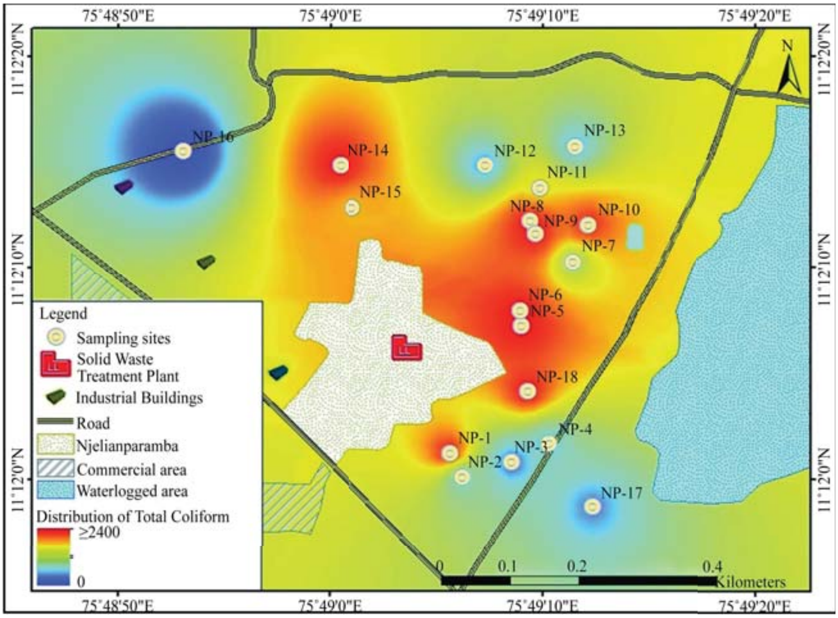

Figure 3. Distribution of total coliforms in groundwater samples.

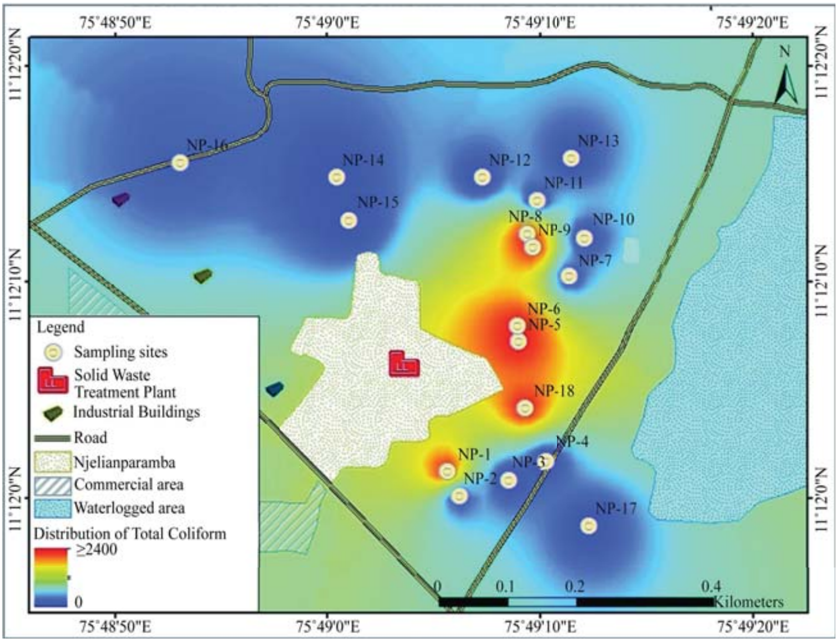

Figure 4. Distribution of fecal coliforms in groundwater samples.

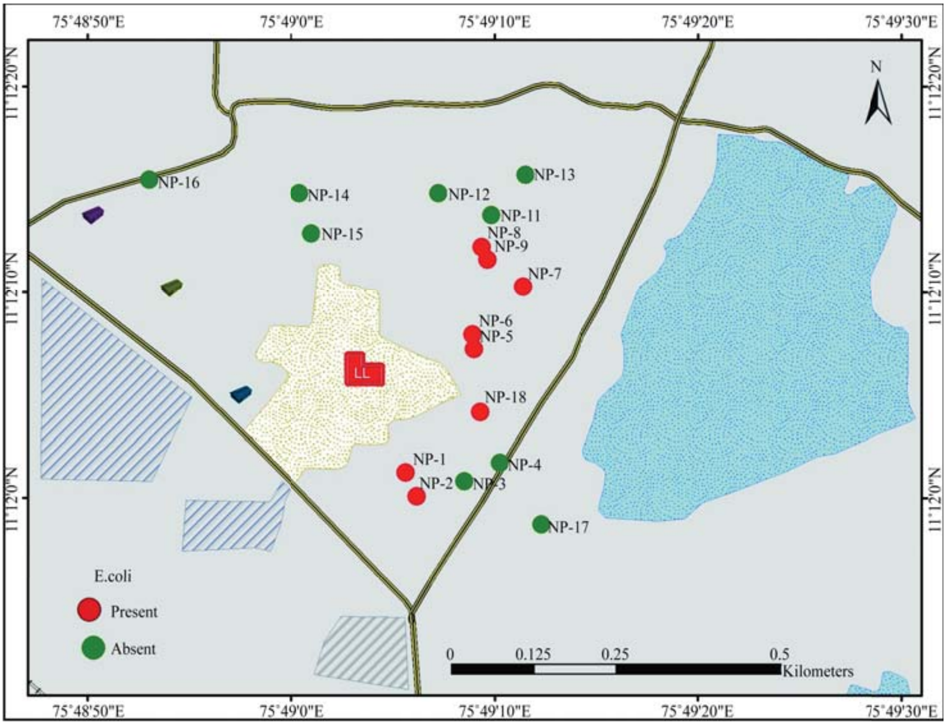

Figure 5. Distribution of *E. coli* in groundwater samples.

Excellent: (CCME WQI values 95 - 100)
Good: (CCME WQI values 80 - 94)
Fair: (CCME WQI values 60 - 79)
Marginal: (CCME WQI values 45 - 59)
Poor: (CCME WQI values 0 - 44)

3.1.8. Spatial Distribution of CCME WQI in the Groundwater Sources

The overall water quality in the study area was represented using CCME WQI. CCME WQI of the study area was calculated in the pre- and post-monsoon seasons. According to CCME WQI, six sampling sites (NP-1, NP-5, NP-6, NP-8, NP-9 and NP-18) showed poor WQI values. All the six sites were located 200 m from the dumpsite. Additionally, eight sites showed marginal water quality and four stations showed fair water quality. A CCME WQI map was created using the CCME WQI classification to understand the groundwater quality in the study area. Figure 6 explains the three classes of water quality in the study area. GIS-based spatial analysis techniques have been shown to be a powerful tool to represent water quality assessed by CCME WQI values. Analysis using this method suggests that the majority of the sites in this study area falls had poor and marginal category. The spatial distribution map clearly showed that portions of the study area close to the landfill had poor groundwater quality. Figure 6 represents the spatial distribution of CCME WQI in groundwater.

3.1.9. Impact of Distance from Landfill on Solid Waste Leachate

The spatial variation of the dissolved solids in groundwater samples and distances from the landfill to the study area were represented using Geographic Information System. Samples were collected spatially at different distances from the landfill site. These two criteria were used to determine the groundwater quality at the sampling

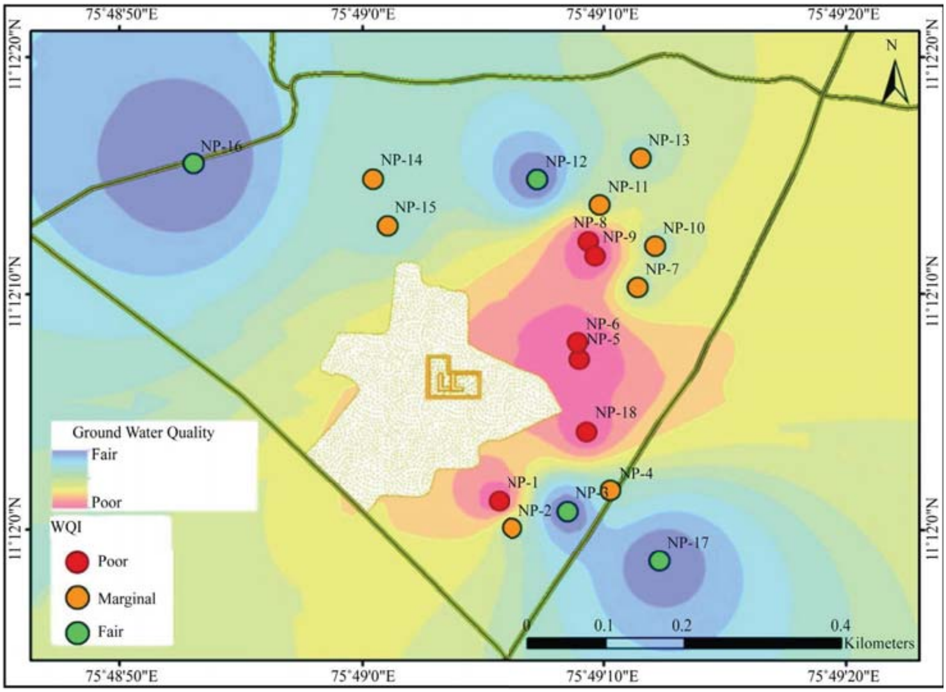

Figure 6. Spatial distribution of CCME WQI in Njelianparamba.

sites with proximity to the landfill. **Figure 7** represents the variation of Total Dissolved Solids (TDS) with distance from the landfill site. The total sampling sites were grouped into three buffer zones based on the TDS concentration. Buffer zone I, which contained most of the sampling sites, corresponds to the distance of 0 - 200 m from the landfill. Sites in zone I included; NP-1 to NP-9, NP-12, NP-14, NP-15 and NP-18. The TDS values of these sites were high, indicating that the water is unfit for any use. Zone II was 200 to 300 m from the landfill site. Although it is not as hazardous as Zone I, use of water from these sites is not recommended. Zone III consisted of 300 - 500 m from the landfill.

Groundwater samples from this zone had low TDS. The zonation map showed that the sampling sites within zone I and II contain more soluble salts in groundwater and cannot be used for any purpose. As shown in **Figure 7**, samples from wells situated close to the landfill site were found to be more heavily contaminated than those located far away. These findings indicate that the gravitational movement of the leachate is hindered by the mass of the soil matter. Over increasing time, the viscous fluid may penetrate deeper and spread all over a longer distance.

3.1.10. Correlation Analysis

Correlation analysis is a descriptive technique to assess the degree of association among variables. Statistical package for Social Sciences (SPSS version 19.0) was used for correlation analysis. In this study, Pearson correlation coefficients were determined for various water quality parameters.

Table 4 shows the Pearson's correlation matrix between the two parameters (TDS and chloride) and their well depth and distance from the landfill site. Chloride is a useful tracer of groundwater contamination (Mor *et al.* 2006) and TDS is a valuable index of total ions in samples. Strong negative correlations (−0.863 and −0.733) were obtained for the concentrations of TDS and chloride respectively with their distance from the landfill site. The significant negative correlation for TDS with distance from the dumpsite shows that the concentration of

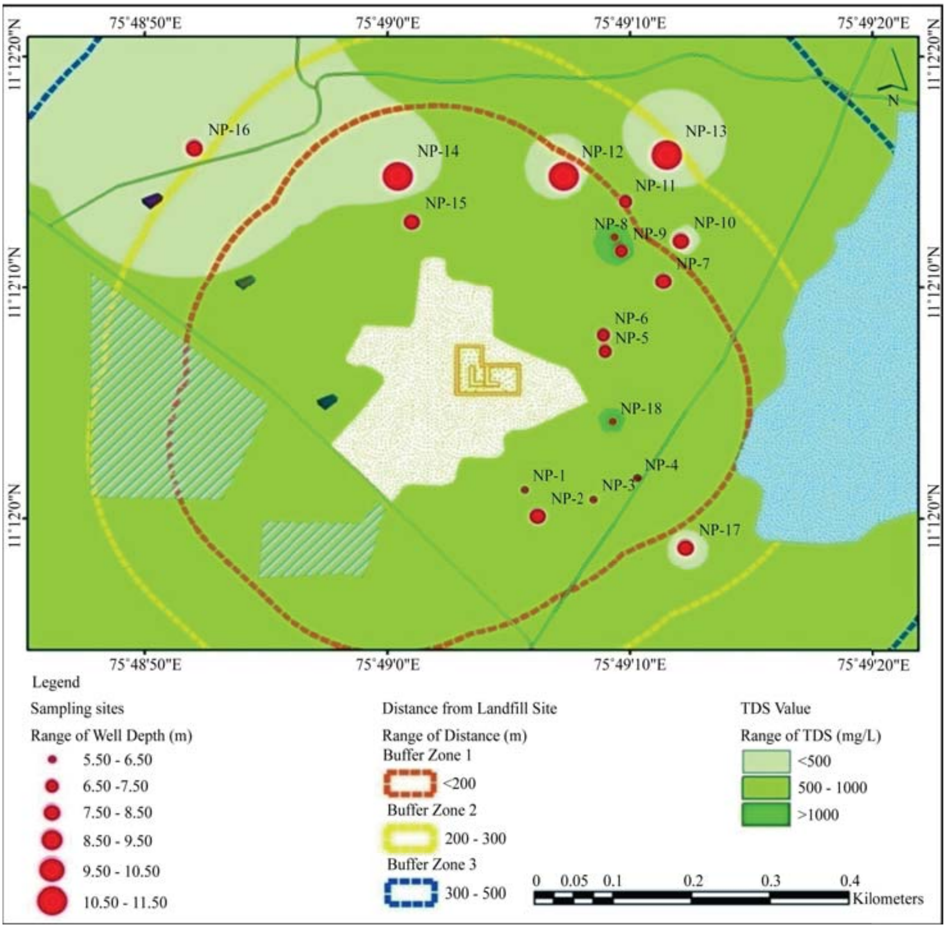

Figure 7. Variation of TDS with distance from landfill site.

Table 4. Correlation coefficient for different parameters.

Parameters	Distance	Depth	TDS
Distance	1.0	0.416	−0.863
Depth	0.416	1.0	−0.510
TDS	−0.863	−0.510	1.0
Chloride	−0.733	−0.516	0.854

Correlation > ±0.6 are in italics.

contaminants in groundwater normally decreases with increasing distance from pollution. A moderately high negative correlation was obtained for TDS and chloride with well depth, which also indicated that the concentration of contaminants in groundwater samples decreased with increasing depth. Correlation analysis confirmed that groundwater quality improved with increases in well depth and the distance of the well from the pollution source.

4. Conclusion

The impact of landfills leachate on the surrounding groundwater quality in Njelianparamba, India is a major environmental concern of the area. In this study, physico-chemical and bacteriological parameters of leachate and groundwater samples collected in and around the landfill site were analysed. The results showed that the wells in close proximity to the landfill (NP-5, NP-6, NP-8, NP-9 and NP-18) were most affected by leachate percolation. Spatial distribution of groundwater quality parameters was measured by GIS. LPI and WQI in the study were applied to assess the overall quality of the leachate and groundwater. This method appears to be more systematic and provides a comparative evaluation of the quality of sampling sites. The LPI value at Njelianparamba for both the seasons exceeded the standard LPI of 7.4 proposed for leachate disposal. CCME WQI map was also generated using the same technique to understand the water potability spatially. The CCME WQI indicted that majority of the study area had poor and marginal water quality. However, the quality improved with increase in distance of the well from the pollution source. The majority of the parameters showed an inverse relationship between concentration and distance. The results of this study indicated that the Njelianparamba municipal dumping site was prone to groundwater contamination through leaching. Because dumping is a continuous process, without proper treatment facilities, groundwater in the surrounding area will gradually become more adversely by this activity.

References

[1] Gupta, N. (2014) Groundwater Vulnerability Assessment Using DRASTIC Method in Jabalpur District of Madhya Pradesh. *International Journal of Recent Technology and Engineering*, **3**, 36-43.

[2] Census of India (2011) Main Sources of Drinking Water 2001-2011. Department of census Kerala, Ministry of Home Affairs, New Delhi.

[3] Rathod, M., Mishra, H. and Karmakar, S. (2013) Leachate Characterization and Assessment of Water Pollution near Municipal Solid Waste Landfill Site. *International Journal of Chemical and Physical Science*, **2**,186-189.

[4] USEPA (United States Environmental Protection Agency) (1984) A groundwater protection strategy for the Environmental Protection Agency. EPA Number: 440684002.

[5] Wijesekara, S.S.R.M.D.H.R., Mayakaduwa, S.S., Siriwardana, A.R., de Silva, N., Basnayake, B.F.A., Kawamoto, K. and Vithanage, M. (2014) Fate and Transport of Pollutants through a Municipal Solid Waste Landfill Leachate in Sri Lanka. *Environmental Earth Sciences*, **72**, 1707-1719. http://dx.doi.org/10.1007/s12665-014-3075-2

[6] Nagarajan, R., Thirumalaisamy, S. and Lakshumanan, E. (2012) Impact of Leachate on Groundwater Pollution Due to Non-Engineered Municipal solid Waste Landfill Sites of Erode City, Tamil Nadu, India. *Iranian Journal of Environmental Health Sciences & Engineering*, **9**, 35. http://dx.doi.org/10.1186/1735-2746-9-35

[7] Akinbile, C.O. and Yusoff, M.S. (2011) Environmental Impact of Leachate Pollution on Groundwater Supplies in Akure, Nigeria, *International Journal of Environmental Science and Development*, **2**, 81-86. http://dx.doi.org/10.7763/ijesd.2011.v2.101

[8] Kanmani, S. and Gandhimathi, R. (2013) Assessment of Heavy Metal Contamination in Soil Due to Leachate Migration from an Open Dumping Site. *Applied Water Science*, **3**, 193-205. http://dx.doi.org/10.1007/s13201-012-0072-z

[9] Jhamnani, B. and Singh, S.K. (2009) Groundwater Contamination Due to Bhalaswa Landfill Site in New Delhi. *International Journal of Civil and Environmental Engineering*, **1**, 121-125.

[10] Kumar, D. and Alappat, B.J. (2003) A Technique to Quantify Landfill Leachate Pollution. *Proceedings of the* 9*th International Landfill Symposium*, Cagliari, 6-10 October 2003, Paper No. 400.

[11] Selvam, S., Manimaran, G., Sivasubramanian, P., Balasubramanian, N. and Seshunarayana, T. (2013) GIS-Based Evaluation of Water Quality Index of Groundwater Resources around Tuticorin Coastal City, South India. *Environmental Earth Sciences*, **71**, 2847-2867. http://dx.doi.org/10.1007/s12665-013-2662-y

[12] IMD (2013) Normal South West Monsoon Rainfall Data. Indian Meteorological Department, Kozhikode District, Kerala.

[13] CGWB (2009) Groundwater Information Booklet of Kozhikode District, Kerala State. Central Ground Water Board, Ministry of Water Resources, Government of India.

[14] APHA, AWWA, WEF (2012) Standard Methods for Examination of Water and Waste Water. 22nd Edition, American Public Health Association, Washington DC.

[15] MoEF (2000) Municipal Solid Waste Management and Handling Rules. Notification Issued by Ministry of Environment and Forests, Government of India.

[16] D'Souza, O. and Somashekar, R.K. (2012) Pollution Potential of Leachate from an Unscientific Landfill and Its Impact on Groundwater. *Electronic Journal of Environmental Science*, **5**, 21-32.

[17] Kale, S.S., Kadam, A.K., Kumar, S. and Pawar, N.J. (2010) Evaluating Pollution Potential of Leachate from Landfill Site from the Pune Metropolitan City and Its Impact on Shallow Basaltic Aquifers. *Environmental Monitoring Assessment*, **162**, 327-346. http://dx.doi.org/10.1007/s10661-009-0799-7

[18] Mor, S., Ravindra, K., Dahiyaa, R.P. and Chandra, A. (2006) Leachate Characterization and Assessment of Groundwater Pollution near Municipal Solid Waste Landfill Site. *Environmental Monitoring Assessment*, **118**, 435-456. http://dx.doi.org/10.1007/s10661-006-1505-7

[19] Kumar, D. and Alappat, B.J. (2005) Evaluating Leachate Contamination Potential of Landfill Sites Using Leachate Pollution Index. *Clean Technology and Environment*, **7**, 190-197. http://dx.doi.org/10.1007/s10098-004-0269-4

[20] D'Souza, P. and Somashekar, R.K. (2013) Assessment of Stabilization, Temporal Variation and Leachate Contamination Potential of Municipal Solid Waste Dumpsites in Bangalore. *International Journal of Environmental Protection*, **3**, 28-35.

[21] Dharmarathne, N. and Gunatilake, J. (2013) Leachate Characterization and Surface-Groundwater Pollution at Municipal Solid Waste Landfill of Gohagoda, Sri Lanka. *International Journal of Scientific Research*, **3**, 1-7.

[22] BIS (2012) Indian Standard Drinking Water Specification. Bureau of Indian Standards, New Delhi.

[23] Hopps, H.C. and Feder, G.L. (1986) Chemical Qualities of Water That Contribute to Human Health in a Positive Way. *Science of the Total Environment*, **54**, 207-216. http://dx.doi.org/10.1016/0048-9697(86)90266-4

[24] Jalali, M. (2005) Nitrate Pollution of Groundwater in Toyserkan. *Western Iran Environmental Earth Science*, **62**, 907-913. http://dx.doi.org/10.1007/s12665-010-0576-5

[25] Kathale, N. (2012) Physico-Chemical Status of the Groundwater of Southeastern Area, Chandrapur, Maharashtra, India. *International Journal of Interdisciplinary Research*, **2**, 165-172.

[26] CPCB (2008) Guideline for Water Quality Management. Central Pollution Control Board, Delhi. http://www.cpcb.nic.in.

[27] Adeolu, A.O., Ada, O.V., Gbenga, A.A. and Adebayo, O.A. (2011) Assessment of Groundwater Contamination by Leachate near a Municipal Solid Waste Landfill. *African Journal of Environmental Science and Technology*, **5**, 933-940.

[28] CCME (2001) Canadian Water Quality Guidelines for the Protection of Aquatic Life: CCME Water Quality Index 1.0 Technical Report. Canadian Council of Ministers of the Environment, Winnipeg. http://www.ccme.ca/files/Resources/calculators/WQI%20User's%20Manual%20(en).pdf