DEVELOPMENT OF SIMULATION MODEL FOR LEACHATE MIGRATION NEAR VAMANJOOR LANDFILL AND TREATMENT OF LEACHATE BY NANOPARTICLES

Thesis

Submitted in partial fulfilment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

By

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APRIL – 2021

DECLARATION

by the Ph.D. Research Scholar

I hereby declare that the Research thesis entitled "**Development of simulation model for leachate migration near Vamanjoor landfill and treatment of leachate by nanoparticles**" which is being submitted to **National Institute of Technology Karnataka, Surathkal** in partial fulfilment of the requirements for the award of the Degree of **Doctor of Philosophy** in **Civil Engineering Department** is a *bonafide report of the research work carried out by me*. The material contained in this Research Thesis has not been submitted to any university or institution for the award of any degree.

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Place: NITK, Surathkal

Date: 30-04-2021

CERTIFICATE

This is to certify that the Research thesis entitled "**Development of simulation model for leachate migration near Vamanjoor landfill and treatment of leachate by nanoparticles**" submitted by **DIVYA ANAND** (Register Number: **145002CV14F03**) as record of research carried out by her, *is accepted as the Research Thesis submission* in partial fulfilment of the requirements for the award of the degree of **Doctor of Philosophy.**

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ACKNOWLEDGEMENT

I express my deep sense of gratitude to my supervisor, Dr S. Shrihari, Department of Civil Engineering and Dr Ramesh. H, NITK Surathkal for their help and valuable suggestions throughout my research work. I also thank them for their in-time assessment and expert guidance in preparing the thesis and technical paper writing.

I am grateful to Research Progress Assessment Committee members, Dr A Mahesh and Dr Subhash C. Yaragal for their critical evaluation and useful suggestions during the progress of the work.

With deep sense of regards, I would like to thank all the previous HODs and present HOD, Dr B R Jayalekshmi, for their kindly in time support

I am greatly indebted to Dr Dwarakish G S, the former Head of the Department of Applied Mechanics Department, NITK, Surathkal, and for granting me the access of software GMS to the maximum extent, which was very vital for the completion of this research.

I thank Mr Manohar Shanbouge, Mr Dheeraj and all the teaching and non-teaching staff of the department for their help.

I thank my fellow research scholars Mrs Anjali, Mrs Sheekha, Ms Poorani, Mr Vinod, Department of Civil Engg. National Institute of Technology Karnataka (NITK), Surathkal

My heartfelt thanks are due to my beloved parents, and all the family members who blessed and supported me to every success in my life. Special thanks are due to my dear husband Dr H.T.Ajay.Rao for his moral support. My heartfelt thanks to my darling daughter Adithi for her love, help and support and to my adorable little boy Anantha Krishna for the good luck brought to me.

Thanks are to all those who directly or indirectly helped me during my research.

Finally, thanks to the almighty GOD for providing me the strength, knowledge, ability and opportunity to undertake this research study and to persevere and complete it satisfactorily.

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ABSTRACT

The impact of leachate from landfill on groundwater has paid a lot of global attention because of its devastating environmental significance. The outputs from landfill induce heavy impacts or risks to the environment forcing the concerned authorities to impose more strict constraints and hence leachate is to be treated before it migrates to the neighboring environment.

The Mangaluru City Corporation is collecting the waste on a daily basis and dumping it into a landfill at Vamanjoor located nearly 8.5 km from city centre. The landfill has got a bottom liner, but the drainage to collect leachate is not fully functional. Hence all the untreated leachate formed at the bottom, finds its trails into the neighbouring environment polluting the underlying aquifer. The water sample from observation wells were analysed and results shows that the wells located in 1 km around the landfill are contaminated with the landfill as point source from where contaminants are continuously injected.

The leachate collected from landfill was analyzed in the laboratory for various physico-chemical parameters and were compared to the Standards of disposal for Indian standards for surface water IS 2296-1982. It showed that most of the parameters exceeded specified standard for the disposal of waste. Since the composition of the on-site leachate changes every day, in order to maintain repeatable composition, synthetic leachate was prepared in the laboratory. The nano iron was synthesized in the laboratory and characterized using Scanning Electron Microscope. The removal efficiency of chemical oxygen demand (COD) from synthetic leachate using nano iron was studied. For analyzing significant factors which favors the reaction such as pH, initial concentration, optimum concentration of adsorbent to be added, batch experiments were conducted using nano iron with and without starch coating. Batch experiments proved that pH of solution was an important parameter while kinetics coefficients were directly related to pH with correlation coefficients $R^2 > 0.90$. The nano iron dosage of 2 mg/l enhances removal efficiency of COD beyond that dosage the effluent will have traces of iron beyond the limit which is undesirable. Based on the removal efficiency which is around 60%, optimum conditions were adopted for continuous fixed-bed study. In a perspex column the nano iron coated with starch is sandwiched between

untreated natural lateritic soil and the synthetic leachate was allowed to pass through it. The removal efficiency was obtained by comparing COD of influent and COD of effluent. A comparison of batch and column reactor has been done where continuous fixed-bed column was found to be more effective in removal of COD with removal efficiency of 68% in the remediation of leachate which may be due to the adsorption by laterite soil. Evaluation of Freundlich, Langmuir and D–R isotherm models were done. The kinetics of the experiments shows that it follows pseudo first order reaction kinetics. Because of its high removal efficiency, nano iron coated with starch has been taken as an effective remedial agent in treatment of leachate. As it showed better removal efficiency during continuous fixed-bed column studies, it can be used as adsorbent in permeable reactive barriers. Permanent reactive barriers are specially designed reactive zone which extends beneath water table which intercepts and degrade the contaminants in groundwater.

The current study focuses on determination of extent of groundwater contamination on a typical tropical coastal aquifer due to a landfill located at Vamanjoor in Dakshina Kannada district, India. MODFLOW which is a standard and popular flow model was used to simulate groundwater flow and MT3DMS was used for simulating contaminant transport because of its ability to model various complexes such as advection, dispersion and chemical reaction involved in the solute transport. The aquifer considered is a shallow, unconfined one with laterite soil which gets good rains during monsoon and will be dry during rest of the year. The adsorption by laterite soil has been considered. The specific yield and transmissivity were estimated to be 7.85% and 213 m^2/day respectively. After calibrating successfully with Nash–Sutcliffe efficiency 0.8, horizontal hydraulic conductivity was set as 7m/day. Validation of model was then done with the field data and is applied for forecasting the spread of contaminant for anticipated future scenarios. The results show that in spite of retardation offered by lateritic soil, contaminant trail is expanding with a velocity of 0.15 m/day in downstream direction.

The solute transport model MT3DMS was successfully applied to simulate the contaminant transport of the study area. Since MT3DMS model involves the model structure involved in MODFLOW, the model domain was not altered. The model was

calibrated and validated with reasonable precision (correlation coefficient $R^2 > 0.7$) which shows that the model performance is good. The simulated results show that the contaminant has spread for a distance of 1 km radius around the landfill which is in accordance with the actual value of the water quality analysis of observation wells.

The model after calibration and validation is applied for the evaluation of general regional impact on the groundwater system for future scenarios. The study revealed that the contamination has spread for a distance of nearly 1 km from the landfill and plume is expanding at a rate of 0.15 m /day. By 15 years the plume will reach a distance of 1.8 km from the landfill. If permanent reactive barrier is installed the expansion of plume can prevented and the pollutant at the observation well located at 1 km from landfill can be reduced less than 400 mg /l. Hence installation of permeable reactive barrier with nano iron can be taken as a remedial alternative in order to control groundwater pollution due to landfill leachate.

Key words: Groundwater, leachate, landfill, nano iron, permanent reactive barrier

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CHAPTER 1

INTRODUCTION

1.1 GENERAL

Landfills are main sources of air and water pollution. Still dumping wastes in engineered landfills is one of the most commonly used method for disposal of solid waste around the world as it is economical and environmentally sustainable option of waste management. When the decomposition of waste starts and when rainwater or groundwater mixes with the refuse, leachate will be formed that normally contains high concentrations of organic and inorganic contaminants like xenobiotic organic compounds, humic acids, ammonia nitrogen various inorganic salt and even heavy metals (Honjiang et al., 2009). Leachate is a stinking liquid dark brown in colour which is heterogeneous in nature that comes out of the wastes. The toxicity of leachate depends upon composition of waste; extent of decomposition of the refuse and also hydrogeological factors. As leachate penetrates in to the soil and reaches the underlying aquifer, it causes groundwater pollution and when it moves in horizontal direction, it contaminates surface water. Hence to prevent the percolation of leachate, the landfill has to be lined with an impermeable barrier and also the leachate formed has to be collected and treated before releasing it to environment.

The emission of leachate from landfill is alarming because of its toxic impact on the environment when it is released unchecked. Even though there are different methods to treat landfill leachate, there are many constraints such as process efficiency, requirement of energy, difficulty in operation and cost effectiveness. New research suggest nanotechnology as economically beneficial as well as eco-friendly way for the treatment of leachate. Nano particles are widely used now a day for environmental remediation due to their exclusive chemical and physical properties (Rajan, 2011). Due to the higher reactive surface area, smaller particle size and also higher dispersivity compared to other nano particles, nano irons are widely used in the environmental clean-up. Nano iron can be used either in situ or ex-situ for the remediation of leachate. It can be injected as slurry mixed with water under pressure, by gravity or by both and can remain suspended for long time thus facilitates in situ treatment or it can be used as a reactive barrier for in situ treatment. Ex-situ treatment can also be carried out with the aid of nano iron where the leachate is taken out for its treatment.

Permanent reactive barriers are in situ treatment method where immobilization or degradation of contaminant takes place as leachate passes through reactive barrier (Obiri et al., 2014). The contaminated water when passed through reactive bed, it transforms the pollutant into environmentally acceptable form. The advantages of permanent reactive barrier are since it is an in situ treatment method, the need for storing, transportation and disposing the leachate are not required. Also as the contaminated groundwater is flowing through permanent reactive barrier under natural gradient, there is no need for energy supply which minimizes the cost of treatment (Thiruvenkatachari et al., 2008).

1.2 GROUNDWATER MODELING

Groundwater modeling helps in simulating the complexes involved in movement of groundwater and can replicate the flow and also can evaluate and forecast its flow and transport. But proper understanding of the landfill site is needed as the reliability of groundwater model is on the basis of accuracy of the data from the field. Groundwater models are developed so as to evaluate groundwater system which is subjected to several assumptions and constrains. Various numerical methods such as finite element method (FEM) and finite difference methods (FDM) are used in modeling of groundwater where the solution of differential equation governing flow of groundwater or solute transport is solved. In finite difference method, the approximation of the flow equation is done by differentiation. The solution is determined in a faster way so that the researchers can compile information on aquifer and address the problems persist in simulation of groundwater.

Contaminant transport modeling can also be efficiently solved by using numerical methods. In order to solve the mathematical model several assumptions are made like aquifer is homogeneous and isotropic (hydraulic conductivity is not changing with position where it is measured within the aquifer and also not changing with direction of measurement) and also steady flow (hydraulic head as well as groundwater velocity is not changing with time). But with the use of computers, more practical situation such as the transient flow in aquifer because of heterogeneity and anisotropy (hydraulic conductivity depends on the position and the direction of measurement) of the aquifer can be dealt. The contaminant transport model calculates the concentration of the contaminant in groundwater from the point where it is introduced to the environment to the site down the gradient. For that a groundwater flow model is required to know the flow velocity as well as the direction of flow of groundwater. The space and time base solution is obtained by solving the partial differential equations governing the flow.

1.3 SCOPE OF THE WORK

The population of coastal region of Karnataka (around 10000 sq. km) as per Indian Network for Climate Change Assessment (INCCA, 2010) is 200 people per sq.km. The source of water for agricultural and domestic use in the area under consideration is met mostly from open wells. Mangaluru city located at coastal region of Dakshina Kannada District is experiencing a rapid growth of population since last decade due to the presence of industries, educational institutions as well as due to the emergence of commercial centers. Also Mangaluru city is the headquarters of many nationalized banks. Groundwater along with piped water supply by Mangaluru City Corporation is used as main water supply for the district throughout the year. According to the City Corporation the city needs around 160 million liters of water per day and the main source of water is from Thumbe vented dam. During severe summer, the city is facing water crises owing to poor water collection in catchment area due to which the industries in the area have to downside their operations.

Figure 1.1 Vamanjoor landfill

The Mangaluru City Corporation is collecting the solid waste on a daily basis and dumping it into a landfill at Vamanjoor (Figure 1.1) located nearly 8.5 km from city centre. The landfill has got a bottom liner, but the system to collect leachate is not fully functional. Thus, all the leachate formed at the bottom, finds its trails into the neighbouring environment polluting the underlying aquifer. In an incident which took place during August 2019, following heavy rainfall the soil cap of the Vamanjoor landfill developed crack and rainwater seeped into the garbage. Because of the force of the water, the garbage began sliding towards the areca plantation which resulted in the damage of the plantation (figure 1.2). As Vamanjoor is a home for many educational institutes and also a residential area urgent attention needs to be paid to the ground water of this region. The current study has been carried out with the aim to find out the trail of contaminant by using Visual MODFLOW and MT3DMS to forecast the transport process in groundwater. As possible remedial measure, an attempt is made to analyze the ability of nano iron to remediate leachate which can be adopted to prevent further contamination.

Figure 1.2 Garbage heap slide during 2019 August rainfall

1.4 RESEARCH OBJECTIVES

The current study is intended to model the groundwater contamination from a landfill at Vamanjoor for the existing climatic and hydro-geologic conditions and also for the forecasted conditions foreseeing the conditions which may occur in the future. The three dimensional simulation was applied by using MODFLOW and MT3DMS to understand the flow of ground water as well as the extent of contamination in a spatial and temporal basis. Also a possible remedial measure for preventing further contamination using nano iron is being suggested. Accordingly, the current study has the following objectives:

1. To assess the spread of contamination due to landfill leachate through physical examination of groundwater samples.
    - To find the number of abstraction wells in the study area and to choose the observation wells
    - To measure the hydraulic head of observation wells during Pre-monsoon and post monsoon season
    - To analyse physic chemical parameters of groundwater from observation wells.
    - To analyse physic chemical characteristics of leachate
2. To analyse the potential use of nano iron in remediating leachate.
    - To prepare synthetic leachate and synthetic iron nano particle
    - To do the characterization of Iron nano particle using Scanning Electron microscope (SEM)
    - To perform batch and column studies using iron nano particle for the treatment of Chemical Oxygen Demand of synthetic leachate
    - To study adsorption isotherms and kinetics.
3. To develop a three dimensional numerical groundwater flow and solute transport model of the study area using MODFLOW and MT3DMS
    - To calibrate and validate the model by comparing simulated and observed values
4. To predict spread of contaminants for various scenarios.

1.5 DESCRIPTION OF STUDY AREA

1.5.1 General

Mangaluru is an important coastal city on the west coast of India located in the state of Karnataka with an average elevation of 22 m above the mean sea level. The city covers an area of 132.45 sq. km and a population of around 488,968 as per 2011 census. The area mainly consists of educational institutions, industries, residential areas and agricultural land. The people in the area mainly dependent on both surface groundwater as the sources of water for the watering their crops and also for domestic and industrial supplies. Topographically the city is relatively plain up to 30 km of the coast region beyond which it changes to undulating hilly terrain towards the east in Western Ghats. Geologically it is characterized by hard laterite soil in the hilly region and sandy soils in the sea shore.

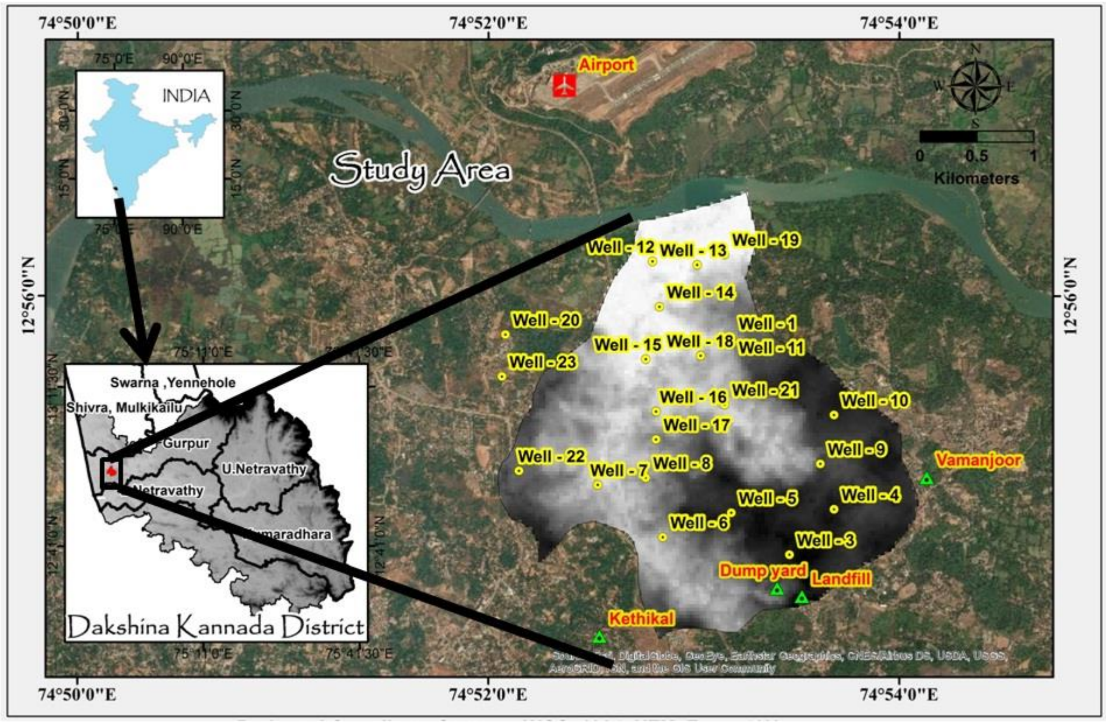


Figure 1.3 Location of Study area

The river Gurupur is one among the main west flowing rivers of Dakshina Kannada district in Karnataka. The basin covers the foothills of the Western Ghats, in the middle lateritic plateaus and towards its mouth is flat coastal alluvium. (Lathashri and Mahesha, 2016). The city is characterized by tropical monsoon climate. Around 200 ton of solid waste is collected on daily basis and disposed into the municipal landfill located at Vamanjoor which is 15 km away from the city lies between 12 ° 54 ' to 12 ° 56 ' N and 74 ° 52 ' to 74 °54 ' 30” E, located in Gurupur basin (figure 1.3).

Many educational institutes including St Joseph College of engineering and SDM college are located in the study area. The study area falls in the jurisdiction of Mangaluru taluk. The crops cultivated are mainly coconut, areca which is irrigated by using groundwater pumped from open wells. Due to the scarcity of water during summer groundwater is used for domestic purposes during these months.

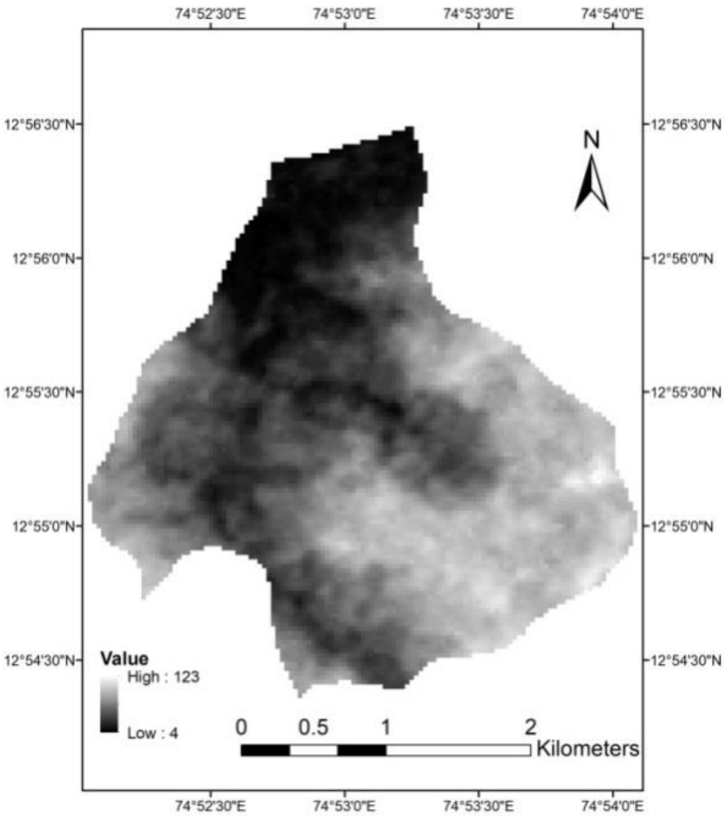


Figure 1.4 DEM of Study area

1.5.2 Topography

The topography of the study area is shown in figure 1.4. In order to get the surface elevation of the model, the SRTM raster Digital Elevation Model (DEM) of resolution 30 m was downloaded. The study area is sloping towards the north where the west flowing river Gurupur exist. The elevation of the region varies from 4 m to 123 m above mean sea level (msl). The topography of the study area is plain to undulating terrain.

1.5.3 Climate of the study area

The annual rainfall data was obtained from meteorological station located at Mangaluru Airport located at Bajpe which is at a radial distance of 4.5 km from the landfill. The rainfall data of last 18 years has been plotted in the bar chart as given in figure1.5. The typical weather of the place is of the tropical climate with more humidity with moderate temperature of 36 ° C during the month of May and 21°C experiencing during the month of December are extreme climate of the year also the relatively higher level of humidity of the region ranges between 65 % and 88 %.

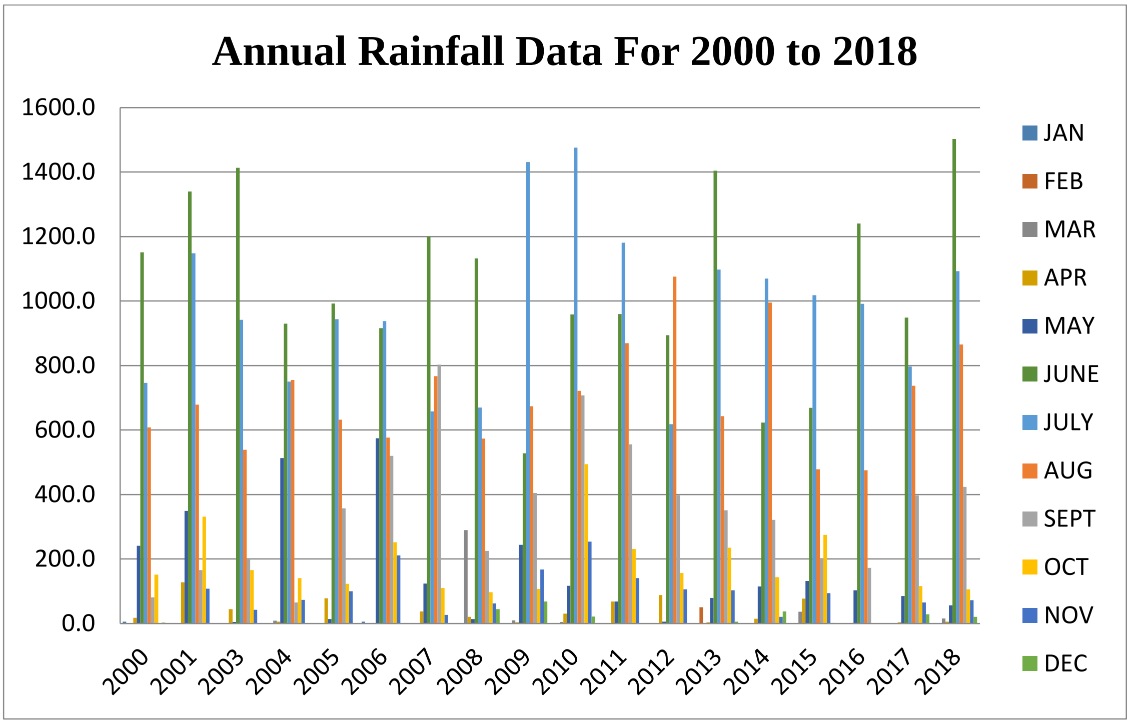


Figure 1.5 Rainfall data at Mangaluru Airport located at a radial distance of 4.5 km (2000-2018)

The Indian Meteorological Department has identified four seasons for the region. Monsoon season which occurs in the month of June to September, post monsoon which is in the months October and November, winter which occur in the month of December and January and pre monsoon or summer during February to May. As per the report annual average precipitation is 3810 mm with mostly about 85 % occurs in the months of June to September.

1.5.4 Geology of study area

The geology of the area is lateritic formation which lies under a very thin layer of clay, granites, gneisses and coastal alluvium throughout the coastal area. The lithological map which is prepared by KSRSAC (Karnataka State Remote Sensing Application

Centre), Bangalore for Dakshina Kannada District (Figure.1.6) was considered. From the previous studies (Rao 1974, Srikantiah 1987) it is evident that the sub-basin is an unconfined aquifer having depth which ranges up to 30 m. The bore log data from Kethikal which is around 2 km from Vamanjoor dump yard was taken for the present study (Bhat et al., 2008). As per bore log data (Figure.1.7), hard laterite is present till 4.5 m and shedi soil is present for a depth of 9 m and then exist weathered rock for a depth of 2.5 m and for 0.5 m soft rock exist and hard rock exist at a depth of 31.8 m from the top soil.

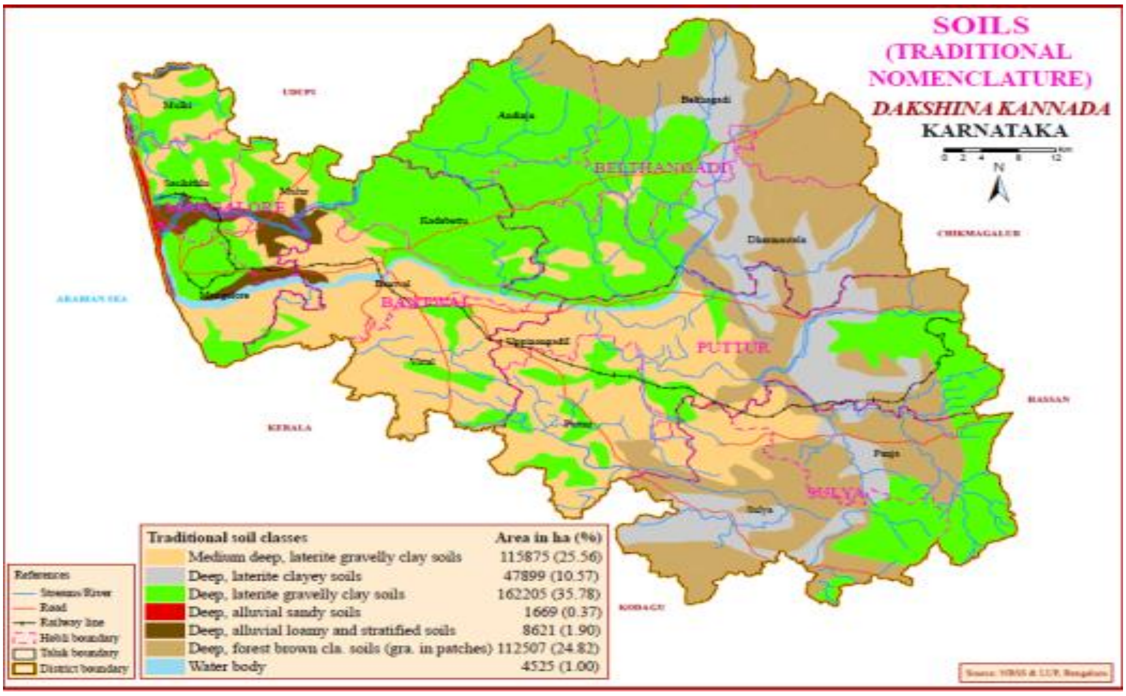


Figure 1.6 Soil map of Dakshina Kannada District (Prepared by KSRSAC, Bangalore)

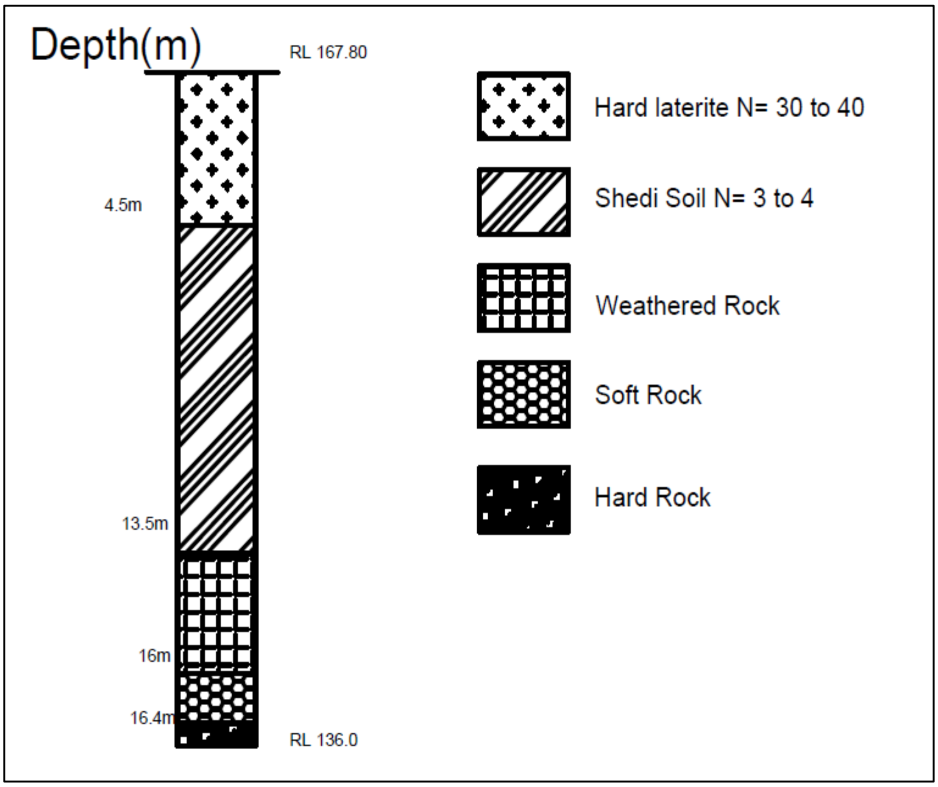


Figure 1.7 Bore log of Kethikal near Vamanjoor (Bhat, 2008)

1.5.5 Land use and land cover

The land use land cover (Figure.1.8) was obtained from LISS (Linear Imaging Self Scanning Sensor) IV multi-spectral sensor data with 5.8 m spatial resolution obtained from RESOURCESAT-2 satellite. It was procured from NRSC (National Remote Sensing Centre) located in Hyderabad during month of February 2016. Signatures for 6 classes were obtained for the classification of the area. The scale of data is 1:250000. Of the 19 classes, the data has been merged into 5 classes which are vegetation built up land, agricultural land, water body and barren land. As per the result obtained from classification, it was observed that the 55.89 % of the total area is covered by vegetation, 11.32 % built up land, 21.25 % agriculture, 4.52 % water body, 1.64 % roads and 5.38 % is barren land.

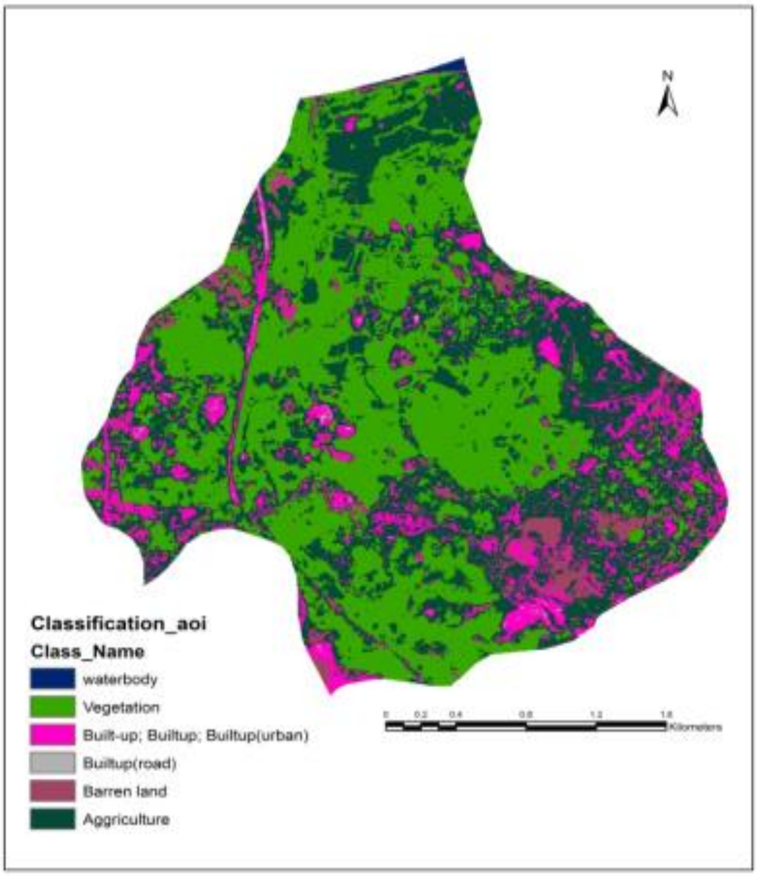


Figure 1.8 Land use land cover map of study area

1.6 ORGANIZATION OF THESIS

The thesis contains seven chapters, list of references and annexure. A brief description of each chapter is presented here.

Chapter 1 gives information on the introduction to the problem, description of study area, objectives of study, research methodology which is adopted

Chapter 2 provides the review of literature of groundwater flow and solute transport model, remediation techniques or the treatment procedure adopted for leachate.

Chapter 3 provides the method adopted details of observation well and a report on water quality analysis

Chapter 4 provides an insight on the characteristics of leachate and batch and column studies using nano iron, adsorption isotherms and kinetics.

Chapter 5 gives the detailed method of development of groundwater flow model for a tropical coastal aquifer located at Vamanjoor in Dakshina Kannada district, India with the help of groundwater flow model, MODFLOW and the applications which is related to the study area and sensitivity analysis

Chapter 6 gives information regarding the application of solute transport model its applications so as to know the path and fate of the contaminant from the landfill and sensitivity analysis

Chapter 7 presents the application of developed model for predicting future scenario for different cases and also to predict the possibility of the remedial measure which can be adopted in the site.

Chapter 8 lists outs the conclusions, the limitations of the study and also the scope of future work

CHAPTER 2

LITERATURE REVIEW

2.1 GENERAL

Landfills are the most attractive route of disposing municipal solid waste as it is economically viable (Schiopu and Gavrilescu, 2010). Mainly solid waste from residential, commercial and industrial area are disposed into the landfills. Even though the alternatives such as incineration, composting are considered as some of the ways of reduction of wastes, the final portion like ash or slag has to be landfilled. The landfill technology has evolved from uncontrolled dumps in an open space to engineered ones which is designed for the elimination or minimization of its adverse impacts on the surrounding environments (Renou et al., 2008). Still the subsequent migration of leachate which is a highly toxic liquid oozing out from the landfill waste to the nearby environment is serious concern and threat to public health at bot old type dump yards and the new engineered landfills. The most significant concern regarding migration of leachate is groundwater pollution. Even if the bottom of the landfill is lined with an impermeable membrane, when leachate reaches the bottom, it migrates laterally to surface or it descends downward to reach the aquifer below affecting quality of groundwater (Kjeldsen et al., 2002; Regadío et al., 2013). Hence landfill leachate is to be collected, treated and discharged safely so as to avoid potential pollution produced by it. (Fatta et al., 1999)

Treatment of landfill leachate should meet the standards fixed by regulatory authority and efficient treatment has to be ensured. The major aim is to develop a technology so as to reduce risks on environment at optimal cost and also volume of final contaminated soil and groundwater is reduced. Nanotechnology plays a wide role in controlling pollution because of its variety of application across wide discipline (Rajan, 2011). Recently metallic nano particles because of its potential applications are becoming more popular in the treatment of leachate. Permeable reactive barriers are one among the widely acceptable innovative technology for the in-situ remediation of leachate contamination.

If contaminant is detected in the groundwater, action has to be taken so as to mitigate it or clean it up or to control it. For that the path as well as the fate of the contaminant has to be forecasted so that the remedial measure can be designed. The construction of mathematical model of study area and its solution will give the prediction of the path of contaminant as well as transport phenomena taking place. But due to the heterogeneity of the domain and irregular boundaries it is difficult to find out the analytical solution of mathematical model. Hence it is transformed into a numerical model which is solved with the aid of computers. By conceptualizing the groundwater system, one can demonstrate the behaviour of the aquifer in the past, also can predict the outcomes and helps the decision making bodies to explore the alternative approaches for its management. (Schiopu and Gavrilescu, 2010)

2.2 LEACHATE GENERATION AND COMPOSITION

The physico-chemical as well as microbial degradation of organic matter present in the landfill when combined with percolated rain water results in the generation of aqueous effluent called leachate (Visvanathan et al., 2007). The characteristics of the landfill leachate depends largely the composition of the waste deposited in landfill and the degree of decomposition (Renou et al., 2008). The following are main factors which influences the degradation of waste in landfill are

2.2.1 Moisture content

Biodegradation of the waste needs moisture and it is the main factor that determines the production of landfill leachate. Moisture in the landfill site is derived from the intrinsic moisture of the waste the amount of the rainfall received in the area, penetration of surface and groundwater in to the landfill and the rate at which the waste is biodegraded. (Kjeldsen and Beaven, 2011) The moisture helps in the distribution of microorganism and flushes away the products of degradation.

2.2.2 Site Characteristics

Landfill site which are deeper than 5 m have more chance of developing anaerobic conditions while shallow ones allow interchange of air subsequently lower anaerobic activity takes place. The anaerobic condition are also developed in the landfill sites provided with caps. (Jain et al., 2005)

2.2.3 Waste Characteristics

The amount of organic matter present in the waste determines the degree of biodegradation of the waste. The waste when shredded before landfilling it increases homogeneity and surface area thereby increasing the rate at which biodegradation takes place. The compaction of the waste also increases the available biodegradable material for degradation. The leachate generated from semi aerobic landfill is more stable than those from anaerobic landfill (Aziz et al., 2010).

2.2.4 Acidity and temperature

Activity of microorganism is influenced by the acidity and it regulates the rate at which biodegradation takes place. Initially the pH of the landfill will be neutral followed by acidic phase. The temperature indicates the type of the microorganism that are active. The compacted waste will be of low temperature due to the lesser availability of oxygen. In most of the case the temperature of the landfill will be in range of 30° C to 35° C and the temperature will vary with the depth of the landfill (Schiopu and Gavrilescu, 2010)

Leachate is commonly characterised by its strong odour, dark brown colour and the presence of mixture of high level of contaminants such as organic compounds which includes dissolved organic materials, volatile fatty acids, xenobiotic organic at low concentrations, pathogens humic acids and fulvic acids (Kamaruddin et al., 2015). The table 2.1 gives information about the parameters which can be used to assess the age of landfill. The age of the landfill also determines the characteristics of leachate. In the young landfills where it is less than five years, around 95 % of organic compounds are made up of volatile fatty acids where as in the stabilized or matured landfill, organic fraction will be of refractory organic compounds (Mishra et al., 2018). Aerobic organism will be acting during initial five years and during second phase (5 to 10 years) which is the transition stage, the degradation takes place mainly due to acid forming organisms. And final phase, generally termed as those which is more than 20 years the activities of microbial organisms will be more or less in steady state. The stabilization period is long which may be due to heterogeneity in composition of waste, time-consuming anaerobic activities or due to specific conditions of site such as prevailing soil condition of site, the water content and the weather of the place (Barlaz et al., 2002).

Table 2.1 Parameters which determine landfill age (Kjeldsen et.al., 2002)

Landfill type	Young	intermediate	stabilised
years	< 5 years	5-10 years	> 10 years
pH	< 6.5	7	> 7.5
BOD5/COD	> 0.3	0.1– 0.3	< 0.1

Besides that the characteristic of landfill leachate changes with time as well as with sites which is due to a combination of different factors such as site characteristics, weather of the place, moisture content, degree of compaction and temperature.

It has been proved that the compression of waste and the biodegradation processes can produce twice or thrice the quantity of leachate (Pantini et al., 2014). The hydraulic conductivity and the porosity will decrease in time because of the overpressure with progressive landfilling and hence degradation also gets reduced over time (Di Bella et al., 2012).

2.3 LEACHATE FATE AND MIGRATION

Leachate after being generated is released into the neighbouring environment and the ability of migration depend mainly on the physico-chemical properties of the contaminant. It also depends on the soil column below which extends from the ground surface to the water table (Gavrilescu, 2005). The concentration of organic matter in the leachate will be reduced while migrating through the sub surface soil due the process such as dispersion, diffusion, and adsorption. The degradation of organic matters also occur by microorganism due to aerobic or anaerobic processes which reduces the pollutant load while migrating (Sykes, et al., 1998). It was seen that the heavy metals can migrate away from the limits of disposal site causing serious threat to the water table and soil below the landfill.

2.4 ENVIRONMENTAL IMPACTS OF LANDFILL LEACHATE

Leachate from landfill is one among the major sources of polluting agents of surface as well as groundwater unless proper treatment is given to it before disposal. Or else it percolates through the soil and reaches the underlying aquifer (Bashir et al., 2009). As groundwater is an important resource for sustaining human life, care has to be taken so as to prevent leachate movement from landfill. Satisfactory management has to be done so as to reduce the risk of migration of leachate from landfill (Patil et al., 2013). Even after the closure of old landfills, numerous environmental worries are arising due to their poor design like defects because of aged liners, uncontrolled leachate and gas emission (Tong et al., 2015). Due to growth of industries and thereby an increase in population, the quality of water is being deteriorated because of disposing urban solid waste and industrial solid waste (Raju et al., 2011).

Table 2.2 Impact of landfill on groundwater various studies conducted in India

Location of landfill	Impact	References
Gazipur, Uttar Pradesh	The physico- chemical analysis of groundwater sample indicated that the groundwater quality is significantly affected by leachate percolation.	Mor et al., 2006
Pirana landfill, Ahmadabad, Gujrat	The traces of heavy metals were present in the groundwater sample indicated pollution due to leachate percolation.	Singh et al., 2008
Bhalaswa landfill, New Delhi	The chloride concentration in the groundwater within 75 m around the landfill was found to be in polluted and study seeks urgent attention to	Jhamnani and Singh, 2009

	be taken for the groundwater supply of the region.	
Urali Devachi Landfill site, Pune	Higher values of BOD, COD and MPN indicated the water samples of the observation wells around the landfill within 1.8 km radius are polluted.	Barde et al., 2014
Landfill sites located in Chandigarh, Panchkula, and Mohali (Sahibzada Ajit Singh Nagar)	Due to the presence of higher concentration of ammoniacal nitrogen, chemical oxygen demand, chloride, sodium and potassium in water samples of observation wells within 1 km radius from the landfill, confirms the leachate is the potential source of groundwater contamination.	Negi et al.,2020
Ramna, Varanasi, Uttar Pradesh	Higher values of parameters such as NO^{3-}, PO_4^{3-}, Fe, electrical conductivity (EC) and total dissolved solid (TDS) during analysis of groundwater samples near the landfill site especially during post-monsoon, indicates that groundwater quality is being significantly affected by leachate percolation.	Mishra et al., 2019
Vendipalayam, Semur and Vairapalayam landfill sites in Erode city, Tamil Nadu	The presence of heavy metals, and higher level of Cl^-, NO_3^-, SO_4^{2-}, NH_4^+ shows that the water samples are polluted because of the percolation of leachate.	Nagarajan et al., 2012
Dhapa, Kolkata	The effect of leachate percolation was evident on the groundwater surrounding the landfill as most of the physico-chemical parameters exceeds their permissible limits. Also heavy	Maiti et al.,2016

	metals such as Pb and Hg were present in surface water and groundwater samples	

Also it is recommended to pay attention to the closed non-engineered landfills which had been in operation years before as the leachate can arise from these landfills over coming decades and pollute the aquifer below.

2.5 LANDFILL LEACHATE TREATMENT METHODS

The infiltration of leachate from landfill to groundwater table possess a great potential risk and hazard to human health as well to environment, which remains aesthetic concern. As the outputs from the landfill induces impacts or risks to the ecosystem, the respective authorities are forced to impose more strict rules for the treatment of landfill leachate. Leachate treatment has to be done so as to meet the standards set by the concerned supervisory authorities and it should ensure an efficient and successful treatment (Gupta and Singh, 2007). The leachate has to be treated according to any one of the following method of a combination of the following methods (i) Treatment of the leachate on-site (ii) disposing it to sewerage system (iii) transport of the same for its treatment elsewhere. The final goal is developing a technology which can further decrease cost of clean-ups, and decrease the remaining volume of polluted soil and groundwater.

2.5.1 Conventional treatment

Conventional treatment methods may include

(i) Transfer of leachate and treating it with domestic sewerage where the leachate is treated along with the municipal sewerage in the treatment plant. As cost of operation and maintenance was less, this type of treatment method was preferred (Ahn et al., 2002). But due to high organic matter which has low biodegradability and due to the presence of heavy metals in the effluent the efficiency of the treatment is reduced. Recycling is one of the conventional treatment methods adopting from pas t as it is the least expensive method where the leachate is recycle back through the tip of the landfill (Lema et al., 1988). It has been reported that the moisture content is increased thereby enzymes are nutrients are provided between methanogens and solids (Bae et al., 1998). But if the volume of leachate is high, the problems of saturation, acidic conditions, ponding around landfill may occur (San and Onay, 2001; Chan et al., 2002).

(ii) Biodegradation which is aerobic or anaerobic treatment is commonly adopted methods because of its economic aspects, simplicity and reliability. It is carried out with the help of microorganisms which degrades the organic compounds present in the leachate to carbon dioxide and sludge in aerobic conditions and biogas which is a mixture CO_2 and methane under anaerobic conditions. The presence of fulvic and humic acids tends to limit the effectiveness of the process (Lema et al., 1988).

(iii) Physical and chemical treatments include

A) Adsorption – The adsorption of pollutant onto some adsorbents such as activated carbons or metallic nano-particles is called adsorption. The process delivers better reduction of COD. Studies show that laterite is an excellent adsorbent for the removal of arsenic fluoride, phosphate, zinc (Maji et al., 2008, Chalermyanont et al., 2009, Gomoro et al., 2012). Because of the adsorptive capacity of laterite soil, along with marine clay, it is assessed to use as liner for landfill (Chalermyanont et al., 2009). As lateritic soil adsorbs various chemicals and heavy metals, the sorption by laterite soil which retards the flow of pollutant has been considered (Nayanthika et al., 2018).

B) Floatation - a step which is performed after treatment for removal of residual humic acids which is non-biodegradable (Rubio et al., 2002).

C) Chemical precipitation is used widely as pre-treatment step for the removal of highly concentrated ammonium nitrogen (NH_4^{+}- N).

D) Coagulation flocculation is given as a pre-treatment step in stabilised or old landfills before biological process (Silva et al., 2004).

E) Chemical oxidation is used widely for the treating landfill leachate. Advanced oxidation process such as Fenton's oxidation process make use of strong oxidants in the presence of ultra violet rays or ultra sound and catalysts, to attain complete mineralisation. The main drawback is that it works in low pH (Lopez et al., 2004).

F) Air stripping is the commonly used method to eliminate high concentration of ammonium nitrogen. But the releasing of ammonia into the atmosphere which causes air pollution is the major drawback of this method.

But the level of treatment is not adequate for reducing the negative impacts of the aged landfill and leachate that are more stabilised in nature. Also the standards set by the regulatory authorities for the disposal of discharge after treatment are getting hardened which suggests proposal of some new technologies for the treatment of the leachates. Hence more effectual methods of treatments on the basis of membrane technology has been emerged as a feasible alternative for the compliance of pending regulation of water quality in most of the countries (Tadkaew et al., 2007, Renou et al., 2008).

2.5.2 New treatment method

New treatment methods make use of membrane processes for the treatment of landfill leachate. The treatment mainly consists of nano-filtration, reverse osmosis micro filtration and ultra-filtration.

(a) In nano-filtration usually the membrane materials are made up of polymeric films. The removal efficiency of COD was found to be 70 to 80\% when combined methods of physical and nano-filtration was employed. But the main drawback is membrane fouling.

(b) Reverse osmosis is one among the efficient method for the rejection of COD and heavy metals (nearly 98%) from the leachate. But the main drawbacks is the application of the membrane process that is pressure driven and membrane fouling (Rautenbach et al., 2000).

(c) Microfiltration eliminates colloids and suspended matter and hence it is carried out as a pre-treatment method before another membrane process. It cannot be used alone as the reduction in COD is only 25 to 35 % (Piatkiewicz et al., 2001)

(d) Ultra filtration is used in a combination of other process as it removes macro-molecules. The removal efficiency of COD when ultrafiltration is used alone is only 10 to 15%. It is proved that ultrafiltration is an efficient pre-treatment for reverse osmosis (Bohdziewicz et al., 2001).

2.5.3 Permanent reactive barrier

Permanent reactive barriers (PBR) are specially designed reactive zone which extends beneath water table which intercepts and degrade the contaminants in groundwater. While passing through the barrier, the pollutants will either get treated to less harmful product or it will become an immobile species. PBR is designed in such a way that it will not hinder groundwater flow and hence installation of PBR may not alter hydrogeology of aquifer. PBR is one among the new technology to treat contaminants which can substitute pump and treat method of treatment.

The advantages of PBR are (i) its ability to degrade the pollutant or immobilize it in situ without taking it up to the surface thereby saving the cost of storing, treating, cost of transportation (iii) power input is not required as the influent flows by a natural slope (iv) only periodic replacement of reactive media is required once it is clogged or it gets exhausted (v) effective remediation of contaminant thus avoiding the problems concerning pump and treat system (Thiruvenkatachari et al., 2008).

Method of installation of permanent reactive barrier includes construction of a trench across the flow path of contaminant either by using funnel and gate system or by constructing a continuous reactive barrier. The gate or the continuous reactive barrier is filled with nano iron which reacts with the target contaminant to form by-products which are biodegradable and non-toxic (Gavaskar et al., 1998).

The removal mechanism by reactive media in the PBR takes place mainly through three mechanism (i) Degradation – by chemical or biological degradation the contaminants will transform to compounds which are harmless (ii) Precipitation – contaminants will get immobilised within the barrier and insoluble compounds are formed (iii) Sorption – contaminant will get immobilised as a result of adsorption and forms a complex (Roehl et al., 2005). Some of the reactive materials used in PBR as per USEPA for target contaminants are activated carbon, bauxite, activated alumina, , ferric oxides and oxyhydroxides, magnetite, peat, humate, lignite, coal, phosphates, titanium dioxide, zeolite. Table 2.3 gives information of reactive media for treating major contaminant.

Table 2.3 Reactive media for treatment of target pollutant (Franklin et al., 2014)

Pollutant	Reactive media	References
Perchloroethene Trichloroethene Dichloroethene vinylchloride	Zero valent iron, granular activated carbon, Hydrogen/palladium, zinc, sand and wood chips, tire rubber	Benner et al., 2002; Chen et al., 2011; Gavaskar et al., 2000; Henry et al., 2003; Lee et al., 2007; Öztürk et al., (2012); Tobiszewski and Namies´nik, 2012; Vogan, 1999
Benzene Toluene ethylbenzene, xylene	Zero valent iron, granular activated carbon, oxygen releasing compounds, compost, saw dust , leaf litter, surface modified zeolite	Aivalioti et al., 2008; Chen et al., 2011; Guerin et al., 2002; Kwon et al., 2011;; Ranck et al., 2005; Yeh et al., 2010
polychlorinated biphenyl, polycyclicaromatic hydrocarbons, dichlorodiphenyl trichloroethane (DDT) Dichlorodiphenyldichloroethane (DDD)	Zero valent iron, granular activated carbon	Katz et al., 2006; Sayles et al., 1997; Yang et al., 2010
Metals like Nickel, Copper, Zinc, lead, Cadmium, Arsenic, Chromium, Mercury	Lime stone, zero valent iron, fly ash, activated alumina	Cappai et al., 2012; Chung et al., 2007; Conca et al., 2002;

		Gavaskar et al., 2000; Genç-Fuhrman et al., 2005; Ludwig et al., 2009; Manios et al., 2003
adsorbable organic halogens, Chemical oxygen demand, nitrate, ammonium	Zero valent iron, Saw dust, Wood chips Compost, Polystyrene, Wheat straw, Softwood and sand, zeolite	Cameron and Schipper 2010; Choe et al., 2004; Chung et al., 2007; Gavaskar et al., 2000; Gibert et al., 2008; Liao et al., 2003; Robertson et al., 2000; Skinner and Schutte, 2006; USEPA 2002; Westerhoff and James, 2003
Phosphate	Zerovalent iron, peat/sand, limestone	Fenton et al., 2009; Gavaskar et al., 2000; Van-Nooten et al., 2010,
sulphate	Zerovalent iron, organic carbon, mushroom compost	Benner et al., 1999; Cappai et al., 2012; Conca et al., 2002; Gavaskar et al., 2000; Lapointe et al., 2006; Skinner and Schutte, 2006, USEPA, 2002
chloride	Zerovalent iron, activated carbon,	Fronczyk et al., 2010

Permanent reactive barrier are benefited in the following ways (i) It is considered as cheaper technology as it needs relatively lower energy cost and also low maintenance and monitoring cost except initial installation cost (ii) It can degrade more pollutants as more number of barriers can be placed (iii) The ground surface above can be used for some useful purpose as the treatment is taking place below the ground surface. (Faisal et al., 2019)

The limitations are (i) contaminants which are flowing in the direction of the barrier are only treated (ii)The site, hydrogeological conditions and also the delineation of the pollutant plume has to be properly understood before installing the barrier (iii) The technology has to be restricted to a depth of 20 m (iv) The problems such as service and monitoring performance can come across as it is below ground surface (v) The replacement of reactive media while in operation is difficult (Franklin et al., 2014).

2.6 NANO IRON FOR ENVIRONMENTAL CLEAN-UP

Remediation using nano iron is one among new generation cost effective solution for many problems concerning environmental clean-up. Because of its higher surface area with higher reactivity makes it a brilliant agent which can remediate the contaminants. The factors such as lower standard reduction potential, quantum size property which is in favour of reaction and the efficacy to transport through the groundwater makes it an excellent in remediating various pollutant (Tosco et al., 2014). As it is effective in transportation through groundwater, injection of slurry of nanoparticles can be done under pressure or by gravitational means to set up a zone which is to be treated. Such a treatment is called in situ treatment. The in situ treatment using nano iron is efficient in remediating chlorinated hydrocarbons. (Elliott and Zhang, 2001; Glazier et al., 2003). It is effective in immobilization of heavy metals and even radionuclides. The reaction periods of nano iron is around 4 to 8 weeks. The studies show that the nano particles can flow up to 20 m distance in groundwater. The reaction of nano iron is comparatively rapid and with high removal efficiency. Due to the agglomeration thereby increasing its size to micron level the chemical reactivity as well as the mobility will be lost. Agglomeration decreases the specific surface area thereby reducing its reactivity. Hence a stabilizer can reduce agglomeration either by adsorbing stabilizer which is charged so that the repulsion between particles is increased. Stabilizer has to be so chosen that it should be environment friendly and cost effective (Wijesekara et al., 2014, Cundy et al., 2008)

For the synthesis of nano iron, many methods had been developed. Some of them are: decomposing iron pentacarbonyl in argon or any organic solvents with the help of laser (Elihn et al., 1999), by the process of thermal cracking (Karlsson et al., 2005), by vaccum sputtering (Kuhn et al., 2002), by reducing particles such as goethite and hematite (Uegami et al., 2003). But the most common method is by the synthesis of nano iron from ferric and ferrous ion using borohydride as reducing agent (Alidokht et al., 2011). The diameter of nano iron ranges between 10 nm to 100 nm and it shows a structure like shell with a core. Because of its larger surface area and many reactive sites, iron nano particles are generally preferred for remediation of leachate (Tratnyek and Johnson, 2006).

Iron nano particle own properties such as adsorption as well as reduction which aids the reduction of various pollutants such as chlorinated organic compounds such as chlorinated methane, chlorinated ethanes, chlorinated benzene, chlorinated phenyls and so on (Elliott and Zhang, 2001) Sometimes the magnetic property of iron is made used of for the recovery of mineral as separation tool after the treatment (Yantasee et al., 2007). It is efficient in treating dense non-aqueous phase liquid (DNAPL) from aquifer (Quinn et al., 2005). Now a days technology based on nano iron in remediating contaminated groundwater is getting transferred from lab to field (Tratnyek and Johnson, 2006). The iron nano particles have been successfully used as reactive barrier for the treatment of contaminant in previous studies (Henderson et al., 2007). But iron nanoparticles must be firmly stabilized on/in the membrane structure through physicochemical treatments so that it will be environmentally less challenging. And these systems are to be properly designed so that they minimally release nanomaterial into the environment.

The main disadvantage of the Permeable Reactive Barrier is that there is limited information about long term performance of the PRB in-situ. (Olson & Higgens, 2009). Also if large rocks below ground structure can create problem during construction. Bio fouling can reduce pore space hence the permeability is reduced. The clean-up and monitoring takes lengthy time is also a disadvantage of reactive barriers. During heavy rainfall, when the porosity or reactivity is considerably reduced, groundwater can back up the up gradient side choosing alternate pathways around the barrier. The lifetime of this material can be reduced due to the contamination coating the surface of the ZVI particles, preventing flow through the barrier due to this build-up. (Thiruvenkatachari et al., 2008) The iron reactivity could also be reduced if it comes into contact with silica or natural organic matter. (Thiruvenkatachari et al., 2008).

During the treatment of wastewater, the adsorbent becomes exhausted and loses its competence to further adsorb the pollutants. Different techniques like thermal, chemical, oxidation and electrochemical are used for the regeneration of exhausted adsorbent for further use in wastewater. This regeneration process also adds extra cost as well as lowers the adsorption efficiency. But the pollutant loaded iron nano particles can be desorbed using a very low concentration of base or acid, and desorbed iron nanoparticle have can be again used as adsorbents for removal and recovery of different pollutants from wastewater. Iron nanoparticles could be reused for more than two cycles without any appreciable changes in the original adsorption capacity. (Nassar, N. N. 2012). More over investigations need to be carried to find out the long term impact on environment. The risks associated such as influence of nano particle in flora and fauna is badly understood which has to be studied before the wide application as a tool of remediation (Nowack and Bucheli, 2007).

2.7 GROUNDWATER FLOW MODEL FOR LEACHATE TRANSPORT

Groundwater models are tools for understanding the aquifer system, its behaviour and prediction of its responses to a stress. Groundwater simulation plays major role in effectively managing groundwater resources and in the prediction of effective measure for its management. Groundwater flow model can be used (i) to understand the flow patterns and interpreting tool to investigate the dynamics of groundwater system; (ii) to predict the response of the system for stresses; (iii) an assessing tool which evaluate recharge of the aquifer, discharge from the aquifer and it storage and also to quantify sustainable yield; (iv) as a tool of prediction for forecasting conditions that may happen in the future or the effects of manmade activities; (v) a supportive tool to plan field survey, collection of data and for the design of solution which is practical; (vi) a managing tool to assess alternate policy and (vii) a conceptualising or visualising tool to communicate key message to the public and the decision-makers (Pathak et al., 2018).

A groundwater simulation model is replication of a groundwater system in a simplified way. It can be a physical model or mathematical model. The physical model demonstrates the physical processes while mathematical one represents the physical process and boundary conditions using governing equations which are usually solved with the help of computers. The simulation of hydraulic head , flow rates within the boundaries as well as across it, time taken to flow and estimation of water balance can be carried out using groundwater flow models. While a solute transport model provide an estimation of the concentration of solute dissolved in groundwater and its migration (Bear and Cheng, 2010)

A number of computer modelling software are available now a days for the application of various problems. Some of them are (i) MODFLOW -finite difference method for the simulation of flow under saturated conditions (ii) FEFFLOW -finite element method for the simulation of flow under saturated and unsaturated conditions, mass transport and heat transport (iii) SUTRA - open source finite element method for the simulation of flow under saturated and unsaturated conditions, mass transport and heat transport (iv) MT3DMS -Software that can be couple with MODFLOW that can simulate mass transport in groundwater (v) SEAWAT – open source that can be combined with MODFLOW and MT3DMS for simulation of saturated flow of solute transport (vi) PEST – Parameter estimation and uncertainty analysis software which is open source designed to estimate parameters of any models (vii) VISUAL MODFLOW – graphical user interphase supports many software such as MODFLOW, MODPATH, MT3DMS, SEAWAT, PEST (Kumar 2015).

MODFLOW is a commercial software which make use of finite difference methods for solving the governing equations of groundwater flow. Because of its user friendly features it is popular among hydro-geologists. The programming of MODFLOW is carried out in FORTRAN 77 language. The newest version of MODFLOW is

MODFLOW 2000 (Harbaugh et al., 2000). The simulation of groundwater flow under steady state and transient state can be performed by using MODFLOW (Guieger and Franz, 1996). To simulate groundwater the data such as hydrogeological, hydraulic parameters, the stresses like abstraction from wells, recharge due to precipitation, loss due to evapotranspiration, recharge or discharge to rivers and lakes, and groundwater head is required which is procured with the help of coupling GIS (Geographic Information System) with MODFLOW (Pathak et al., 2018). For heterogeneous aquifer, the parameters such hydraulic conductivities, storage coefficients which varies spatially can be assigned to the specific cells in the horizontal or vertical layer of cell which will replicate the anisotropic condition of aquifer. The simulation of aquifer can be done as confined or un-confined aquifer.

MT3DMS is solute transport software used to simulate the movement of solute in variably saturated, heterogeneous medium subjected to a variety of boundary conditions (D An et al., 2013, Srivastava and Ramanathan, 2018) with add-on reaction packages to address phenomenon such as advection, dispersion and chemical reaction. It is designed for working with any numerical flow model which is cell centred and it can model time dependent conditions of aquifer (Cecan and Schneiker, 2010). After calibration of groundwater flow model, information regarding the flow model is saved as an external file which is retrieved for solute transport model which saves memory of computer and time of execution (Shi et al., 2010). The structure of the model allows the simulation of processes like advection, dispersion of diffusion, chemical reaction and mixing of source or sink in a separate way without taking much space of computer memory. Further-more addition of new packages which involves other transport process is possible without modifying the code which readily exists (Zheng et al., 2012). The model calibration are carried out by adjusting the parameters such as hydraulic conductivity of aquifer, its storage properties, longitudinal and lateral dispersivities, and porosity manually or by optimising mathematically till the output matches satisfactorily with the field values (Zheng and Bennett, 2002). MT3DMS can be used as an efficient decision making tool to evaluate, mitigate or to manage contamination caused by various pollutants (Sathe et al., 2019).

2.7.1 Application of groundwater flow models for contaminant transport

Some relevant case studies are briefly presented under this section which evaluate the groundwater flow and contaminant transport.

i. Shang Gao et al., (2018) studied leakage from landfill located at Taihe City, China. The leakage of landfill leachate was getting diffused to area surrounding the landfill and slowly moving downwards and reaching the karst aquifer beneath. The simulation results shows that the concentration of pollutants is comparatively less and the migration of the pollutant in the horizontal direction after the expiry of service period was also found to be less. The migration in the vertical direction was also found to be less. The limitation of the study is that the researchers has not considered the biodegradation. Hence the result of the study shows that the impact of landfill is less on groundwater environment.
ii. For the proposal of remedial solution of a decommissioned landfill site Tainan City, Taiwan, simulation of groundwater contaminant transport was carried out by Chen et al., (2016). The information regarding hydro geology, precipitation were incorporated for the simulation of model. The spread of ammonia nitrogen and chloride was predicted for coming 10 year. It is evident from the results that of not only the soil and groundwater of landfill site is heavily polluted but also the nearby Hsuhsian creek is polluted. The spread of the pollutant is taking place in a faster way which will spread to the nearby river contamination the entire water system which is an irreversible change. Study suggest to take some remedial action to prevent the spread of contaminant.
iii. Singh et al., (2019) studied the possibility of virtual reactive barrier to remove chromium and iron generated from Bhalswa landfill, Delhi. The analysis focusses two virtual PRB modelling (i) selection of barrier (ii) analysis of different barrier and its impact with time. MODFLOW coupled with MT3DMS was used for the simulation of contaminant transport. The simulation results shows that funnel and gate performs better than continuous reactive barrier system. Higher the ratio of barrier and hydraulic conductivity larger contaminant plume pass through the aquifer which hence removal efficacy is

improved. Study suggest PBR as a better option for the remediation of aquifer nearby landfill site.

iv. D An et al., (2013) studied the transport of arsenic from an unregulated landfill which penetrated into aquifer and was migrating in the direction of groundwater flow. The study revealed that the plume is expanding with time. The possible remedial measures such as hardening of ground, providing leak-proof barrier, option of pumping and providing ditches for drainage were considered and the extent of contamination was studied. But the limitations found were (i) hardening of ground- the total contaminant were not decreasing by the control of contamination infiltration; (ii) pumping well – the remedial cost was found to be high (iii) leak proof barrier – for prolonged usage the effectiveness may be reduced and underlying aquifer will get contaminated (iv) drainage - it was a better remedial alternative but when large quantity of discharge water comes then the treatment cost will become high. Hence it was proposed to provide a combined method of hardening of ground with drainage ditches so that it can achieve profitable as well as efficient method of treatment.

v. In a study which assess the effect of landfill leachate located at Varanasi India, on the quality of groundwater, it is unfit for drinking and domestic purposes as per WHO and Bureau of Indian Standards. It was found that nitrate, phosphate, iron electrical conductivity and total dissolved solids were found to be more near the observation wells located near the landfill especially during post monsoon season. This indicates that the quality of the groundwater is significantly deteriorated due to the percolation of leachate. Simulation of groundwater indicates that the rise in hydraulic head during post monsoon season is the reason for the flow of the pollutant in the downward direction. The study suggest urgent attention to be given so as to minimise the impact of landfill on quality of groundwater. (Mishra et al., 2019)

vi. Varghese et al., (2015) made use of MT3DMS along with genetic algorithm for developing a tool which helps in tracking a polluter where information such as location or characteristics of the source of the pollution is not available. Hypothetical case was considered for the study and the results were found to be reliable for fixing accountability of contamination on pollution causing agent.

The results of the study shows that even with 2% error in observed data, the prediction can be accurately mage with an error of 8%.

vii. Ahmed et al., (2019) studied impacts of landfill in desert region with help of flow model MODFLOW and MT3DMS for finding the fate of heavy metal transport. The results fitted satisfactorily well with experimental values. The adopted model generated by MODFLOW and MT3DMS for the fate and transport of heavy metals from the surface into groundwater was fitted well with the experimental measurements. Sensitivity analysis results based on this match showed also clearly the influence of the studied parameters such as contact time and locations. The results indicated as the contact time and rate of pumping increases the safe distance to withdraw water from aquifer decreases. Hence in order to find out a safe distance to withdraw water from aquifer a simple mathematical equation was developed. Based on which the safe distance of the location of well was found to be 113 m from leachate collection centre.

2.8 LITERARURE GAP

In spite of extensive study in relation with groundwater contaminant transport by various researches, the process provide a wide scope of more studies in relation to the hydro-geology, climate and underlying formation of the study area. Even though several simulation studies has been conducted to know about the contaminant transport, seldom focussed on landfills located in unconfined coastal aquifer which receives lot of monsoon rains. The current study involved in the two distinguish areas are the development of groundwater flow model to find out the extent of contamination of groundwater due to landfill leachate and the possible remedial measure which can be applied so as to prevent the contamination from the landfill.

The present study has been undertaken by considering the following points indicating the research gap

- The dearth for a research to find the extent of groundwater contamination due to a landfill located on typical tropical shallow unconfined aquifer with underlying laterite layer which gets good monsoon rains with the help of groundwater flow model, MODFLOW and MT3DMS.

- The assessment of the application of starch coated nano iron as reactive media sandwiched between lateritic layers for the remediation of COD of leachate.
- The prediction of events that can occur in the anticipated future and the prediction of fate of contaminant when remedial alternatives are adopted.

From the previous studies it can be seen that intricate simulation studies has not been done in the study area, though many geophysical examination has been performed. The present study focuses on determination of extent of groundwater contamination on a typical tropical coastal aquifer due to a landfill located at Vamnjoor in Dakshina Kannada district, India with the help of groundwater flow model, MODFLOW and MT3DMS. The study analyses the possibility of starch coated nano iron as reactive barrier for the remediation of leachate and predicts the reduction in contaminant when the remedial alternative is adopted in the field.

CHAPTER 3

METHODOLOGY

3.1 GENERAL

Groundwater resource is precious and need to be conserved. It is necessary to curb water pollution by controlling the discharge from urban and agricultural areas which contributes nutrients and pathogens to water bodies (Yadav et al., 2019). Groundwater is affected by the leaching of organic and inorganic contaminants from the landfill. Generally landfills create lots of environmental problems like combustion of landfill gases, foul smell and leachate leakage. But the most severe of all the problem is the leakage of leachate from landfill which severely affects the surface and groundwater. A study has been conducted in order to assess the extent of contamination from the landfill at Vamanjoor and the possible remedial measure which can be adopted there so as to control the groundwater pollution. In order to find out the extent of contamination a preliminary survey has been undertaken such as finding out the number of abstraction well in the study area, measuring groundwater level and analysis of physic chemical parameters of groundwater on seasonal basis. The study then proceeded with the development of conceptual model of the groundwater flow using MODFLOW and contaminant transport using the software MT3DMS. For that the collection of various input parameters which include geology or topography of the area, hydrogeology of the area, boundary and initial conditions been done

3.2 OUTLINE OF RESEARCH WORK

In order to estimate the impact of leachate percolation on groundwater quality, various physic chemical properties were analysed in leachate and groundwater samples to understand possible link on groundwater contamination. A field survey was conducted to find out number of abstraction well in the study area and it was found that there are 68 abstraction well of which 23 were chosen as observation wells. On seasonal basis, the groundwater samples were collected from 23 observation wells around the landfill, and analyzed the water quality. The hydraulic head of the observation wells was measured seasonally so as to know the groundwater fluctuations.

Studies were conducted to find the feasibility of nano iron in the remediation of leachate. The leachate from landfill was collected and various physic chemical parameters were analyzed. As the physic chemical parameters of the leachate changes with time, synthetic leachate of known COD was prepared in laboratory. By conducting batch experiments in the laboratory, the condition most favorable for the reduction of COD from synthetic leachate was determined. Depending on the outcomes of batch experiments, continuous fixed-bed adsorption studies were carried out using nano iron particle sandwiched between untreated natural laterite soil so as to find the removal efficiency of COD from synthetic leachate. The analysis of isotherms and the kinetics of the reactions were studied.

The various steps involved in the simulation of the model are represented in the flow chart below (figure 3.1) In order to create digital elevation model (DEM), the toposheets 48/L/13/NE and No 48/L/13/NW with contour interval 1: 25000 were obtained from Geological survey of India and considered. The boundaries of study area and drainage network were delineated using ARC GIS (version 9.3). The various data inputs like meteorological data, the geology of the site were obtained from various government agencies. The data regarding aquifer characterization such as pumping test were taken from the earlier researches conducted in the study area. Initially the program MODFLOW is run and then the transport parameters were given to run MT3DMS model. The calibration was performed by using the observed level of water as well as the data obtained on the water quality analysis from the study area. The validation of model was then carried out and the model was used to predict the (i) scenario to find the current contamination level (ii) scenario to find the contamination spread in another 15 years (iii) scenario where the spread of contaminant for maximum rainfall (iv) scenario when the reactive barrier of nano iron is installed around the landfill and predicted the concentration of COD transported from landfill.

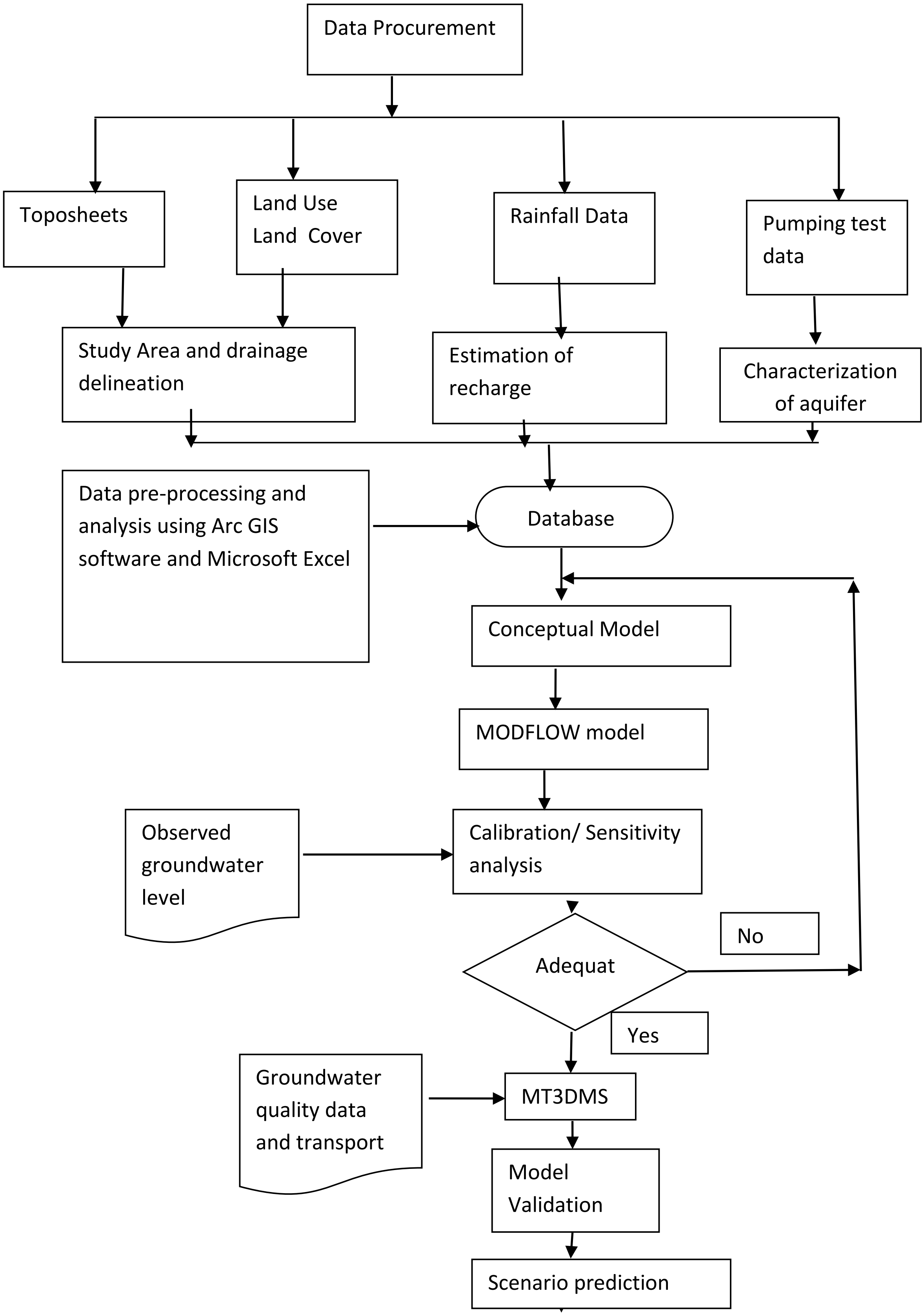


Figure 3.1 Methodology adopted for the simulation of model

3.3 DATA COLLECTION

The water level as well as water quality analysis of 23 observation wells located around the landfill were conducted on seasonal basis and were compared with the data obtained from Government agencies. In the present study, the groundwater level data from the year 2000 to 2018 was procured in person from Central Groundwater Board, Zila panchayath office complex. The last 15 years water quality data on a fortnightly basis maintained by Karnataka Pollution Control Board was procured personally. The rainfall data maintained by the meteorological station located at Mangaluru International Airport was collected personally which included daily rainfall data from years 2000 to 2018. In order to have a proper knowledge of hydrogeology of site and information of watershed, the data of the previous researches done in the study area is also taken into consideration while developing conceptual model (Lathashri, 2018; Honnanagoudar, 2015).

3.4 HYDROGEOLOGY

The significant hydraulic characteristics of the aquifer are hydraulic conductivity of the aquifer, its transmissivity and specific yield. The hydraulic conductivity is defined as the quantity of the fluid flowing per unit cross sectional area in unit gradient and is expressed in m / day. Transmissivity is the rate of flow of water through vertical strip of aquifer under a unit hydraulic gradient which extends through the saturated thickness of aquifer. It is expressed as m^2 / day. The specific yield for unconfined aquifer is the effective porosity of the aquifer. From the pumping test data conducted in the study area for the previous researches, the transmissivity was obtained in the range of 210 to 250 m /day, hydraulic conductivity of range 1.85 m / day to 49.5 m / day, the specific yield was ranging between 0.6% to 21% (Honnanagoudar, 2015, Lathashri, 2018)

3.5 WELL INVENTORY

In order to understand the behaviour of fluctuation in groundwater level and its depth to water table well inventory studies have been carried out in the study area. A local survey was conducted to find the number of wells in the area. Total number of 68 abstraction wells were discovered which is included in the development of conceptual model in MODFLOW which influences the groundwater level of the sub-basin. Of the 68 abstraction wells in the study area, 23 were chosen as observation wells (figure 3.2). Table 3.1 provides the location of the observation wells of the study area. The water level was measured and the groundwater was collected for the analysis of various physiochemical parameters on seasonal basis (post monsoon during October 2016, pre monsoon May 2017 and May 2018). The main factors which control the groundwater head in the study area are geological formations of the area, the physiography, the rainfall of the region and the abstraction of groundwater for utilizing it for domestic as well as agricultural purposes. The water level data of the observation well measured by groundwater department was considered for the validation studies. Also the fortnightly water quality tests conducted by Karnataka Pollution Control Board for the observation well was collected personally considered for the current study.

Table 3.1 Location and depth of water level of observation wells taken on October 2016

Well No	Location		Elevation of Water Head from ground level (m)	Well depth (m)
	Latitude	Longitude		
1	12°55'48"	74°53'11"	10.7	8.67
2	12°54'42"	74°53'10"	7.8	6.24
3	12°54'46"	74°53'28"	6.8	7.35
4	12°54'59"	74°53'41"	7.9	9.21
5	12°54'58"	74°53'11"	6.4	4.25
6	12°54'51"	74°52'51"	7.9	9.4
7	12°55'6"	74°52'32"	7.9	10.1
8	12°55'8"	74°52'46"	8.1	6.75
9	12°55'12"	74°53'37"	7.8	8.38
10	12°55'26"	74°53'41"	6.3	4.3
11	12°55'48"	74°53'11"	6.2	5.76
12	12°56'10"	74°52'48"	6.9	8.0
13	12°56'9"	74°53'1"	7.1	9.2
14	12°55'57"	74°52'50"	9.7	8.4

15	12°55'42"	74 °52'46"	9.8	6.9
16	12°55'27"	74 °52'49"	8.5	9.8
17	12°55'19"	74 °52'49"	8.1	10.4
18	12°55'43"	74°53'12"	7.9	8.2
19	12°56'12"	74 °53'9"	8.4	8.9
20	12°55'49"	74°52'45"	9.9	10.6
21	12°55'29"	74°53'49"	6.9	7.8
22	12°55'10"	74°52'39"	8.5	7.9
23	12°55'37"	74°52'34"	10.1	11.4

Groundwater quality analysis

Water samples were collected from the 23 observation wells of the sub-basin for detailed quality analysis. After immediate collection of samples, pH, temperature and electrical conductance were measured by using portable meters. For the analysis of other parameters, the samples were taken to the laboratory in polyethylene cans. The cans were rinsed before sampling and were tightly sealed and labeled after collecting the water samples. Samples were collected after the pumps were started for 5 to 10 minutes. The laboratory analysis was done without much delay to analyze various relevant physico-chemical parameters as prescribed by APHA 1994 methods. All the experiments were carried out thrice so as to reduce the error and found that the results can be reproducible with $\pm$ 3 % error. From the water quality analysis it is seen that water sample near the landfill is polluted while the wells which are away from the landfill are not much contaminated. The level of contamination is high during the post monsoon period which may be due to more amount of infiltrated water which transports the contaminant plume to distant wells.

The various physico-chemical parameters analysed includes pH, chlorides, total dissolved solids, Chemical oxygen demand (COD), and conductivity are represented graphically. The pH was in the range of 5.5 to 7.8 as shown in figure 3.3. Though the water samples taken away from the landfill are neutral the one which is near the landfill showed acidic

The electrical conductivity is defined as the measure of dissolved salts in water. It was found to be high in the wells in the vicinity of the landfill (figure 3.4). The total dissolved solid (TDS) provides information on the quality of water or its salinity. The range falls between 200 mg / l to 700 mg / l. The high chloride level can be seen in the wells near the landfill which may be due to the leaching of leachate from the landfill. (Figure 3.5) The salinity in the wells near the river also is high which may be due to the intrusion of the sea water during summer. High TDS is an indicator of groundwater pollution near the dumping sites (Olaniya and Saxena 1977). The TDS was found to be high for the groundwater in the observation wells near the landfill (figure 3.6). The consumption of water with high concentration of TDS can cause gastrointestinal problems in humans (WHO, 1997).

Chemical Oxygen Demand (COD) determines oxygen required by the organic matter for its oxidation and it gives an index on pollution. The high COD value in the sample near the landfill indicates the presence of organic contaminant in the water sample as shown figure 3.7.

Chloride concentration is taken as an index of pollution and hence it can be taken as a tracer for contamination of groundwater. The chloride concentration was found to be high in the groundwater sample High concentration of chloride can be due to domestic effluent fertilizers which are injurious to human as it can cause heart disease and kidney disorders (WHO, 1997).

From the physico-chemical analysis of various parameter it can be concluded that the groundwater in the vicinity of the landfill is polluted and the extent of pollution can be found with the help of groundwater flow models which is discussed in detail in the following chapters.

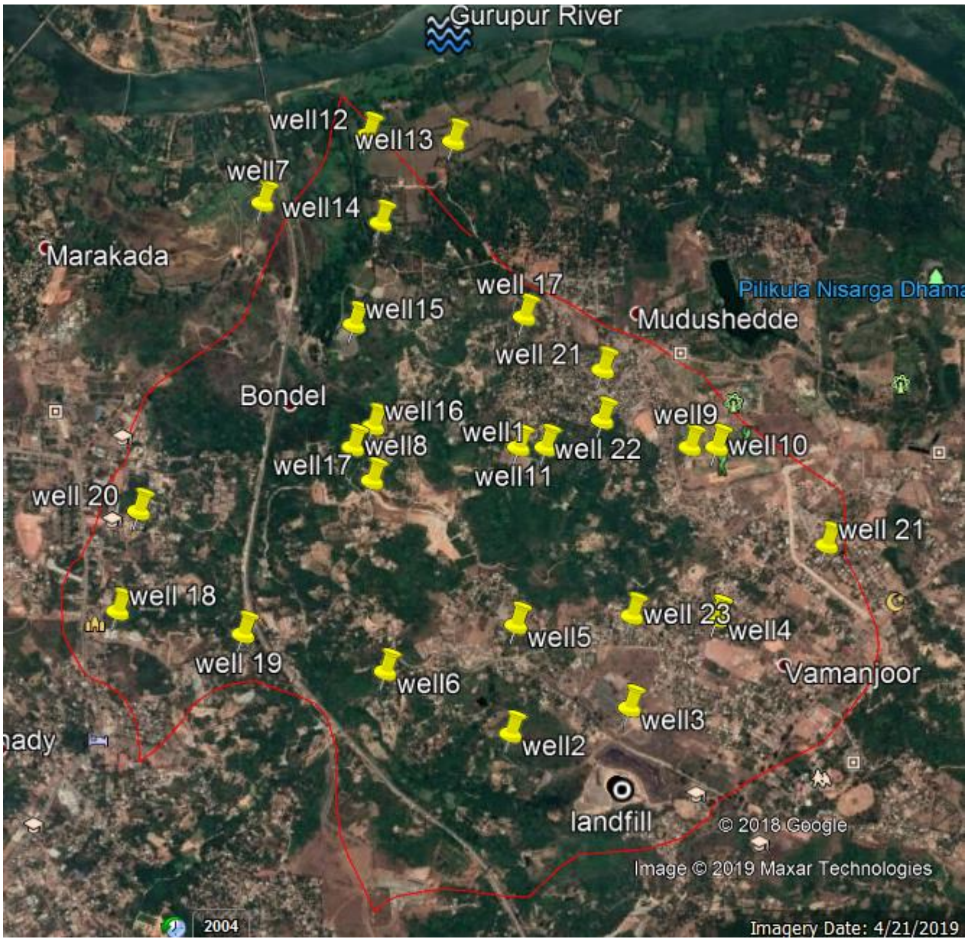


Figure 3.2 Google earth image showing the location of observation wells, landfill, Gurupur river at Vamanjoor

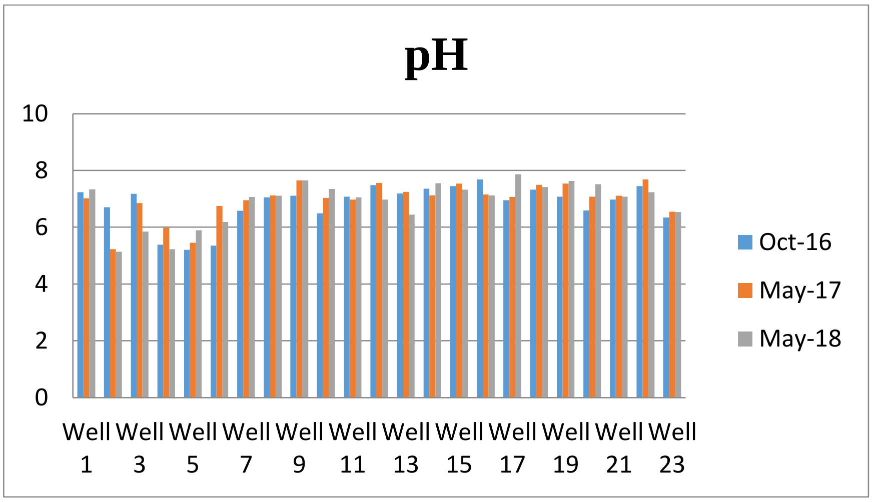


Figure 3.3 pH level of water in observation wells during October 2016 (post monsoon season) May 2017 (pre monsoon) May 2018 (pre monsoon)

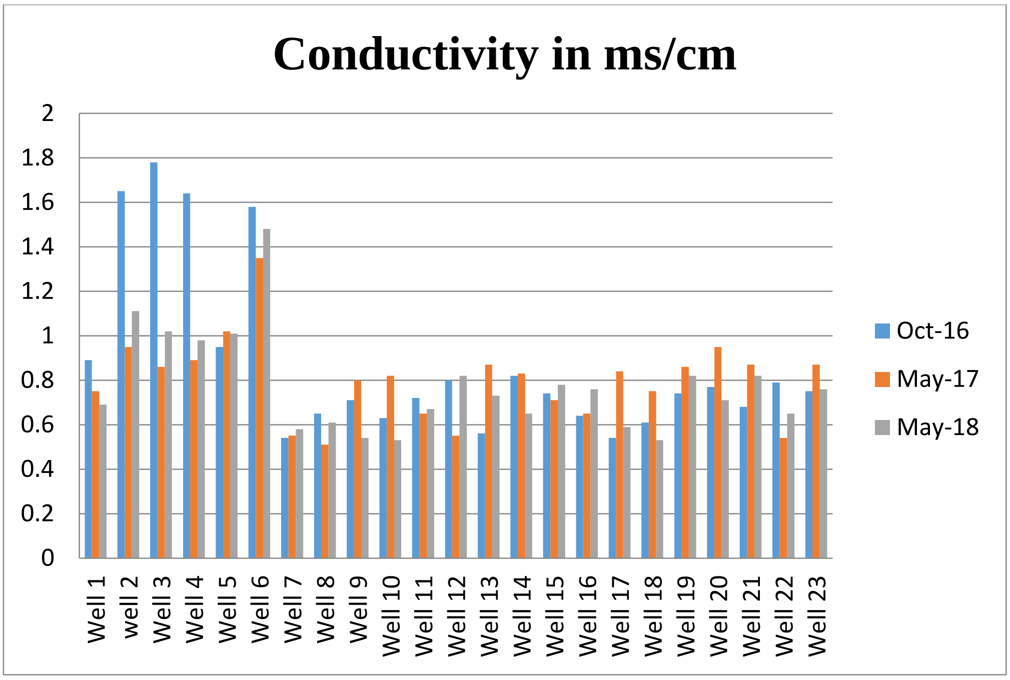


Figure 3.4 Conductivity of groundwater in observation wells during October 2016 (post monsoon season) May 2017 (pre monsoon) May 2018 (pre monsoon)

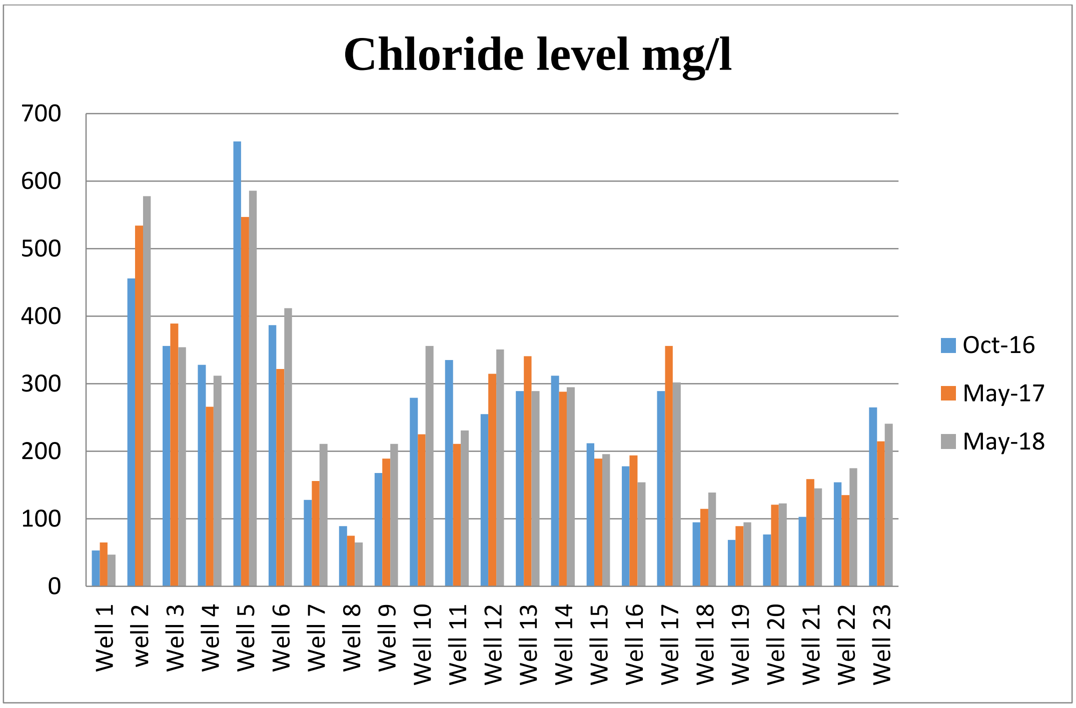


Figure 3.5 Chloride level of groundwater in observation wells during October 2016 (post monsoon season) May 2017 (pre monsoon) May 2018 (pre monsoon)

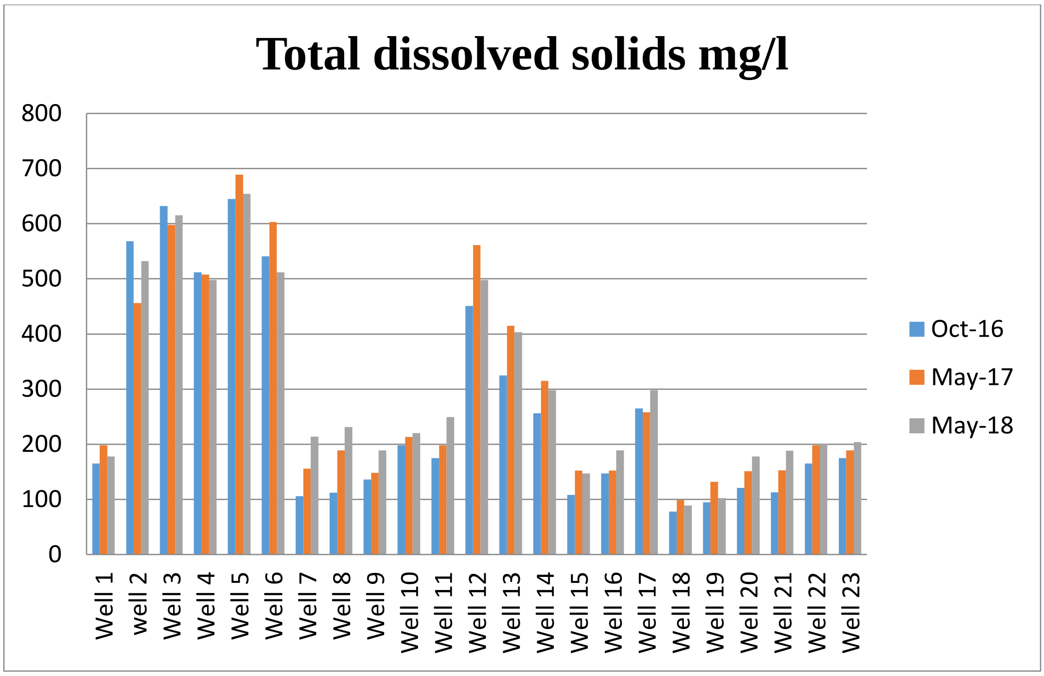


Figure 3.6 Total dissolved solid level of groundwater in observation wells during October 2016 (post monsoon season) May 2017 (pre monsoon) May 2018 (pre monsoon)

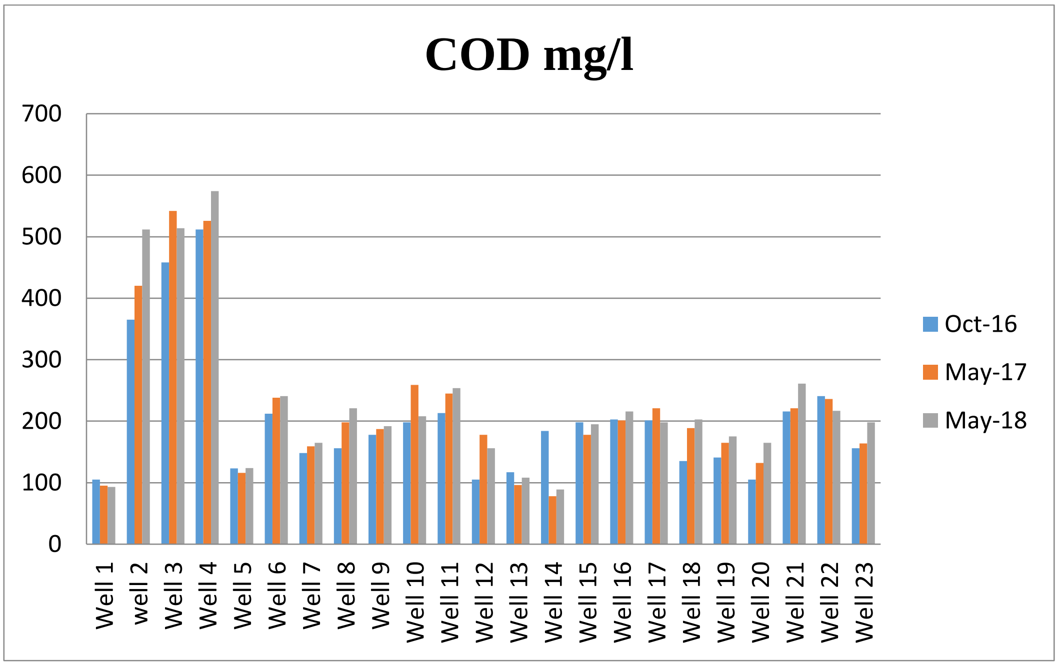


Figure 3.7 COD level of groundwater in observation wells during October 2016 (post monsoon season) May 2017 (pre monsoon) May 2018 (pre monsoon)

3.6 CLOSURE

Before developing a conceptual model it is necessary to have knowledge about the site and the studies conducted in the area. A detailed study about the geology, hydrogeology, location of wells as well as the quality of the groundwater of the area is examined. From the previous studies it was understood that the aquifer beneath is an unconfined shallow one with hydraulic parameters such as transmissivity varies between 210 to 250 m /day, hydraulic conductivity - 1.85 m / day to 49.5 m / day, and specific yield - 0.6% to 21%. A local survey was conducted to know the location of abstraction wells and found 68 observation wells from which 23 were chosen as observation wells. The water level head was measured for pre monsoon and post monsoon period and also the water quality was analysed. The results of the analysis suggest that the wells near the landfill are contaminated with the landfill as point source from where contaminants are continuously injected.

CHAPTER 4

LEACHATE CHARACTERIZATION AND TREATMENT

4.1 GENERAL

Sanitary landfilling method is widely accepted for disposing solid waste because of its economic benefits. Compared to various solid wastes management method such as composting or incinerating, disposal of waste in landfill is found to be cheapest in capital charge. But the main disadvantage is that it generates heavily polluted leachate which varies both in volumetric inflow and in its chemical compositions. Leachate mainly contains humic acid, heavy metals, biogas which mainly contain methane, carbon dioxide, non methane gases which results in bad odour, can cause explosion, can be a reason for global warming also effects the health of the population. (Kjeldsen et al., 2002; Regadío et al., 2013, Barlaz et al., 2002). The stabilization period is long for the leachate because composition of waste is heterogeneous, the anaerobic process which is slow in nature and also conditions prevailing in the site such as the water content, the climatic conditions the geology of the site (Barlaz et al., 2002). The various toxicity analysis conducted for the leachate confirms the need for the treatment of same so that the specific standards are met before disposal.

4.2 VAMANJOOR LANDFILL

Due to improved lifestyle and the immense growth in industrial and commercial sectors Mangaluru is experiencing a surge in human population in the past decade which results in increase in production of solid wastes. The Mangaluru city corporation collects nearly 200 Tons of solid waste on daily basis and dumping it in the municipal landfill located at a distance of 8.5 km from city centre (Figure 4.1). The collected waste are source separated waste which means the biodegradable waste is excluded at the source itself and only non-biodegradable waste is being brought to the landfill where it is sorted again. The fractions which contains glass, metals, paper or cardboard waste which can be recycled is removed and the rest of the waste is deposited in the landfill. Manual and mechanical sorting is being employed here to separate the recyclable waste.

Figure 4.1 Vamanjoor landfill

Vamanjoor being located along national highway, many educational institutes as well as residential homes and quarters are located there. The google earth image of the sub-basin where landfill is located is shown in figure. 4.2. Mainly the domestic waste such as that from houses, markets, slaughter houses and industries are being dumped in this landfill.

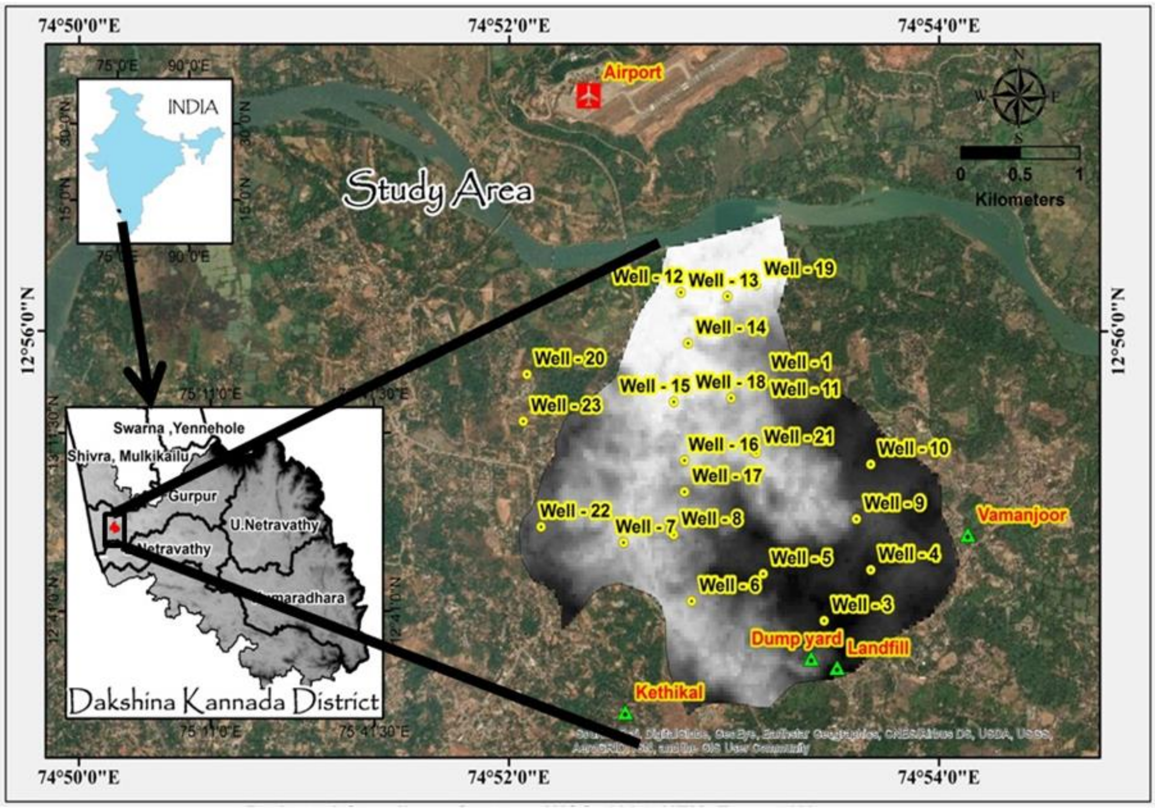


Figure 4.2 Google earth image of the sub-basin where landfill is located

Since 1980s the landfill at Vamanjoor is reported as a main source of air as well as groundwater pollution. It is reported that aftermath a heavy rainfall during August 2019, the sliding of garbage from landfill took place, drowning a part of a village called Mandara near landfill destructing around 10 acres of land and nearly 25 houses (figure 4.3). The landfill has got a bottom liner but the system to collect the leachate formed at the bottom of landfill is poorly managed. And hence the leachate reaches the nearby environment contaminating the aquifer beneath. It is severe peculiarly during monsoon as the water in the wells in the nearby location turns into black and bad odour comes which leads to various illnesses for the nearby residents. Thus it is necessary to have an understanding about the trail of contaminant and feasible remedial measure which can be adopted so as to control the contamination.

Figure 4.3 Garbage slide at Mandara a village near landfill

4.3LEACHATE SAMPLING AND ANALYSIS

The leachate samples were collected during the month of October 2016 from the bottom of Vamanjoor landfill in polythene cans which was properly washed. The sample were analysed for basic constitutes and properties such as pH, temperature, conductivity in the field itself. Immediately thereafter, the samples were cooled to 4°C and transferred to the laboratory for determination of the parameters viz pH, Electrical Conductivity, Total Dissolved Solids, Chemical Oxygen Demand, Nitrate, Nitrite, Ammonia – Nitrogen, Sulphates, Chlorides, Phosphate, Iron, Sodium, Potassium, Total Organic Carbon, zinc, nickel, and various volatile fatty acid. The various physico-chemical parameters of the leachate were analysed as per APHA standards and presented in the table 4.1. The pH of the leachate collected was alkaline which represent the biological stabilization of organic compound present in leachate. (Fatta et al., 1999). The high concentration of electrical conductivity and total dissolved solids shows the presence of inorganic compounds mainly anions and dissolved salts. The concentration of chloride was very high that give justification for the high value of total dissolved solids and Chemical oxygen demand (Motling et al., 2013). High value of sulphate may be due to various inorganic wastes present in the leachate. The source of phosphate may be from the domestic waste, fertilizers, detergents, water from industries and so on. The ammonia nitrogen might have released due to the anerobic and aerobic degradation of solid waste. As the waste is sorted before dumping into the landfill, traces of heavy metals were found to be less except for iron zinc and nickel (Maiti et al., 2016). The chemical oxygen value was found to be high which indicated large concentration of biodegradable organic as well as inorganic compounds. Generally for stabilized leachate COD ranges between 5000 mg/l to 20000 mg/l, hence the collected leachate is considered as a stable one. (Li and Zhao, 2002)

Table 4.1 Characterization of leachate

Sl. no	Parameter	Value	Unit	Permissible limit	Process
1	pH	8.02		6.5- 8.5	Instrumental method by using digital pH meter
2	Electrical Conductivity	15.89	m S	-	Instrumental method by using electrical conductivity meter Conductivity meter
3	Total Dissolved Solids	9260.00	mg/l	500	Oven drying method (APHA 2005, Method 2540C)
4	Chemical Oxygen Demand	14500.0	mg/l	-	Closed reflux method(APHA 2000, Method 5220C)
5	Nitrate	35.50	mg/l	45	Ultraviolet Spectrometric Screening Method (EPA method 352.1)

6	Nitrite	6.98	mg/l	-	Ultraviolet Spectrometric Screening Method (EPA method 352.1)
7	Ammonia – Nitrogen	2038.00	mg/l	50	Nesslerisation Method (IS3025(part 34)-1988)
8	Sulphates	36.00	mg/l	200	Turbidimetric method (IS :3025(Part 24)-2003)
9	Chlorides	6000.00	mg/l	1000	MOHR'S METHOD titrationg with silver chloride (IS:3025(Part 32)-2003)
10	Phosphate	12.60	mg/l		Stannous Chloride Method(APHA, Method 4500P)
11	Iron	4.50	mg/l	3	Colorimetric method
12	Sodium	3345.00	mg/l		flame photometry
13	Potassium	1947.00	mg/l		flame photometry
14	Total Organic Carbon	6000.00	ppm		TOC ANALYSER
15	Zinc	0.3	mg/l	15	Heavy metal analyser
16	Nickel	0.17	mg/l	3	Heavy metal analyser
17	Volatile Fatty Acid				GAS CHROMATOGRAPHY
	Acetic Acid	29.29	%		
	Propionic Acid	51.20	%		

	Isobutryic Acid	1.16	%		
	Butyric Acid	1.35	%		
	Isovaleric Acid	4.25	%		
	Valeric Acid	2.70	%		
	Isocaprioc Acid	2.75	%		
	Hexanoic Acid	3.63	%		
	n-Heptanoic Acid	3.20	%		

4.4 PREPARATION OF SYNTHETIC LEACHATE

The sample of leachate contains various components organic and inorganic and it degrades with time. The leachate from the site is highly unstable and the physical and chemical properties will change with time. In order to avoid such as situation, synthetic leachate samples are prepared in the laboratory. The apparatus and the instruments used for the experiment were washed with nitric acid and washed thoroughly and rinsed with distilled water. Then the apparatus were dried. The waste water composition is supposed to approximate the composition of municipal waste water and had a wide range of different carbon sources (Renou, 2008). The preparation of synthetic leachate for the study area has been adopted from the previous studies. (Azar et. al. 2011)The major components include Acetic acid (7ml), Propionic acid (5ml), Pentanoic acid and Hexanoic acid (1ml), $MgSO_4$ (156mg), $CaCl_2$ (2882mg), Na_2CO_3 and $NaHCO_3$ (324mg, 3012mg) NaCl (1440mg), $CuCl_2$ (40mg), $(NH_4)_2CuSO_46H_2O$ (2000mg), $BaCl_2$ $2H_2O$ (50mg), $MnSO_44H_2O$ (500mg), Sulphuric acid 96% and Distilled water to make it to 1l as final Volume. Synthesis of reagents and sample preparation was done with de ionized water. The chemicals used were of analytical reagent grade. For weighing the chemicals high precision electrical weighing meter was employed. Mechanical shaking device was used for shaking. The de ionized water was examined for iron concentration before starting the experiment and was found under detectable level.

4.5 SYNTHESIS OF NANO IRON

The synthesis of nano iron was prepared as per previous studies (Alidokht et al., 2011). Solution of 0.15 M $NaBH_4$ was added slowly at a rate of 1 to 2 ml / min into 0.1 M $FeCl_3.6H_2O$ aqueous solution at room temperature and vigorously stirred at 400 rpm). During this reaction, ferric ions were reduced into black particles by sodium boro hydride as the reductant. The black precipitates were filtered and then washed with deionised water. Previous studies have indicated that nano iron particles aggregate quickly, which decreases the surface area for reaction and also limiting mobility. (Li et. al. 2006) To control nano particle agglomeration, various particle stabilizing strategies have been reported. In that surface modification with surfactant is one of the most important approaches. Surfactants, such as starch, could be coated on existing nano iron particles in a post-synthesis process; or synthesizing nano iron in the presence of polymer in a pre-synthesis process. The post-synthesis stabilization approach has been shown to decrease reactivity whereas the pre-synthesis approach has improved reactivity and significantly increased surface area. In the present study, nano iron was stabilized by starch in a pre-synthesis process as starch is a nontoxic, biodegradable, and inexpensive substance that can be used as an effective dispersant for iron nanoparticles. The surface morphology was determined with the help of scanning electron microscope. The image from scanning electron microscope of synthesized nanoparticle without and with starch is shown in the figure (4.4) and figure (4.5) respectively.

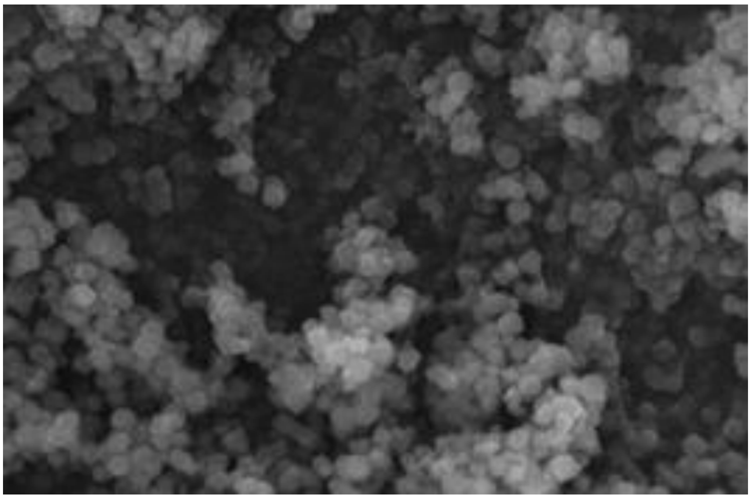


Figure 4.4 SEM image of nano iron

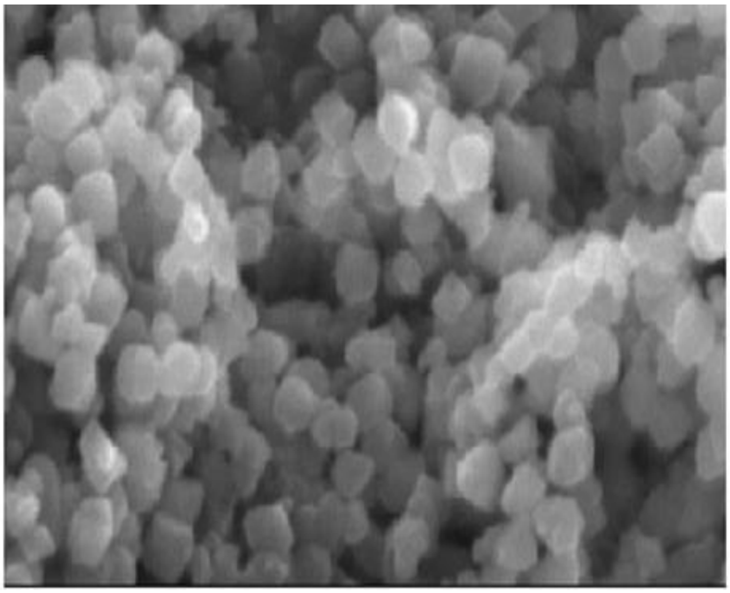


Figure 4.5 SEM image of nano iron coated with starch

4.6 BATCH EXPERIMENTS

The batch experiments were conducted so as to know the efficiency of iron nano particle for the removal of COD from the synthetic leachate. The test was done so as to find the finest condition for columns tests. In addition, useful information could be obtained about the effect of some key parameters. The important factors such as pH, initial adsorbent dosage were analyzed for their optimum dosages. The effects of several main variables were investigated in batch tests, one parameter changed while others were kept constant. Batch experiments were carried out in sealed flasks at room temperature. Predefined quantity of nano iron (0 – 10 mg/l) was added to the synthetic leachate of known initial COD (approximately 6000 mg/l) and the suspension was stirred in a horizontal mechanical shaker shaking at a speed of around 400 rpm (figure 4.6). Aliquots of the samples were taken at certain time intervals and analyzed for COD immediately. All experiments were conducted in duplicate and the results were averaged. The removal efficiency can be defined as difference of final concentration and the initial concentration to initial concentration of COD.

Figure 4.6 Experimental set up for finding optimum condition for the removal of COD

4.7 EFFECT OF SOLUTION pH

Generally, pH of solution is an important factor for the removal of contaminant by nano iron. pH of solution was adjusted by adding Hydrochloric acid or sodium hydroxide. Figure 4.7 presents the results of batch experiments in which known quantity of nano iron is added to synthetic leachate of known initial COD with different pH values. At pH <4.0 or >6.0 after 60 min, less COD was degraded, while more than 50% removal efficiency was obtained after 60 min at pH 5. The results suggest that rapid reduction of COD occurred when pH less than 6, and adsorption was optimized by adjusting the pH greater than 4. Thus, it can be concluded that pH around 5 favours for COD removal by nano iron is mostly because of Van der waals and non-ionic force which exist be leachate and sorbent.

It is clear that starch-stabilized iron nano particles show better removal efficiency (~60%) than that one which is not coated with starch in 60 min of reaction (figure 4.8). It was observed that nano iron nano particles stabilized by starch could maintain a good state of dispersion in the solution resulting in higher removal efficiency rather than non stabilized particles. At higher pH, the magnetite surface becomes negatively charged leading to enhance the electrostatic repulsion between magnetite and various anions, and thus the removal efficiency is reduced. Here removal rate was high at lower pH values and decreases as pH increases, because, in the acidic condition, the accelerated nano iron corrosion enhances the reaction rate

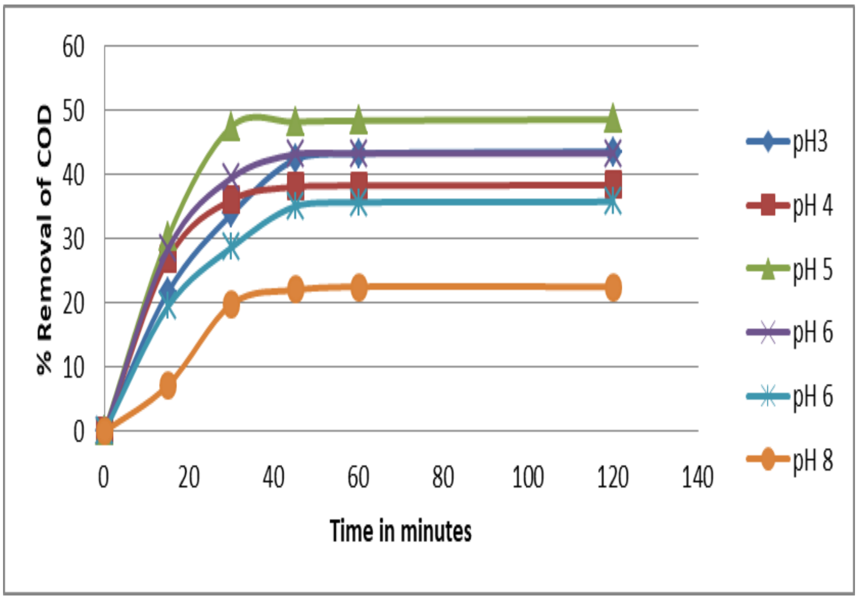


Figure 4.7 Effect of pH on percentage removal of COD when treated with nano iron

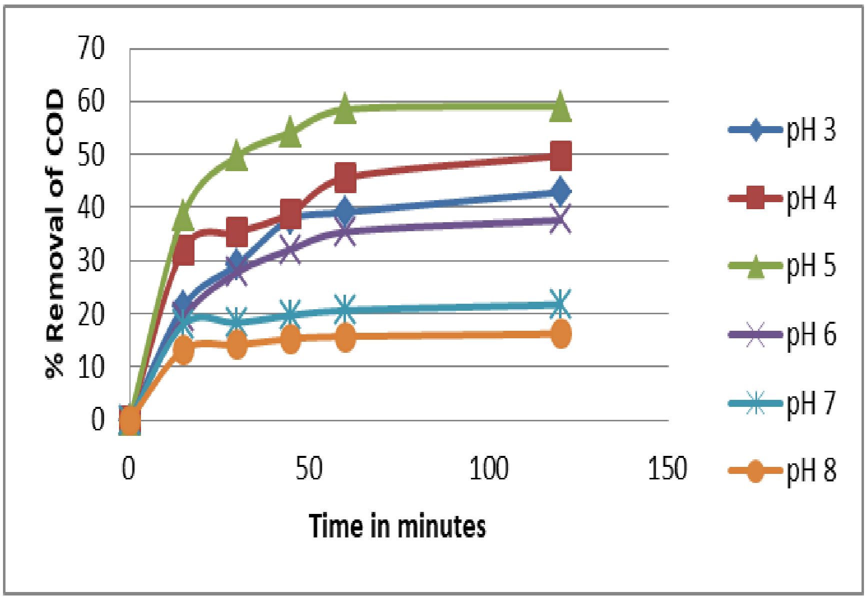


Figure 4.8 Effect of pH on percentage removal of COD when treated with nano iron coated with starch

4.8 COLUMN STUDY

A continuous fixed-bed adsorption study was carried out with a perspex column (internal diameter 5.5 cm, length 30 cm). The experimental set up is shown as figure 4.9. Untreated natural laterite of 0.425 mm average diameter particles was selected from a site near the landfill as column sorbent material. The bed depth of about 25cm was selected for the fixed-bed adsorption of COD. The bed was supported on a strainer. The inlet which feed synthetic leachate solution of known COD of constant flow rate of 10m/day was regulated using an infusion set. The initial pH at 5 was introduced. The flow through the column was continuous. All of the experiments were carried out at room temperature and atmospheric pressure. Samples were collected at regular intervals of time from the outlet and analysed for COD and iron content.

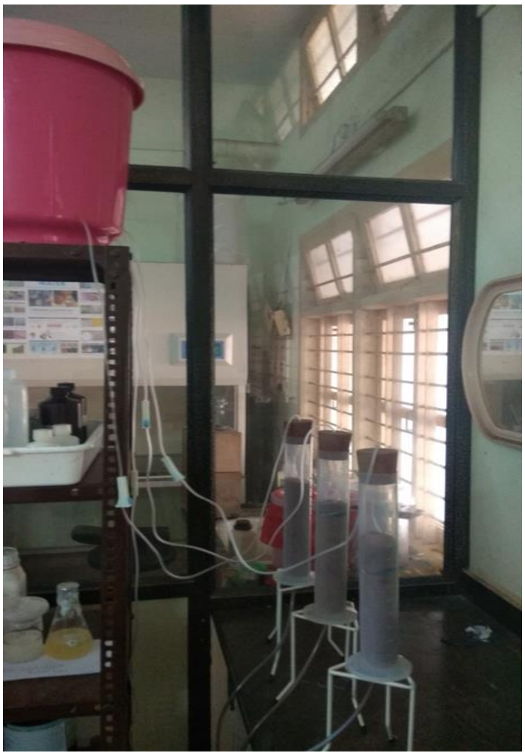


Figure 4.9 Experimental Setup for the fixed-bed adsorption study

The column study was planned based on the results of the batch experiments. The nano iron is kept between two filter papers at a depth of 5 cm from the top of the column and then lateritic soil is placed at the top of it in order to hold nano particle in position. The treatment is carried out in 5 initial loading of nano iron of 0.1, 0.25, 0.5, 1 and 2mg/l, and experiments were conducted in bench-scale model. The synthetic leachate of known COD was allowed to pass through the column in down flow mode under gravity. Other conditions such as seepage velocity were taken as 10 m/d and pH 5 were kept constant. The flow rate was so chosen that sufficient amount of effluent will be got per hour for experimental purposes. The initial COD level of synthetic leachate is nearly 6000 mg/l. Better removal efficiency (~68%) was obtained in continuous fixed-bed with laterite soil which may be due to the adsorption of contaminants by laterite soil.

An effort was done to find out the adsorption capacity of laterite soil alone. Similar column bed studies have been conducted to know about adsorption capacity of lateritic soil. The column was packed with laterite soil alone. Synthetic leachate of known Chemical oxygen demand (COD) was allowed to flow through the column filled with lateritic soil. The COD of the effluent was found. The COD removal efficiency of laterite alone was found to be 12%. COD was quantified by using closed reflux method.

4.9 ADSORPTION ISOTHERMS

Freundlich and Langmuir isotherms explain the distribution or the arrangement of adsorbate in between the adsorbent in a particular temperature at equilibrium. These are the most widely used models. Langmuir isotherm is derived on the assumption that the adsorption is maximum when a layer of uni molecular adsorbate covers the surface and the Freundlich is simply empirical. From the analysis of adsorption isotherm, the behavior of adsorbent can be examined in a systematic way. In order to evaluate the outcomes of the experiment, the results of experiment were applied to the linear form of Freundlich and Langmuir isotherms. The study was performed with concentration of adsorbent varying. The equation for the adsorbate which is adsorbed during equilibrium at a particular temperature will follow the equations below

$$\frac{1}{q} = \frac{1}{Q_{max}} + \frac{1}{bQ_{max}}\left(\frac{1}{C}\right) \qquad \text{.....(4.1)}$$

And Freundlich isotherm as

$$\ln q = \ln k_f + \frac{1}{n}\ln C \qquad \text{.....(4.2)}$$

Where q_e = amount of adsorbate adsorbed /unit mass of adsorbent

b = adsorption constant

*C*e = equilibrium concentration of adsorbate in mg/L,

*Q*max = the maximum adsorption capacity in mg/g

n = adsorption intensity

*k*f = adsorption capacity which depends on adsorbent and adsorbate

Linearized Freundlich isotherm was plotted with log C on x axis and log q on y axis (figure 4.10) and to know sorption pattern over reactive surfaces and the equation was obtained as log q = 0.7029 (log c) + 1.3455 with R^2 =0.945.

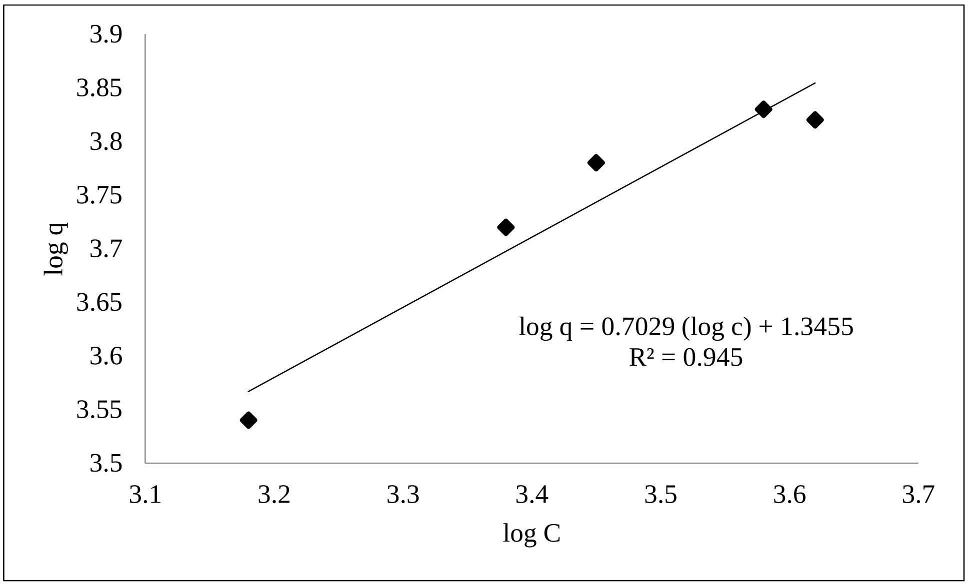


Figure 4.10 Freundlich Isotherm for the adsorption of COD using iron nanoparticle

Langmuir isotherm was plotted with 1/q on x axis and 1/c on y axis (figure 4.11) and the equation was obtained as 1/q = 1.880 (1/c) + 4.808 and R^2 0.96. The Qmax which is the maximum adsorption was found to be 0.208 mg / g.

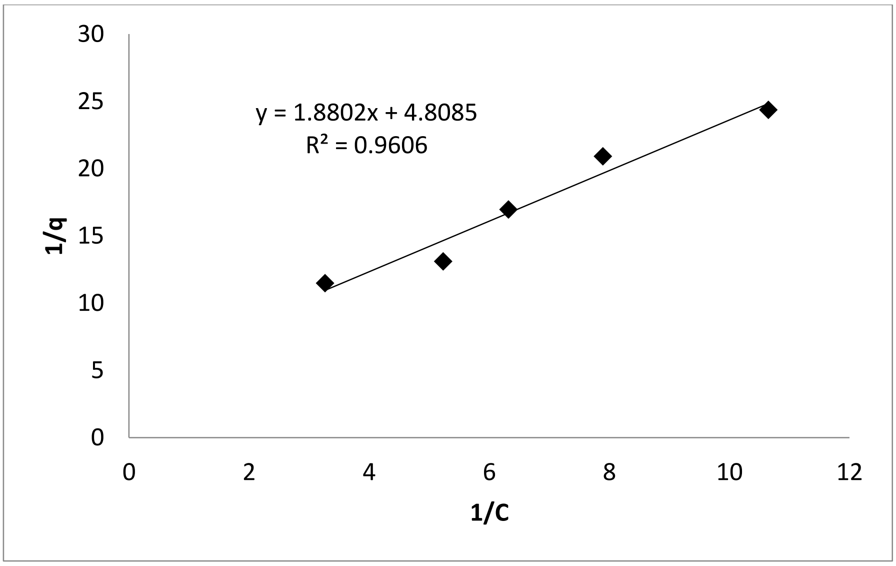


Figure 4.11 Langmuir Isotherm for the adsorption of COD using iron nanoparticle

In order to get a proper understanding of the type of mechanism, the data is applied to Dubinin Radushkevich isotherm model

$\ln Q = \ln Q_m - k\varepsilon^2$……………………………………….(4.3)

Where ε is given by

$\varepsilon = RT \ln [\ 1 + (\frac{1}{C_e})]$…………………………………………(4.4).

Where R universal gas constant

T temperature in Kelvin

Ce equilibrium concentration of adosrbate in ppm

Qm adsorbtion capacity

Q quantity of adsorbent adsorbed.

D-R isotherm was drawn with ln Q on y axis against ε^2 on x axis. (figure 4.12). The constant k and Qm are given by the slope and y intercept of the graph. The k was obtained as 0.093 $mol^2\ kJ^{-2}$ and Qm was got as 0.053mg/g. The free energy variation when one mole of ion is getting transferred to the solid surface from the solution known as mean free energy adsorption (E) and is calculated as

$E = -\ (2k)^{-0..5}$……………………(4.5)

The value of E determines the type of adsorption. The magnitude of E if it is in between 8 and 16, then adsorption takes place due to ion exchange and if it is less than 8 then the adsorption type is physisorption. Here the value of E we got as 2.3 hence it indicate that the adsorption phenomenon is physical.

The efficiency of adsorption is predicted by determining the parameter R_L

$R_L = \frac{1}{(1+bC_0)}$…………..(4.6)

Where $C_{0,}$ the initial concentration and b, the Langmuir isotherm constant.

For adsorption to be favorable, the value of R_L has to be less than 1. And those which is more than 1 it unfavorable for adsorption. In this case the value we obtained is 0.324 which is less than 1. Hence it is favorable for adsorption.

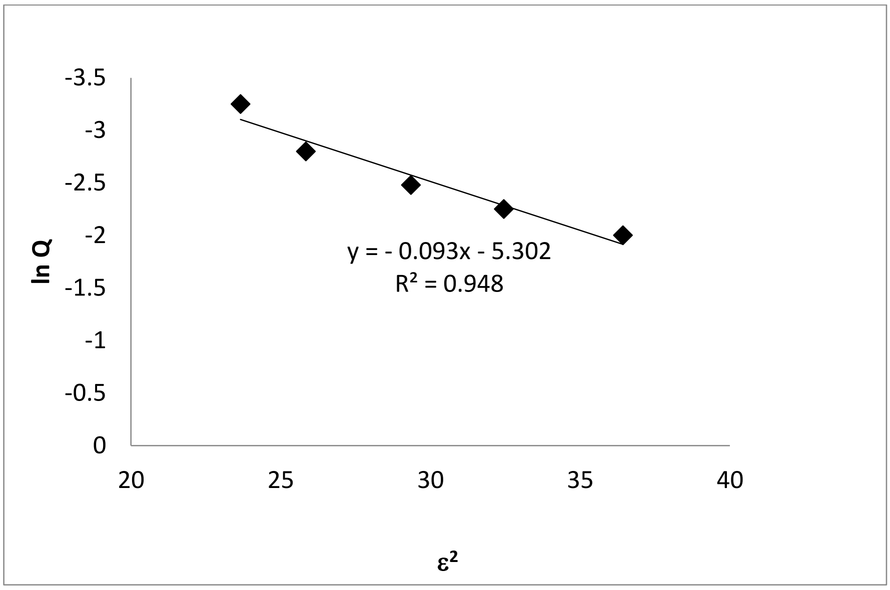


Figure 4.12 D-R adsorption isotherm for the adsorption of COD using iron nanoparticle

Based on the results of our experimental data fitting on these isotherms, nano iron shows a good ability to reduce various contaminants of synthetic leachate which can then be absorbed by the nano iron easily. Furthermore, data fitting by using the Langmuir model give a better fit. This can be seen from the fitting data obtained that the correlation of determination is higher for the Langmuir adsorption isotherm (~0.96) compared to that of the Freudlich model (~0.945).

4.9.1 Adsorption studies for COD adsorption by lateritic soil

In order to know the adsorption capacity of laterite soil, similar adsorption studies were conducted with lateritic soil. The synthetic leachate of known COD was allowed to pass through laterite column of internal diameter 5.5 cm, length 30 cm. The untreated natural laterite of average grain size 0.425 mm was selected from a place near the landfill. The bed depth of about 25cm. and was supported on a strainer. Similar to above experimental set up the inlet which feed synthetic leachate solution of known initial COD of constant flow rate of 10m/day which was regulated using an infusion set. The initial pH at 5 was introduced. The flow through the column was continuous. All the experiments were carried out at room temperature and atmospheric pressure. Samples were collected at regular intervals of time from the outlet and analysed for COD and iron content.

Adsorption isotherm was plotted to know the relation between the quantity of adsorbate adsorbed and the equilibrium concentration of adsorbate which was expressed by linear form of Langmuir adsorption isotherm. The linear form of Langmuir isotherm was drawn as shown in figure 4.13 with 1/Ce on x axis and 1/ qe on y axis. The liner equation was obtained as 1/qe = 0.168x + 8.079 with R^2 0.978 and the maximum adsorption capacity was obtained as 0.12mg / g

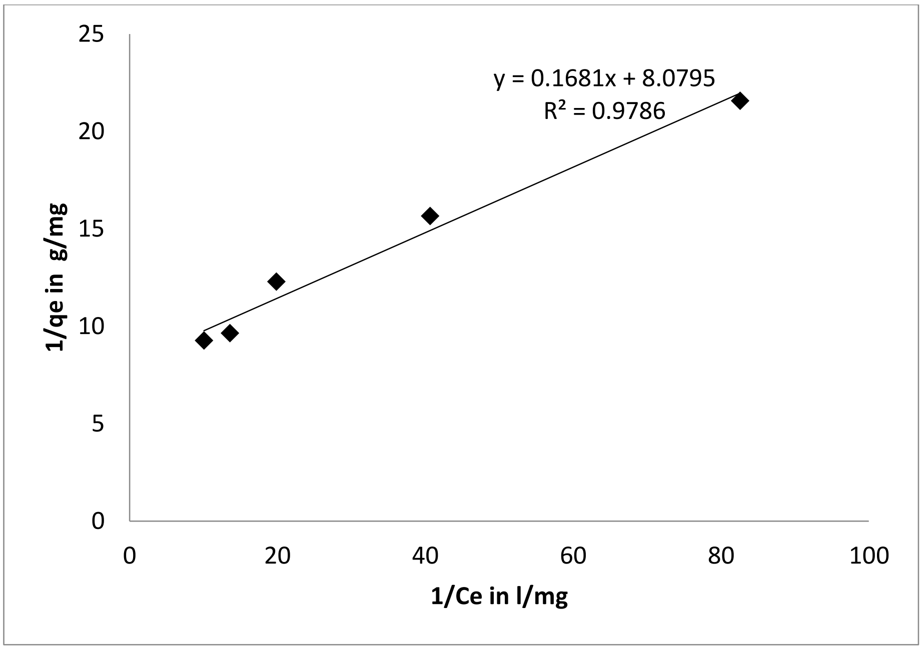


Figure 4.13 Langmuir isotherm model for COD adsorption on laterite soil

Freundlich isotherm was drawn (figure 4.14) with ln Ce on x axis and ln qe on y-axis for the adsorption of COD on lateritic soil. The equation obtained was ln qe = 0.689X -0.153 with R^2 = 0.87. From both the isotherm it can be inferred that Langmuir isotherm fits better with slope of isotherm being 0.17

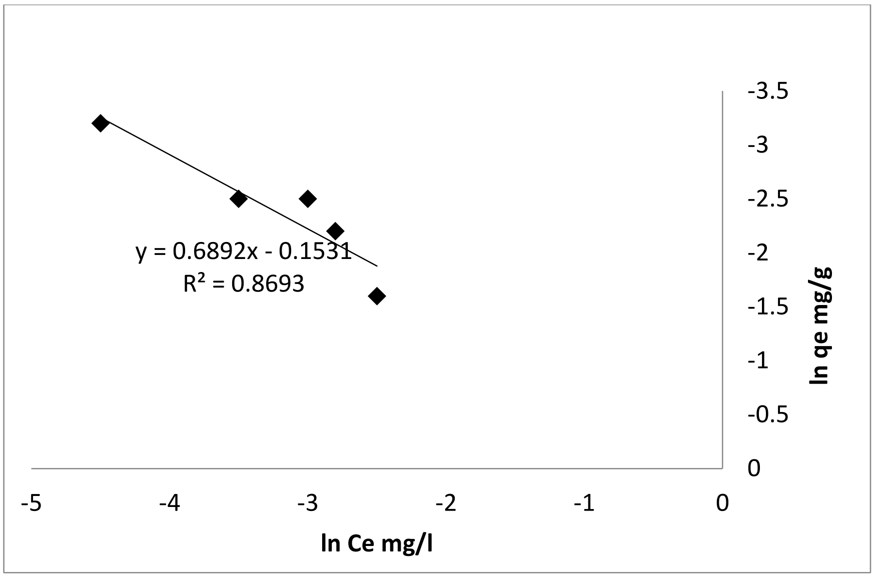


Figure 4.14 Freundlich isotherm model for COD adsorption on laterite soil

4.10 KINETICS OF COD REDUCTION

The adsorption kinetics was studied to determine the required time to achieve equilibrium adsorption of synthetic leachate on the adsorbents. It was reported that nano iron can remove the various ion from aqueous solutions by mechanisms like electrostatic adsorption, complex formation, reduction, and precipitation. (Tehrani et al., 2015). From the previous researches it is seen that when nano iron was used, it captures various pollutant ions easily and rapidly because of their large surface areas and high reactivity. In this research, the kinetics was investigated experimentally for optimum value obtained as a result of batch experiment.

The kinetics of the batch experiment was studied in order to find the contact time for the evaluation of reaction coefficient. So four kinetic models (i) first order (on the basis of concentration of solution) (ii) pseudo first order (on the basis of solid capacity) (iii) second order (on the basis of concentration of solution) and (iv) pseudo second order (on the basis of sorption of solid phase) were investigated.

4.10.1 First order reaction model

First order reaction model is based on the principle that the concentration of solution decreases as the time increases which can be represented as

$\frac{dC_t}{dt} = -k_1 C_t$……………..(4.7)

Where k1 is the reaction constant and Ct is the concentration at time t

Rearranging the terms and integrating we get

$\ln C_t = \ln C_0 - k_1 t$…………(4.8)

Where C_0 is the initial concentration and t is the time in minutes

Plotting ln C_t versus t we get the plot for first order equation which is shown in the figure 4.15. As the R^2 is 0.737 ,it is indicated that the adsorption is not following first order kinetics.

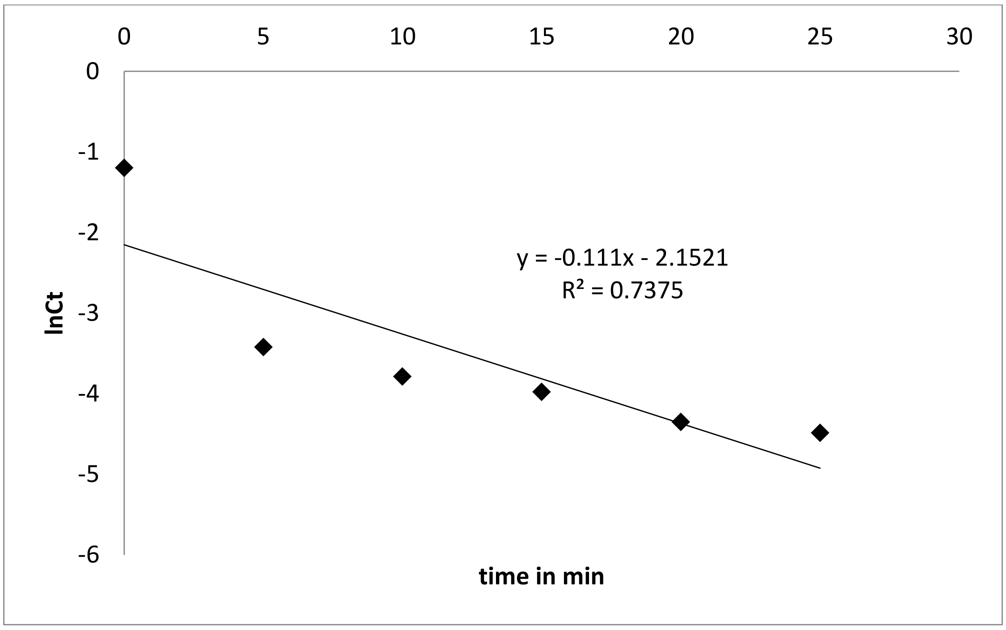


Figure 4.15 First order kinetics for the adsorption of COD using iron nanoparticle

4.10.2 Pseudo First order reaction model

The pseudo first order reaction kinetics is applied on the principle of sorption capacity of the solids and the equation is given by

$\frac{dq_t}{dt}$ = k_2 (q_1 – q_t)………………….(4.9)

Where k_2 is the pseudo first order reaction constant

q_1 and q_t amount of solute sorbed per mass of sorbent (mg/g) at any time and equilibrium respectively

By integrating we get the equation as

$\ln(q_1 - q_t) = \ln(q_1) - k_2t$………………….(4.10)

Plotting ln (q_1 - q_t) Vs time in minutes we a get a linear plot as shown in figure 4.16.

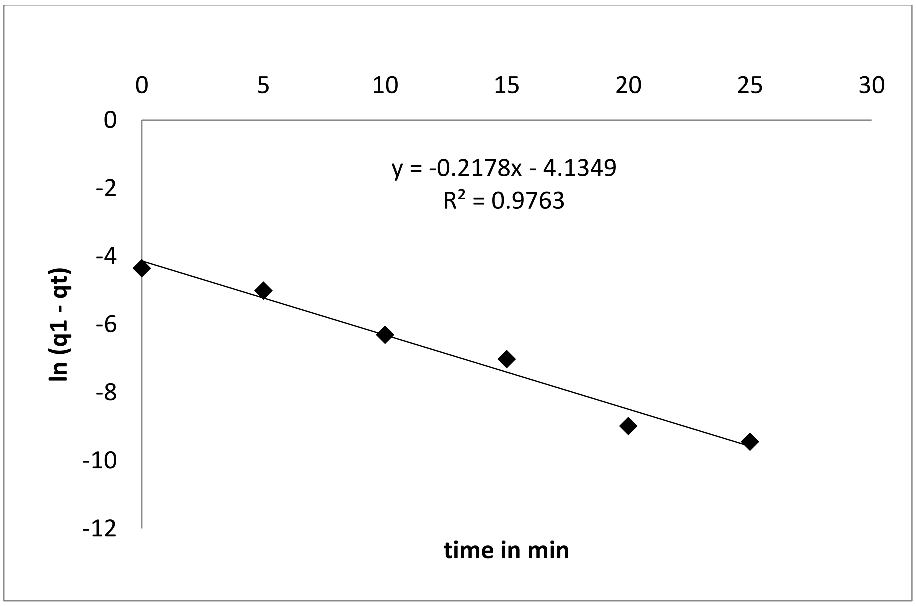


Figure 4.16 Pseudo first order kinetics for the adsorption of COD using iron nanoparticle

According to the coefficient of determination R^2 value which is 0.976, it is better than the first order reaction

4.10.3 Second order reaction kinetics

The second order reaction kinetics is based on solution concentration and equation is given by

$$-\frac{dC_t}{dt} = k_3C_t^2 \text{..}(4.11)$$

Rearranging and integrating the above equation for time t from 0 to t and concentration from 0 to C_t we get

$$\frac{1}{C_t} - \frac{1}{C_0} = K_3 t \text{..........................}(4.12)$$

Where Co is the initial concentration and C_t is the concentration at time t K_3 is the equilibrium constant and t is the time in minutes

A graph was plotted with time on x axis and $1/C_t$ on y axis as shown in figure 4.17.

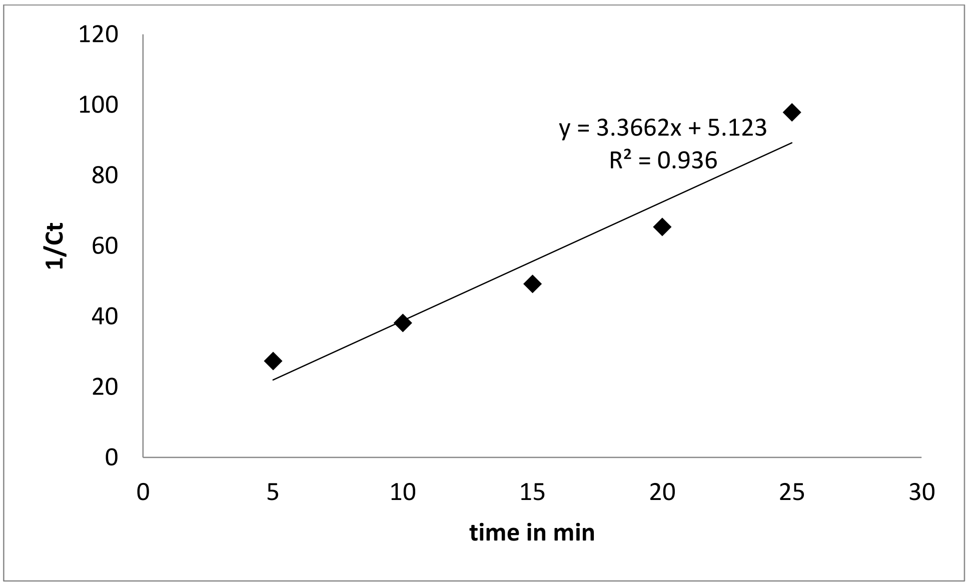


Figure 4.17 Second order reaction kinetics for the adsorption of COD using iron nanoparticle

A correlation of determination R^2 0.956 is obtained which shows that pseudo first order is a better curve than second order. Second order reaction kinetics often used for metal ion adsorption.

4.10.4 Pseudo second order adsorption

It is on the basis of equilibrium capacity and can be expressed as

$$\frac{dq_t}{dt} = k_4[q_e - q_t]^2 \text{..............................(4.13)}$$

By rearrangement and integration of above equation we get

$$\frac{1}{q_t} = \frac{1}{h} + \frac{1}{q_e}t \text{.................................(4.14)}$$

Where $h = k_4 q_e^2$. A plot of t/qt vs t was drawn as shown in the figure 4.18. which clearly shows that pseudo first order curve is the best fit for the adsorption of COD with nano iron.

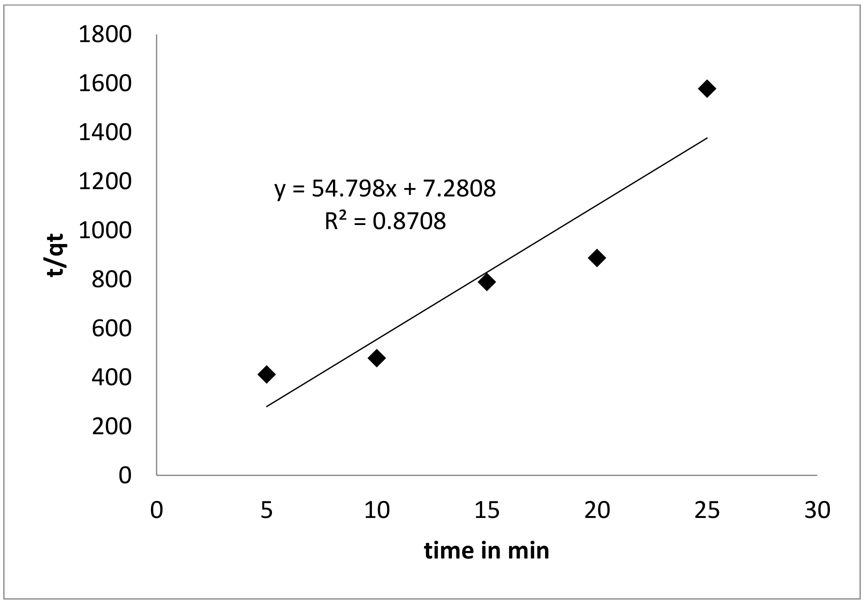


Figure 4.18 Pseudo Second order reaction kinetics for the adsorption of COD using iron nanoparticle

4.11 CONCLUDING REMARKS

The leachate collected was analyzed in the laboratory for various physico-chemical parameters. The results showed that most of the parameters exceeded the IS specified standard for the disposal of waste. As the chemical and physical composition of the landfill changes with time, synthetic leachate was prepared in the laboratory. The nano iron was synthesized in the laboratory and characterization of the same has been carried out using Scanning Electron Microscope. The removal of chemical oxygen demand from synthetic leachate using nano iron was studied. Findings of this study indicated that starch coated iron nano particles has a good feasibility for in-situ leachate remediation in contaminated water. Batch experiments proved that the pH of solution was an important parameter as kinetics coefficients were directly related to pH with coefficient of determination $R^2 > 0.90$. The nano iron dosage of 2 mg/l enhances removal efficiency of COD beyond that dosage the effluent will have traces of iron beyond the limit which is undesirable. A comparison of batch and column reactor was made where continuous fixed-bed column was found to be more effective in removal of COD in the remediation of leachate which may be due to the adsorption by laterite soil. Evaluation of Freundlich, Langmuir and D–R isotherm models were conducted. The kinetics of the experiments show that it follows pseudo first order reaction kinetics. The findings of the study can be further used for applying in the field. Because of the fast reaction kinetics and high removal efficiency, nano iron coated with starch has the fine potential to become an effective remedial agent in treatment of leachate and also it can be used in permeable reactive barriers because of its excellent removal efficiency shown during continuous fixed-bed column studies.

CHAPTER 5

GROUNDWATER FLOW MODEL

5.1 GENERAL

Groundwater flow model simulates the hydrogeological conditions using mathematical equations the solution of which is found using computer programs. In order to simulate a model first step is replacing the partial differential equation governing groundwater flow and accompanying boundary and initial conditions into numerical model which is written in terms of discrete variables. In the current study the simulation model of groundwater flow is developed by using MODFLOW 2000 (Harbaugh et al., 2000). GMS package © (Groundwater Modeling Software) version 10.0.1 was used. GMS provides a user friendly interface and hence it enhances the productivity of model and also it minimizes the complications which is coming across in the simulation processes. Many hydro geologists made use of the graphical interface provided by GMS to understand and solve various types of issues related to groundwater. Originally the program was in FORTRAN 66 (Mc Donald and Harbaugh, 1988)

The simulation of groundwater for the study area is carried out by taking post monsoon water level data which is during the month October 2016. The parameters such as specific yield, hydraulic conductivity are then found by giving input parameters such as annual average rainfall of the region, pre monsoon and post monsoon water level data which was collected during the years 2016 – 2018 to model.

5.2 MODELLING PROTOCOL

Groundwater flow models are replications of groundwater systems that are mathematically represented with some assumptions and are simplified in order to satisfy some specific purpose. Figure 5.1 gives the modeling protocol followed for the development of conceptual model.

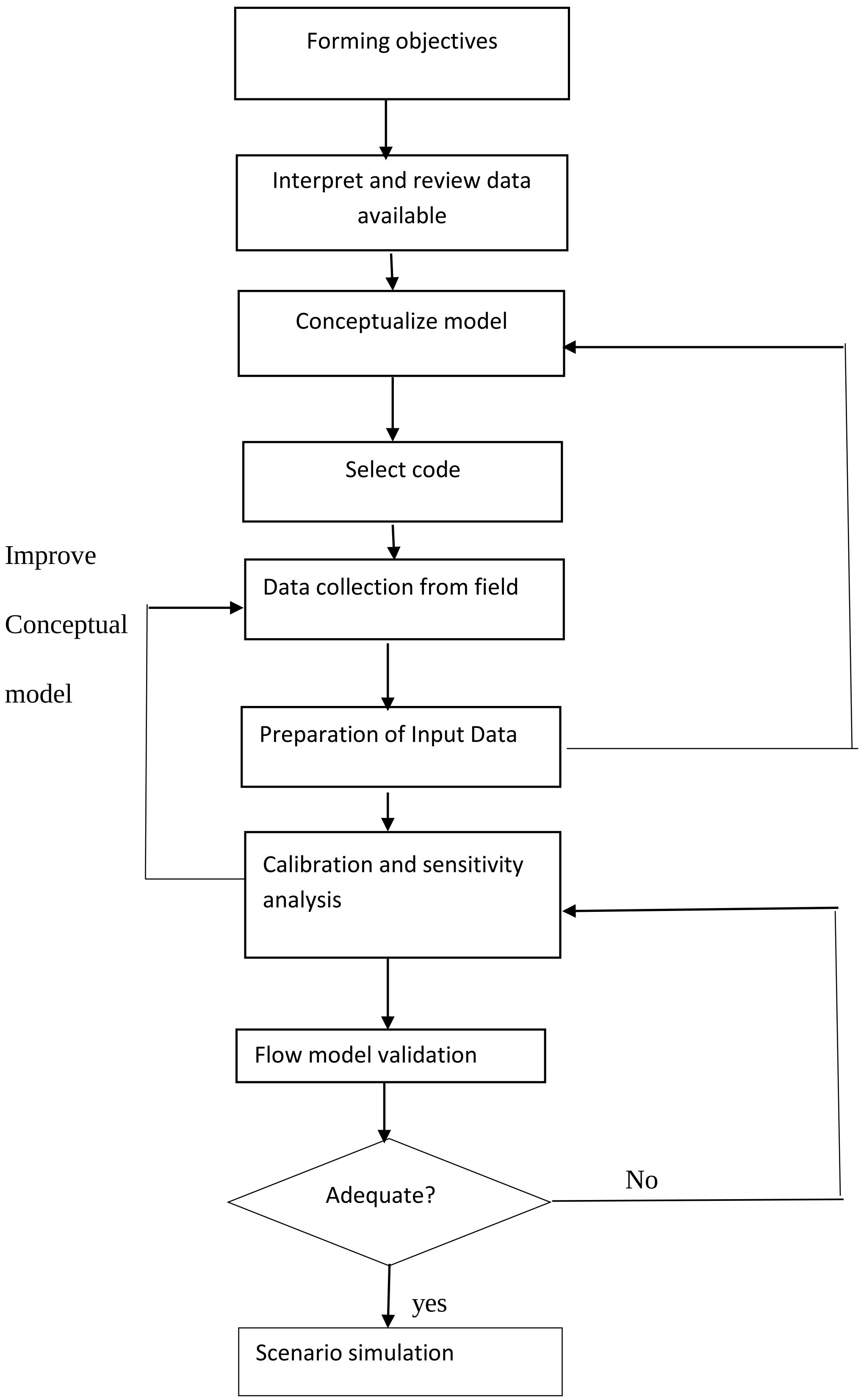


Figure 5.1 Groundwater modeling protocol

The groundwater models were developed to know various hydrogeological process of groundwater flow, its transport and the transformation and also for several other applications. With the improvement in computer technology, the purposes of the applications also increased. Now a days it is widely used to estimate generation of leachate from a landfill, to evaluate remedial alternatives which can be adopted in the site, to assess the risks associated which involves various complications and uncertainties. But the authenticity of the result will depend on how effective the model is in depicting the groundwater system. All models should have a well-defined goal or objective. To achieve that object the various information such as hydrogeology as well as geochemistry of the study area are to be gathered to make the conceptual model. Next step is to select the computer code which can be either two dimensional or three dimensional. Following that the input files are to be prepared and are to be incorporated with the equation governing the flow. Then the calibration has to be done until simulated values match with the field observations with a reasonable degree of accuracy. Subsequently the sensitivity analysis has to be performed so as to know overall reactiveness or sensitivity of the model to the input parameters. Following validation which is the verification of flow model, the predictive simulations can be performed.

5.3 PROGRAM STRUCTURE

MODFLOW – 2000 program is modularized into four entities namely procedures, packages, modules and process.

The program executes 3 procedures ‘define’, ‘allocate’ and ‘ read and prepare’ where ‘define’ will denote model size, whether transient simulation or steady state simulation, the options like stress period, hydrologic data and the scheme for the solution. ‘Allocate’ will allot the memory which is necessary for the program. And the ‘read and prepare’ will read the input which are not functions of time and also work as individual sub routines when main program calls it. The MODFLOW program contains a main program and many independent sub programs called “module” which are group of “packages” to deal with salient features of the aquifer system to be modelled. Table 5.1 lists the MODFLOW packages used for the simulation with a brief description of its operation. The "process" solves the groundwater flow equation using numerical method. The solution of finite difference equation is obtained by simulating it in loops; a loop which consider the stress period, inside the loop the one which consider the time, inside which contain the loop of iteration.

5.4 EQUATION GOVERNING GROUNDWATER FLOW

The three-dimensional flow of groundwater of constant density through the porous media is defined by a partial difference equation which is the governing equation for groundwater flow. (Mc Donald and Harbaugh, 1988).

$$\frac{\partial}{\partial x}\left(Kxx\frac{\partial h}{\partial x}\right)+\frac{\partial}{\partial x}\left(Kyy\frac{\partial h}{\partial y}\right)+\frac{\partial}{\partial x}\left(Kzz\frac{\partial h}{\partial z}\right)-Q=Ss\frac{\partial h}{\partial t}\ldots\ldots\ldots(5.1)$$

Where, K_{xx}, K_{yy}, K_{zz} = hydraulic conductivity along the x, y, z direction which are assumed, m/sec;

h is the piezometric head in meter;

Q is the volumetric flux / volume representing source / sink terms,

S_s is the specific storage coefficient defined as the volume of water released from storage per unit change in head per unit volume of porous material,

t is the time in seconds.

For steady state condition, the term in the right side should be equal to zero. When accompanied with initial and boundary conditions, the equation will describe groundwater flow in transient state in a heterogeneous anisotropic media. The system is considered as grids of cells called nodes where head is computed.

5.5 APPROACH TO CONSTRUCTION OF MODEL

Building conceptual model is the primary step which helps to understand the problem formation in the physical way which further helps in modeling approach. Following this approach will make the problem simpler and piles the data which is required in an organized way for analysing easily. Also it helps in identification of missing data before the conceptual model is constructed. Table 5.1 gives the idea of parameters considered while conceptualizing the system.

Table 5.1 Parameters considered in the conceptualization of the system

Feature	Description	Comment
Boundaries	Location and type of boundaries for area to be modelled	Boundary type include specified flow, specified head, head-dependent flow etc
Geological framework	Geological units, and corresponding hydro-stratigraphic units and model layers and associated aquifer parameters .Bedrock configuration and aquifer or aquitard characteristics	Hydrostratigraphic units comprise of geological units with similar aquifer properties. Several geological formations may be combined into one hydrostratigraphic unit (or model layer) or a geological formation may be subdivided into aquifer and confining units (or several layers)
Hydrological framework and stresses	Recharge and discharge processes and dominant aquifer flow mechanisms	Definition of aquifer media type (porous medium and fractured rock)

Human-induced factors	Anthropogenic influences on the system.	Pumping, drainage etc.

The various data given as input are discussed in the section below.

5.5.1 Groundwater data

The input data collected in relation with groundwater table in the sub-basin are monthly data from Central Ground Water Board from the year 2000 in a well located near Kavoor and the fortnightly water quality data collected from Vamanjoor High School by Karnataka Pollution Control Board which was collected personally from the respective offices located at Mangaluru. Also the water head and water quality data of the observation well were collected in seasonal basis (Post monsoon October 2016, pre monsoon May 2017, Premonsoon May 2018).

5.5.2 Basin discretization

The physical boundary of the basin where Vamanjoor landfill is located is represented by Gurupur river flowing at the north of the basin and the ridge line across all the other direction. The conceptual model in the area is defined as an unconfined aquifer with vertical thickness based on the hydrological and geological properties of the sub-basin, and the model elevation ranges from -30 m to 123 m with respect to mean sea level.

Spatial discretization

The simulation model of study area is represented as a two dimensional grid in a horizontal plane with fairly accurate dimension of cell 100 m X 100 m. The vertical section is denoted by one grid with dimensions which varies. The interpolation of digital elevation model (DEM) (figure 1.4) has been prepared to get the topmost elevation of the grid. Corresponding to the base of aquifer which is shallow, the model base was kept as -30 m which is 30 m below mean sea level. The model representation is shown in figure 5.2 and spatial discretization of the sub-basin is shown in table 5.2.

General Assumptions made to simulate groundwater flow model are

1. Darcy's law can be applied for facture and weathered zones as it is considered as porous medium.
2. Vertical flow is assumed to be negligible
3. As vertical anisotropy, fractures or faults, aquifer heterogeneity effects the distribution of hydraulic conductivity in space, places with same hydraulic conductivity is assumed to be in a single zone the value of hydraulic conductivity is given to that specified zone.
4. Net recharge is not uniform because precipitation got on an area is different because of the difference in hydraulic conductivity, difference in the rainfall received, the slope of the region and geology of the region.

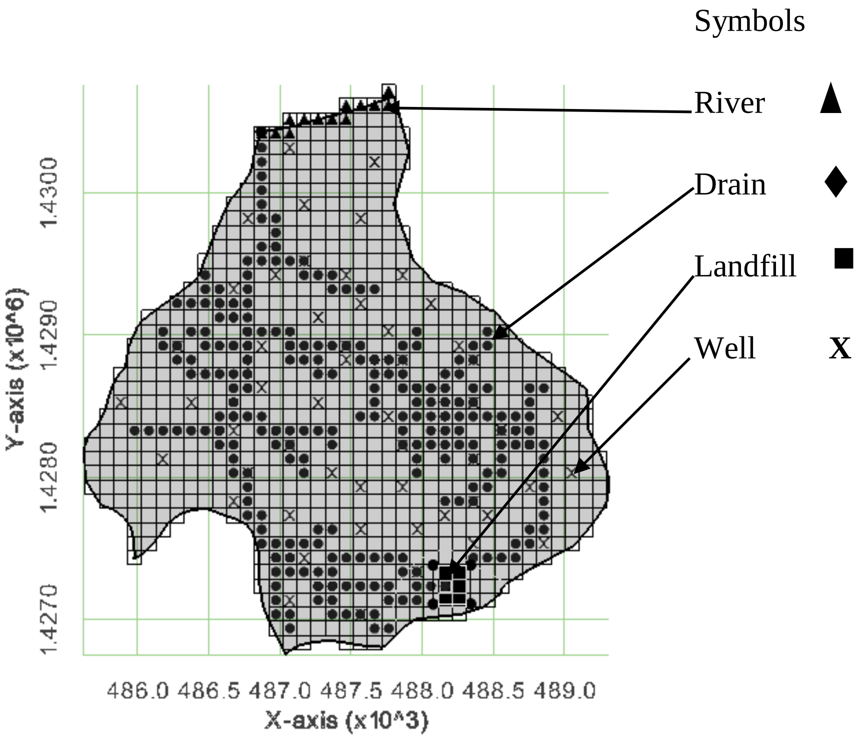


Figure 5.2 Model representation of sub-basin

Temporal discretization

The process of conversion of general time steps into distinct values which is applied over a specific range of time is called temporal discretization. Time steps play a major role in the analysis of groundwater system the length of which is depending on dynamic nature of hydro-geologic process which is to be simulated. In order to obtain initial head, steady state simulation is carried out. Later the system is simulated for transient state for every day time step. The data such as rate of pumping, rate of recharge, river stage and river bed conductance has been assigned.

Table 5.2 Discretization of model.

Sub-Basin	Origin		No of cells		No of active cells	Surface elevation in meter
	X direction	Y direction	X direction	Y direction		
Vamanjoor	485640E	1427956N	41	41	1622	0 - 123m

5.5.3 Sources and sinks

According to continuity equation, the sum of flow entering in and leaving out from the cell is the rate of change in storage inside the cell. This concept is adopted for developing the flow equation. So the equation (5.1) will represent the inflow, outflow, the recharge and sink. In the current study, the recharge includes predominantly from precipitation, and the sinks are due to groundwater extraction for pumping for agriculture and so on.

Recharge of groundwater.

The recharge is quantified as a proportion of the effective precipitation received in the area. But it is difficult to quantify recharge as it depends on the topography of the area, the type of the soil, land use and so on. Hence recharge coefficient, which is the ratio of recharge of the area to the precipitation received in the area has been used in the current study. The recharge for the current study is simulated by the Recharge package represented as (RCH)

The recharge of the area is naturally replenished because of the monsoon rains gets in the area. The rainwater infiltrates and percolates through the sub surface soil and reaches the aquifer. The current study area gets an average annual rainfall of 3810 mm.

For lateritic type of soil, the co-efficient of recharge value recommended by Groundwater Estimation Committee of India (GEC, 1997) is 7 %. Previous works also suggest the value of coefficient of recharge varied between 8 % and 26.5 % (Udayakumar, 2008). The rainfall data was obtained from meteorological station located at Mangaluru Airport. The value of recharge was assigned to the topmost layer and was modified in a suitable range of values so as to get a better value during calibration.

Abstraction data

The groundwater of the area of the sub-basin is widely used for agricultural and domestic purposes. A total number of 68 wells were located in the study area. As per Mangaluru Electricity Supply Company (MESCO) irrigation pumping set installation data was procured and it was found that the average well draft of the study area is 29.16 m3/day. The withdrawal of water from wells from aquifer in the specified rate during the stress period is modelled with the help of a package called well (WEL) package in MODFLOW. The well discharge is handled in the well package by specifying the rate Q at which each individual well removes water from the aquifer, during each stress period. In the absence of actual well draft data, the withdrawal per well is allocated as per the requirement of water for the crops. (Arecanut requires nearly 19 to 23 l /day. And coconut requires nearly 55 l /day). From the previous study it was observed that the evapotranspiration for the study area is 7mm/day, 6mm/day and 5mm/day during the pre-monsoon, monsoon and post monsoon seasons (Kumar, 2010). The agricultural areas are identified using LULC map (Figure 1.8). Accordingly the abstraction for the sub-basin was calculated.

5.5.4 Boundary Conditions

Mathematically boundaries are grouped into 3 categories namely (i) Dirichlet which is constant head or constant concentration; (ii) Neumann which is based on specific flux and (iii) Cauchy which is having mixed conditions or which is head dependent on flux. Other than these, boundaries also includes features like water bodies for example river, streams, drains, injecting or pumping wells or even evapotranspiration or recharge that enforce boundary condition are taken into consideration.

Neumann boundary

Neumann boundary is used in all the part of the model other than on the northern boundary. Neumann boundary (type 2 boundary) is representing the condition where the slope of the dependent variable will be always normal to boundary. For groundwater flow model, due to this boundary condition, specific flux of water will enter or goes out of the simulated area and for solute transport, the gradient of concentration will be normal at boundary. The boundary cells will be assigned no flow cells where the flow equations will not be solved. Also there won't be any flow between no flow cell and its adjacent cell.

Cauchy boundary

It is also called as type 3 boundary and represented by head dependent condition of flow for modeling flow. Here a control head is specifically prescribed. But on the boundary, the head is computed during simulation but in accordance with control head along with a conductance term. The packages river (RIV) and drain (DRN) engage some limited value of flow. Figure 5.3 shows the boundary conditions taken for the present study area.

The flow from or into Cauchy boundary can be calculated as

$Qb = C_{on} (H_c – H_{ijk})$………………………………..(5.2)

Where C_{on} is the conductance term, Hc the specific control head, H_{ijk} the computed head

The interaction of river and aquifer has to been represented as river conductance. The Gurupur river which is flowing in the northern boundary represents Cauchy boundary and assigned it (RIV) river package. The 2 elevation has to be specified (i) the elevation or height of the bottom of the river; (ii) the head in the river. The entry or exit of water to groundwater system will depend on the water head in the river. The flux is determined by multiplying conductance term with the difference of head in cell.

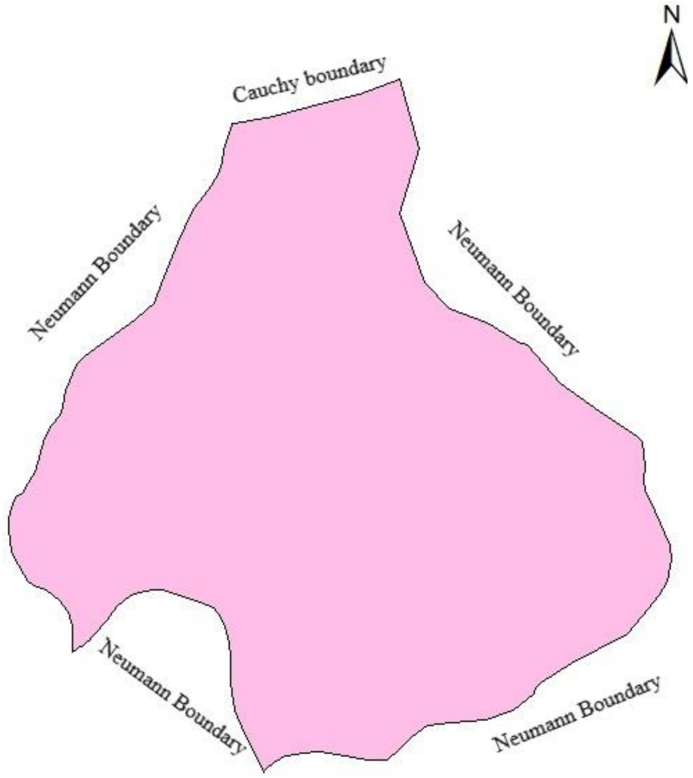


Figure 5.3 Boundary conditions of the study area

The input data required for river (RIV) package are (i) River stage which defines the elevation of surface water body; (ii) bottom of river bed which is the height of the bottom is seeping layer (iii) Conductance which is defined by the parameter that represent flow resistance offered by the seepage layer to the surface and groundwater flow.

From the previous studies, the river bed slope is taken as 1: 6000 for Gurupur river. (Radheshyam, 2009). The data such as river stage got from website of National Remote Sensing Centre and Minor irrigation department was reduced to model elevation and given to starting and ending node. The river bed conductance is given by

$$C_{riv} = \frac{K\,l\,w}{m} \qquad \text{.................................(5.3)}$$

Where *K* represents the hydraulic conductivity of river bed, *l* the length of reach, *w* the width and *m* the bed thickness.

The river bed material was sand of fine to medium grain size and hence the hydraulic conductivity is taken as 2.5 m / day for the fine grained sand and that for the medium grained is taken as 12 m / day (Todd and Mays, 2005). The program will calculate length of river automatically. The width of the river was measured with the help of Google earth and the average of the value of 154 m was assigned. The bed thickness was taken as 1 m.

In order to simulate the drainage network the DRN drain package in MODFLOW was used. The required inputs are conductance and the reference water head. It was assumed that the drain has a depth of 1.5 m from its surface and the width was assumed as 3 m. The drains were considered active during the time of monsoon only. It is assumed that the water can enter from the drain to the aquifer only but not back from aquifer to drain. Or in other words the removal of water is possible only when the elevation of water table is above the drain and if it is below, the effect of drain will not be there.

5.5.5 Initial conditions

The initial conditions given at the start are water head for the flow of groundwater, the concentration given for solute transport. The calibration for the steady state was carried for the post monsoon period which is during October 2016.

5.6 CALIBRATION OF MODEL

During calibration of model, the hydraulic parameters are altered in a specific range (got from previous studies conducted in the area or can be obtained from areas of similar conditions) so that groundwater head obtained as a result of simulation matches the observed groundwater head for the betterment or accuracy of the simulated model. The variation of parameters can either be done manually or by the computer program during calibration. In the current study, Parameter Estimation software (PEST) version 12.2 was used for the calibration of model. In order to get better result, the various input parameters are varied and by trial and error method the model is run for many times to get a fairly accurate range of values which was given as input for PEST.

The simulated and measured values of groundwater head of the study is compared by the following four methods:

Slope – y intercept method

This method is based on the principal that no error or ideal data would have the exact same observed and simulated values. Or all the observed values will fall on a line making 45° angle and intersects the x and y axis at origin. Hence the observed and simulated values are plotted where the x axis and y axis are having same intervals and a line with slope is 1 and passing through the origin is drawn. The line inclined at an angle 45° and zero y intercept indicates a perfect model.

Coefficient of determination (R^2)

R^2 coefficient of determination is defined as the proportion of variance which is explained by the regression model for predicting the dependent variable from the independent ones. Or else it explains how good the co linearity is between observed and simulated value and also explains the variance in the data measured. It is dimensionless or it doesn't depend on units and achieves a maximum value of less than one for discrete models. R^2 value is independent of the sample size. (Nagelkerke , 1991). Even though the range of value for R^2 is 0 to 1, the value higher than 0.5 is generally considered to be good with less error.

Root mean square error (RMSE)

The root mean square error (RMSE) has been used as a standard statistical metric to measure model performance in several studies. It is a good indicator of average model performance. It indicates the error between the simulated values and observed values. For a perfect fit curve, RMSE value will be equal to zero. The formula for RMSE is

$$RMSE = \sqrt{1/n \sum (Xobs - Xsim)^2} \ldots\ldots\ldots\ldots\ldots\ldots(5.4)$$

Where *X obs* is the observed data and *X sim* is the model simulated data.

Nash Sutcliffe efficiency (NSE)

It is the method which is recommended by ASCE to evaluate model and is popularly used by hydrologists. NSE gives a comparison of the residual variance of simulated data with that of measured data. The formula for NSE is given by

$$NSE = 1 - \left[\frac{\sum(Xobs - Xsim)^2}{\sum(Xobs - Xmean)^2}\right] \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(5.5)$$

Where X obs is the observed data, X sim is the corresponding simulated data, The NSE value to be acceptable, has to be 0 – 1. If it is less than 0 it is not acceptable.

5.6.1 Observation wells

The water level of 23 observation wells was measured during post monsoon season in the month of October 2016 (post monsoon), pre monsoon season (May 2017) and pre monsoon season (May 2018) and tabulated below (Table 5.3). A local survey was carried out to get the exact location of observation well and the water level. Trimble Juno 3 series handheld GPS instrument was used in the study. The details of the observation wells considered for the current study is presented in the Table 3.1. The water head is measure on seasonal basis October 2016 (post monsoon season) May 2017 (pre monsoon season), May 2018 (pre monsoon season) and compared with the simulated head.

Table 5.3 Measured water head of observation wells during October 2016 (post monsoon) May 2017 (pre monsoon), May 2018 (pre monsoon)

Well No	October 2016	May 2017	May 2018
1	6.2	7.7	7.5
2	7.5	9.2	9.5
3	8.3	10	10.2
4	9.8	11.5	11.3
5	7.6	8.9	8.7
6	6.8	7.9	8.1
7	9.8	10.9	11.2
8	10.3	11.1	13.2

9	12.1	13.5	9.1
10	8.1	9.6	8.9
11	8.6	9.3	9.1
12	9.6	10.6	10.4
13	11.4	12.1	11.9
14	10.3	11.4	10.9
15	8.9	9.9	9.7
16	7.9	10.4	11.4
17	9.4	11.2	9.6
18	8.6	9.4	8.7
19	8.3	9.1	7.5
20	7.6	8.5	8.4
21	8.9	9.7	9.5
22	7.9	8.2	8.5
23	6.9	7.5	7.2

5.6.2 Steady state calibration

When level of water is not changed for duration of time, the balancing of flow takes place and the aquifer attains steady state. The groundwater system has to be analysed before so as to know the actual time of steady state condition. From the previous data, the groundwater flow was found to be near in the post monsoon period which is during the month of October. Hence the water head during month of October 2016 was taken for the present study .This data was taken for running and calibrating the model in steady state and the hydraulic conductivity and porosity was obtained. The head thus obtained is taken as the initial head for the transient run. For calibration purpose simulation of water head was done by taking water head during the month of May 2017 (Pre monsoon period) and .The head obtained there off is assigned as the starting head for the transient simulation. The groundwater head obtained from steady state simulation is compared with the 30% data of observation well obtained for the sub-basin and also the record of Honnanagoudar 2015. The values of statistical parameter obtained as an indication of model performance such as coefficient of correlation (r) = 0.89, coefficient of determination (R^2) = 0.79 and RMSE value of 0.53m which shows that the results shows a convincingly good agreement with observed and simulated groundwater head.

5.6.3 Transient calibration

While transient calibration, models are calibrated with more constraints or it has degree of freedom is less which increases the reliability of the model. The head obtained as a result of steady state calibration has been taken as the starting head and transient calibration was performed from May 2017 to May 2018 for a period of one year. For transient model, daily time step has been adopted and applied hydrogeological conditions of period under consideration. For the transient calibration, the parameters such as hydraulic conductivity of the aquifer, porosity of the aquifer and specific yield are required which was taken as the same values got as a result steady state calibration. After successful calibration, the optimal values of parameters got are tabulated in the table 5.4.

Table 5.4 Optimal values of parameters obtained after calibration

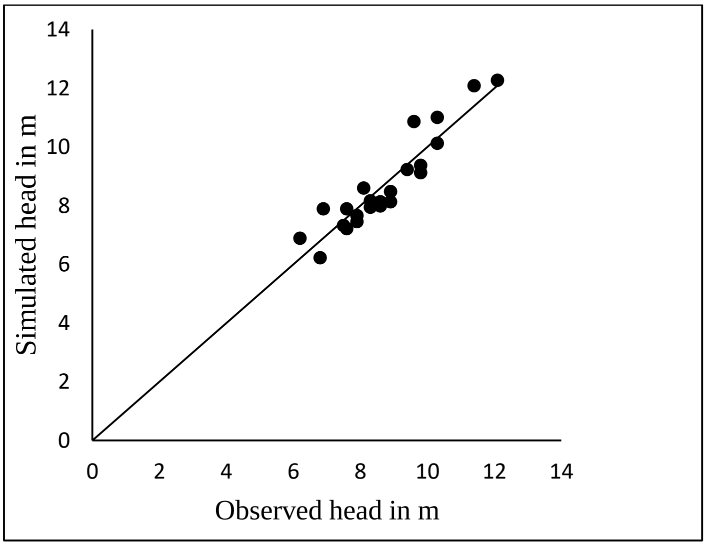
Parameter	Value
Hydraulic conductivity	15 m/day
Recharge coefficient	10 %
Porosity	30 %

From coefficient of determination (R^2), RMSE, and NSE values (Table 5.5) it is indicated that the performance of model is reasonable as all the simulated values are within range.

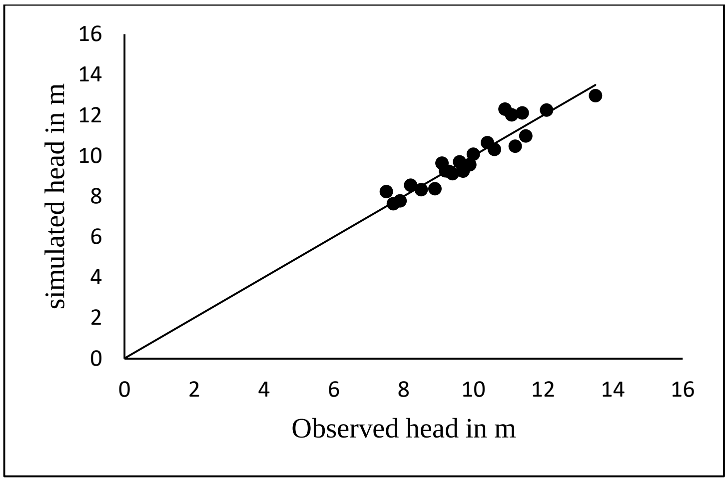
Table 5.5 Simulated model efficiency values on seasonal basis

Month	R^2	RMSE (m)	NSE
October 2016	0.92	0.57	0.475
May 2017	0.89	0.50953	0.588
May 2018	0.9	0.4885	0.423

The evaluation of the model has been carried out with graphical plot and scatter on seasonal basis and presented in figure.5.4 for the study area. Here from the plot between observed groundwater level and simulated groundwater it can be seen that the model rather fits well since all points lie close to the line $y = x$ having slope 1 and passing through origin.



(A)



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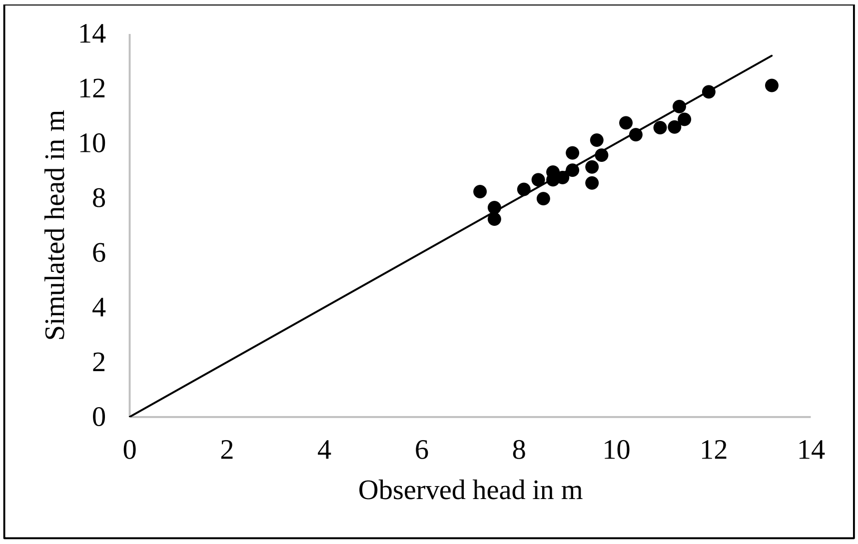
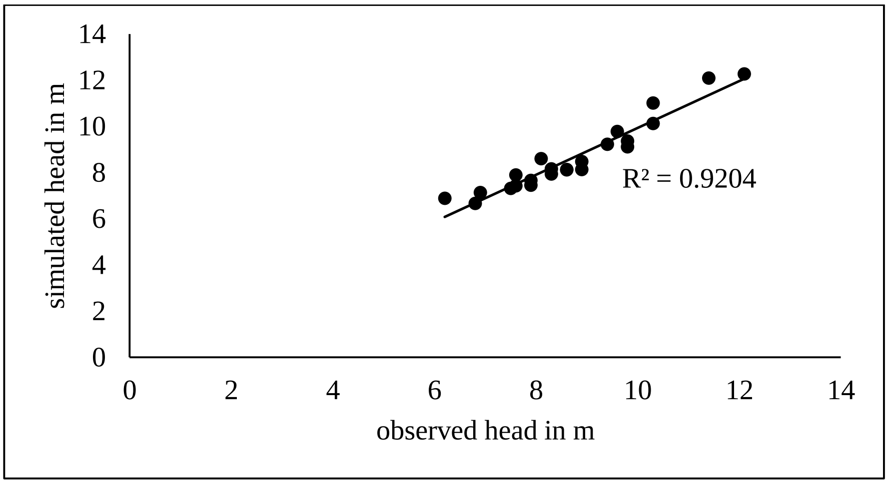


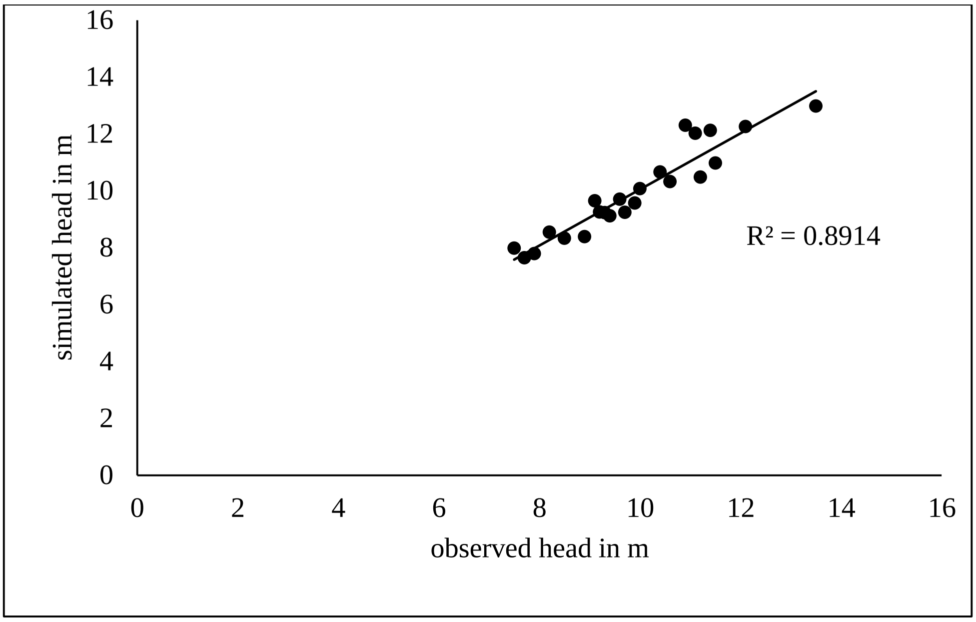
(C)

Figure 5.4 Simulated and observed groundwater heads with line y = x drawn (A) Post Monsoon (October 2016) (B) Pre monsoon (May - 2017) and (C) Pre monsoon (May - 2018)

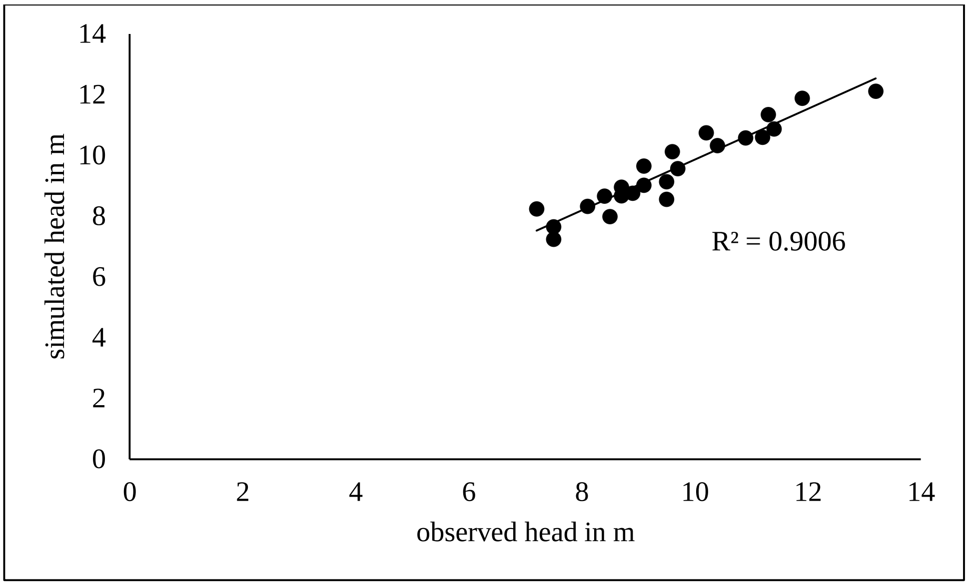
The coefficient of determination (R^2) determines the strength of the linear relationship between the observed and simulated values. From the graphical plots, (figure 5.5) as the R^2 value is nearly equivalent to 0.9 in all the cases, it conveys that the model performance is satisfactory.



(A)



(B)

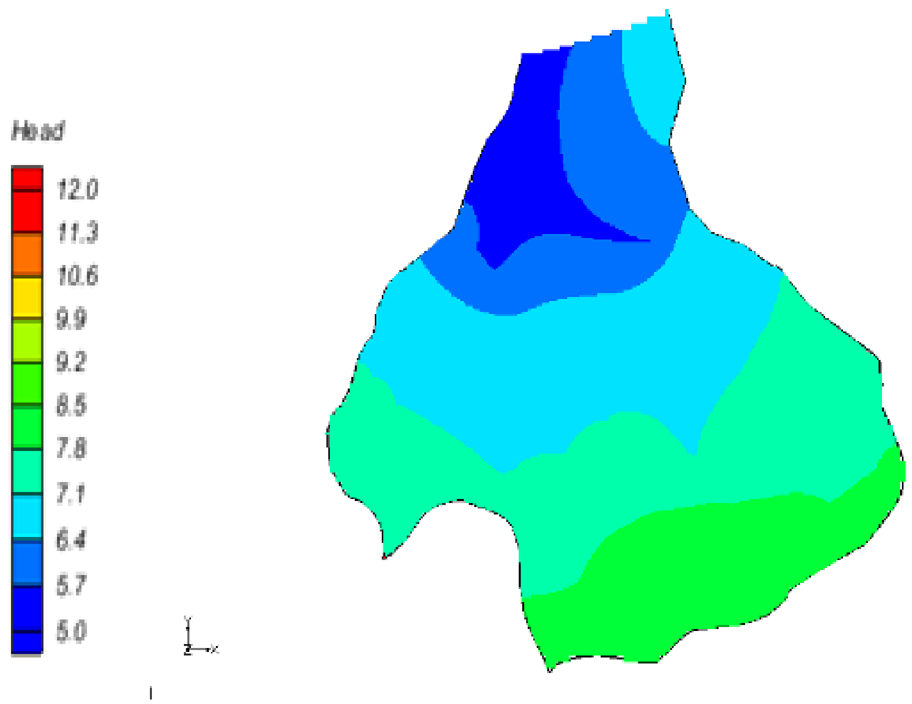


(C)

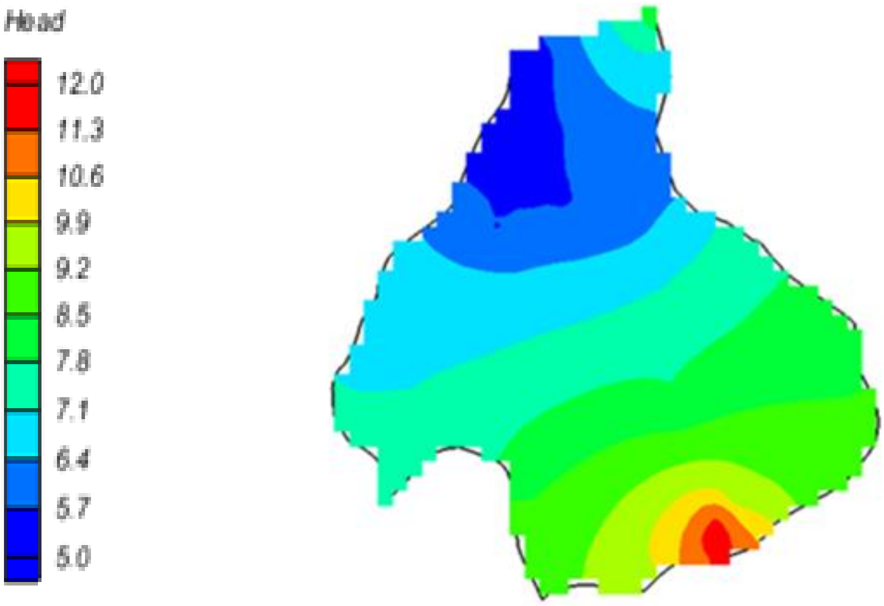
Figure 5.5 Simulated and observed groundwater head during calibration period (A) Post Monsoon (October 2016) (B) Pre monsoon (May - 2017) and (C) Pre monsoon (May - 2018)

Figure. 5.6 shows that the calibrated groundwater flow patterns for the month of October 2016 (post monsoon), May 2017 (pre monsoon) and May 2018 (pre monsoon).

The modelling result of sub-basin shows that the groundwater table is gradually increasing from the river side to the high elevated land area. The water head ranges between 12 m at the elevated areas to 4 m near the river during severe summers which is in accordance with the measured head from the observation wells. And in the post monsoon season it was observed that the head decline to around 7 m which is due to the increase in drainage density in the sub-basin. It is obvious from the figures that the Month of May which is prior monsoon is drier than the month of October which is post monsoon month.



(A)



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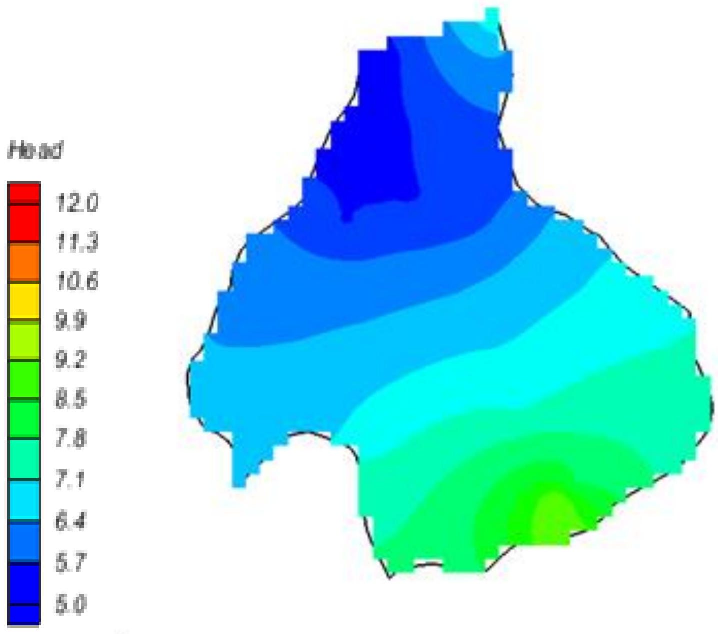


(C)

Figure 5.6 Flow contour of groundwater during the month (A) October 2016 (B) May 2017 (C) May 2018

5.7 MODEL VALIDATION

The accuracy of the model is to be checked before it is applied for predictive simulations. This is done by the process of validation of the model. Hence prior to predictive scenario simulation, validation was performed by taking pre monsoon data (May 2018) following calibration run. A comparison of the simulated water head data with that of observed head which was maintained at the Central Groundwater Board and Department of Mines and Geology, Government of Karnataka (which was collected personally) has been done. The R^2, RMSE and NSE values obtained after analyzing the observed and calibrated groundwater head were 0.736, 0.61m, and 0.651 for the sub-basin. The results are found to be consistent with that of calibrated results and therefore model is considered to be reliable for future prediction. For the perception of the agreement between the simulated and observed values of groundwater head, scatter plot has been drawn (figure 5.7) and it can be observed that the values show a good agreement as it lies close to the line $y = x$ which inclined at angle of 45°

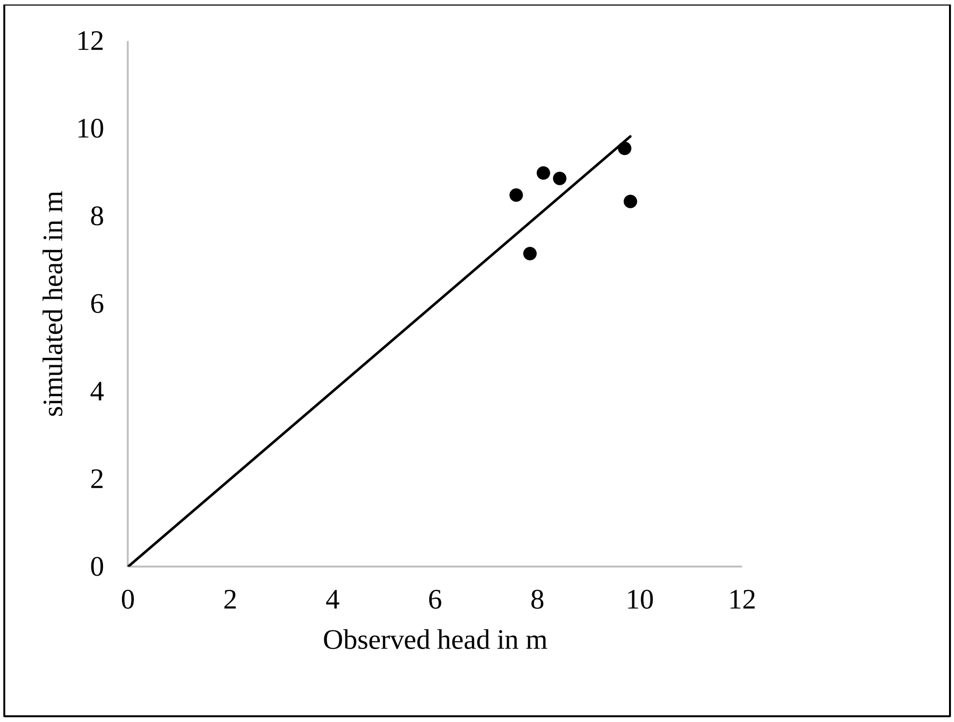
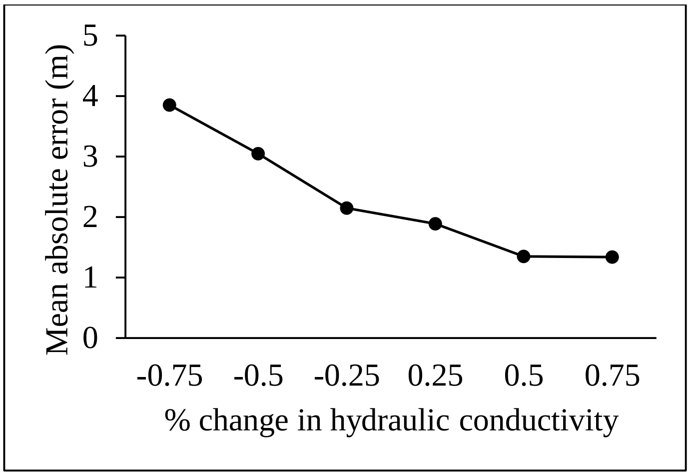


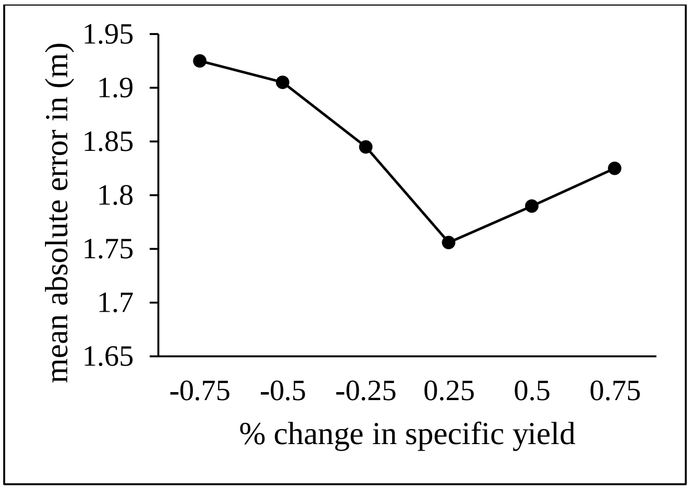
Figure 5.7 Simulated and observed groundwater head for validation

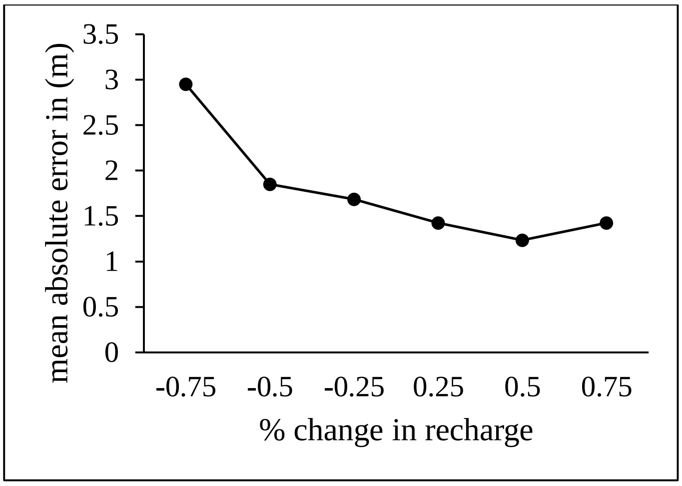
5.8 SENSITIVITY ANALYSIS

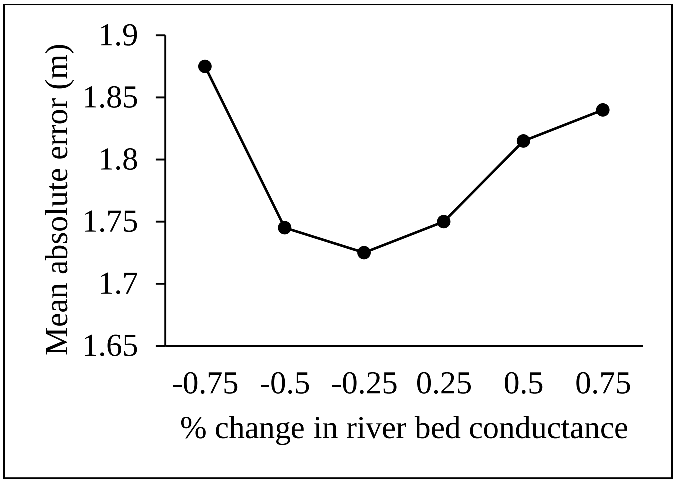
In order to find out the parameters which are affecting the most on model results, sensitivity analysis has been conducted. The parameters such as hydraulic conductivity of the basin, its specific yield, the recharge or precipitation received on the basin, and also river bed conductance has been increased as well as decreased by 25%, 50% and 75% and its variation of results of the model has been analysed. For comparing the influence of various parameters, a plot of Mean Absolute Error versus change in parameter was drawn. By dividing the sum of absolute value of error (magnitude of error) with the number we get mean absolute error.

The parameter hydraulic conductivity is increased and decreased by 25%, 50%, 75% each and mean absoluter error of observed and simulated head is found. From the graph 5.8 (A) it can be inferred the mean absolute error varies from 3.85 m to 1.35 m when the parameter varied between the range -75% to 75%. i.e., mean absolute error varies considerably with a very small change in hydraulic conductivity. When the specific yield is varied in the same range which is -75% to 75%, the mean absolute error was found to vary from 1.95 to 1.75. (Figure. 5.8 B) This infers that the sensitivity of the parameter specific conductivity is lesser when compared with hydraulic conductivity. When percentage recharge is varied between -0.75 to 0.75 it was found that the mean absolute varied in the range between 3 m to 1.5 m which infers that the parameter is medium sensitive (Figure 5. 8 C). While river bed conductance is found to be less sensitive as the mean absolute error varied from 1.87 m to 1.74 m when the river bed conductance varied between -75% to 75%. (Figure 5.8 D). Hence the parameter hydraulic conductivity is considered as the most sensitive parameter and the rate of recharge is medium sensitive while the changes in other parameters are not showing much significance on the model.


Mean absolute error (m)
5
4
3
2
1
0
-0.75
-0.5
-0.25
0.25
0.5
0.75
% change in hydraulic conductivity
(A)


mean absolute error in (m)
1.95
1.9
1.85
1.8
1.75
1.7
1.65
-0.75
-0.5
-0.25
0.25
0.5
0.75
% change in specific yield
(B)


mean absolute error in (m)
3.5
3
2.5
2
1.5
1
0.5
0
-0.75
-0.5
-0.25
0.25
0.5
0.75
% change in recharge
(C)



(D)

Figure 5.8 Sensitivity analysis conducted for the sub-basin by varying (A) Hydraulic conductivity, (B) specific yield, (C) recharge, (D) bed conductance.

5.9 CONCLUDING REMARKS

The finite difference model MODFLOW is successfully used in the simulation of groundwater model situated in the tropical region which is getting lots of monsoon rains. The study area comprises of a shallow unconfined aquifer with lateritic soil and fairly good potential of groundwater. The conceptual model of aquifer in the lateritic formation which is getting plenty of monsoon rains was prepared. The groundwater head was simulated and compared with the observed head. The model was calibrated and validated.

The result of calibration is analysed for the reliability using both analytical or statistical and graphical methods. The analysis results show that a fairly good accuracy ($R^2 > 0.89$) exists between the observed and simulated water levels. The RMSE values as well as the NSE values also show that model is reasonably good.

Model calibration was done successfully, and obtained the parameters as recharge co efficient as 10% of total rainfall, porosity - 30% and river bed conductance - 15m/day. Also the horizontal conductivity was estimated to be 7m/day. The validation of model was done with a reasonable precision of R^2>0.74 for further application.

The outcomes of sensitivity analysis show the hydraulic conductivity of the aquifer is the most sensitive parameter while recharge rate has no much significance in the current study.

CHAPTER 6

GROUNDWATER MASS TRANSPORT MODEL

6.1 GENERAL

Even though management of waste hierarchy is considering landfilling as an option with last priority, the sanitary landfilling in a controlled way is preferred universally for discarding both municipal and industrial waste. Although there are many benefits in landfilling like it is the cheapest alternative in terms of initial cost and management costs, the main disadvantage of landfills are generation of highly concentrated leachate, where its quantity, its volumetric rate of flow and chemical composition are highly unpredictable. In addition to that, outputs from landfills stimulate great impacts as well as risks to the environment thereby forcing concerning authorities to enforce more strict constraints.

The contaminants when enter the groundwater system, the fate of the contaminant and its concentration is affected by a number of processes such as physical chemical or biological which can take place between pollutant and the elements in the subsurface environment. Movement of contaminant and dispersion within the aquifer spreads the pollutant over a wider area. The groundwater flow model can be used as an effective tool not only forecasting hydraulic head but also to predict concentration change for the evolution of pollutant plume and for evaluation of the strategies to be adopted for the protection of aquifer. Even though numerous methods are there for the simulation of groundwater flow and transportation of contaminants, the most popular methods are finite difference method and finite element method. MT3DMS uses a modular structure similar to that implemented in MODFLOW. It is possible to simulate advection, dispersion and sink/source mixing and chemical reactions in this model structure independently without setting aside the memory space of computer for unused alternatives. MT3DMS assuming that the flow field will not be affected by the changes in concentration field which permits the user to build, calibration and validation of the flow model separately. Once the simulation of flow is over, MT3DMS gets the computed hydraulic heads and various flow terms which are saved by MODFLOW to place the foundation for modeling and forecasting behaviour of transport of solute of groundwater systems.

6.2 PRINCIPLES AND CONCEPTS OF MT3DMS

The MT3DMS is the modular three dimensional multi species transport model which can accommodate add on packages. It is assumed that the flow will not be affected by the variation in concentration of the pollutant in the flowing liquid. (Zheng and Wang, 1999). The modular structure of MTDMS is much similar to that of MODFLOW as it consist of one main program and it is accompanied by number of sub program called modules which are grouped as packages such as advection, dispersion, chemical reaction so on. MT3DMS is said to be exceptional because it comprises of solution techniques for 3 main classes like finite difference, particle tracking and higher order finite volume methods so that it can solve wide range of transport problems with high accuracy.

The transport of solutes in the saturated zone is governed by the advection dispersion equation in which for a porous medium with uniform porosity distribution is formulated as follows

$$\frac{\partial c}{\partial t} = -\frac{\partial}{\partial x_i}(cv_i) + \frac{\partial}{\partial x_i}\left\{D_{ij}\left(\frac{\partial c}{\partial x_j}\right)\right\} + R_c \quad i, j = 1,2,3 \ldots\ldots\ldots\ldots\ldots\ldots (6.1)$$

Where *c* is the concentration of the solute;

Rc is sources or sinks;

Dij is the dispersion coefficient tensor;

vi is the velocity tensor.(Kumar, 2012)

The term which represents chemical reaction in the above equation which is $\frac{\partial c}{\partial t}$ comprise of the general effect of biochemical reaction and geochemical reaction on the fate and transport of the contaminant. Or the above equation means that in a given time, the change in storage of mass either sorbed or dissolved will be equal to difference in the mass inflow and mass outflow because of advection, source or sink, dispersion and chemical reaction. The governing equations for the transportation assume single porosity for the medial ant it is taken as effective porosity which is lesser than the actual porosity. The hydraulic head is obtained from the solution of groundwater flow model MODFLOW. The advection term $\frac{\partial}{\partial x_i}(cv_i)$ means the transportation of the miscible pollutant which is having same velocity of groundwater. Dispersion is the spread of pollutant to a bigger area. MT3DMS allows using 2 transverse dispersivities one in horizontal direction and the other in vertical direction. The source or sink term represented by Rc in the above equation refers to amount of solute mass which is entering from source to the domain of model or which leaves from the domain model to sink. MT3DMS is also capable to simulate equilibrium or non-equilibrium of liner as well as nonlinear sorption, radioactive decay, biodegradation and even complicated chemical reactions by adding some of the add-on packages.

6.3 APPLICATION OF MT3DMS IN THE STUDY AREA

The MT3DMS model necessitates the model from MODFLOW within its conceptual structure. MT3DMS takes up the structure created for hydraulic head from MODFLOW. Hence the comprehensive report to describe the MT3DMS is excluded here. So for MT3DMS, discretization of domain, sources, sinks, boundary conditions are all adopted as that from previous chapters and included in MT3DMS.

6.3.1 Initial condition

In the governing equation of mass transport model, the transient change in the concentration of solute is described. Hence in order to obtain the solution of the governing equation, initial conditions are essentially needed. The concentration of chloride is an important indicator of leachate pollution. The physico-chemical parameters of the leachate of Vamanjoor landfill was measured during the month of October 2016 (Table 4.1). The measured concentration of chloride was given as the input value for concentration of percolated solution. The resultant simulated concentration of chloride level is compared with the observed chloride concentration of groundwater of observation well. The source of pollution is being set as a point source where the continuous injection of pollutant take place which means the pollutant is entering the aquifer continuously.

6.3.2 Transport and density parameter

Along with the aquifer parameters, in order to solve the mass transport equation, the transport parameter such as hydrodynamic dispersivity is needed. Initially it is assigned according to the available data which later on adjusted using trial and error method during calibration. It was assumed that longitudinal dispersion is much larger than the transversal dispersion for transport simulation. Again as per Cobaner et al., 2012 the horizontal transverse dispersivity of 1 / 10th of longitudinal dispersivity. The longitudinal dispersivity ranges between 15 to 150 m as suggested by Bhosale and Kumar (2001) for similar conditions of aquifer.

The sorption and de-sorption of the contaminant is assumed to be a simple function of the contaminant concentration. The relationship between concentration and sorbed mass is defined by a linear isotherm. This theory assumes that the sorption is instantaneous. By contrast, a rate-limited sorption option is also available. Turning on sorption has the effect of slowing the rate that the plume moves through the system. This effect can be expressed as a retardation factor that represents the ratio of the ground water flow rate to the plume migration rate. The retardation factor is computed as:

$R = 1 + \frac{\rho Kd}{n}$……………………………………..(6.2)

Where ρ = bulk density of laterite soil taken as 19.5

Kd = distribution coefficient (slope of the isotherm) = 0.17 (from figure 4.13)

n = porosity taken as 0.3

6.4 MODEL CALIBRATION

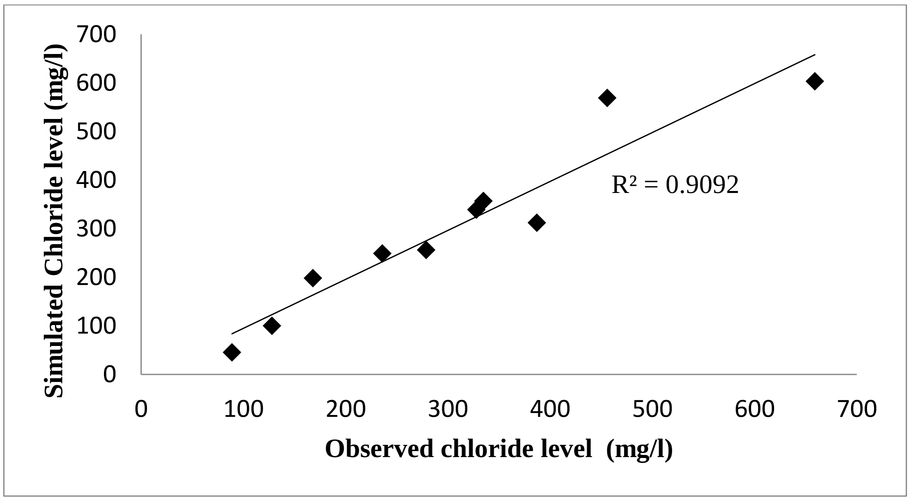
6.4.1 Calibration for transport parameter

As the parameter for the aquifer obtained from running the program MODFLOW are directly used in running MT3DMS, it is necessary to know about the authentication of the model through calibration. The process of calibration of transport parameters is executed like that of the flow parameters. The accuracy was checked by using the same four evaluation techniques that was being used in flow model.

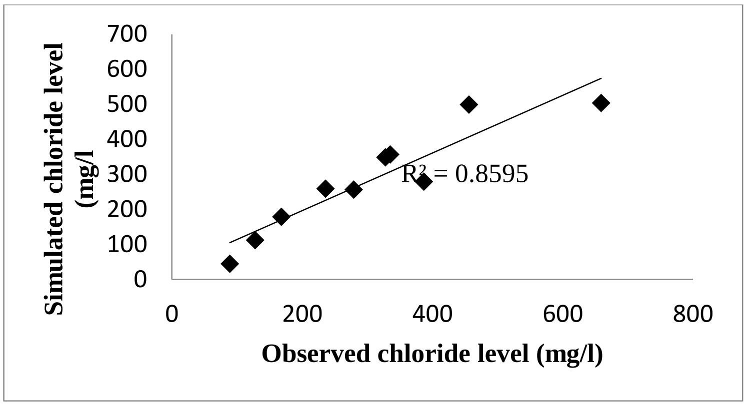
The chloride concentration is measured and compared with the values of the previous researchers and was taken for calibration. The steady state simulation was done by comparing the observed and simulated values of chloride level during the month of October 2016. The transient calibration was performed taking into account the seasonal performance of model. The R^2, RMSE and NSE values of the calibration period are listed in the table 6.1.

Table 6.1 Solute transport efficiency values

Month	R^2	RMSE	NSE
October 2016	0.909	98 mg/l	0.87
May 2017	0.859	134 mg/l	0.912
May 2018	0.757	178 mg/l	0.856



(A)



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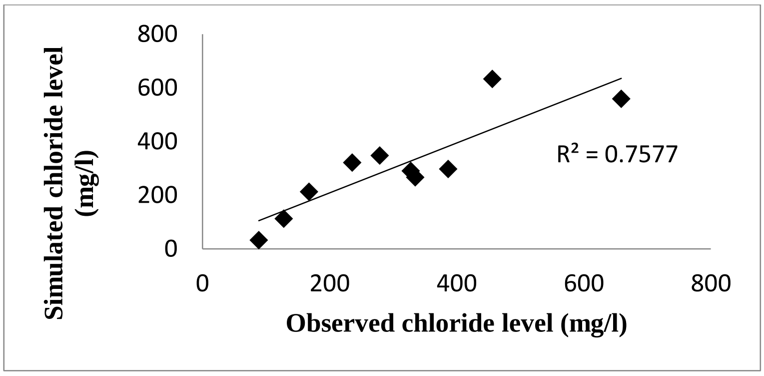


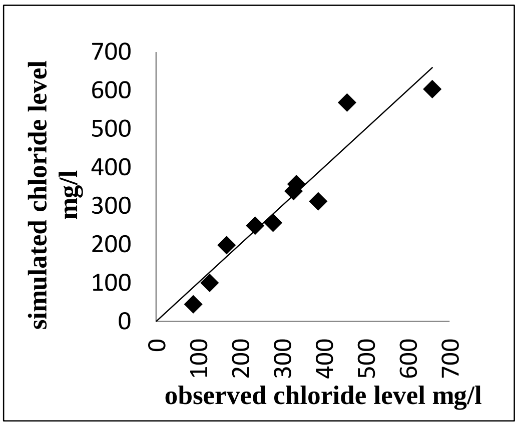
(C)

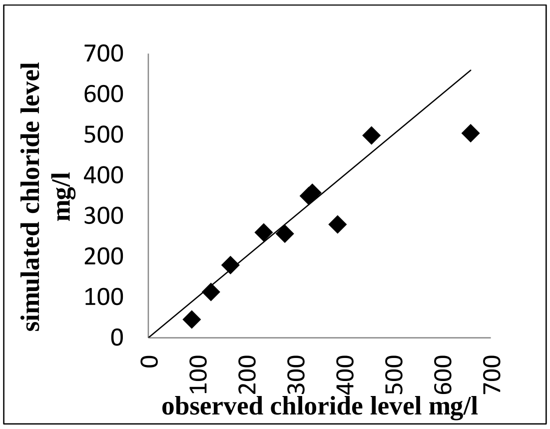
Figure 6.1 Scatter plot of observed vs. simulated chloride for the month October (2016 (post monsoon), May 2017 (pre monsoon), May 2018 (pre monsoon)

The observed chloride level is plotted against simulated values along X and Y axis. A line with slope equal to 1 passing through origin is drawn. It is evident from the figure 6.1 that the points are lying close to the line. Some observed chloride level near the river is slightly high which may be due to the sea water intrusion during summer. The solute transport parameters which were obtained after calibrating successfully is listed in the table 6.2. Figure. 6.2 shows that the observed and simulated chloride level for the month of October 2016 (post monsoon), May 2017 (pre monsoon) and May 2018 (pre monsoon). Figure 6.3 show the plan view of simulated chloride distribution in the study area on seasonal basis. (October 2016-post monsoon, May 2017-premonsoon, May 2018-post monsoon). A good agreement was found between simulated and observed chloride level for the situation prevailed.

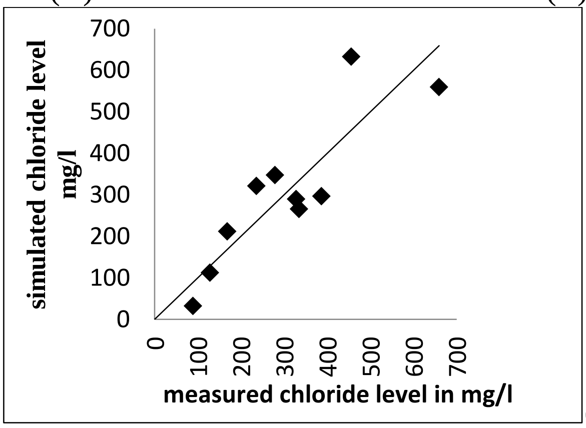
Table 6.2 Solute transport parameters

Parameter	Value
Hydraulic conductivity in m / day	15
Coefficient of recharge in %	10
Effective porosity in %	30
Longitudinal dispersivity in m	25
Transverse dispersivity in m	2.5



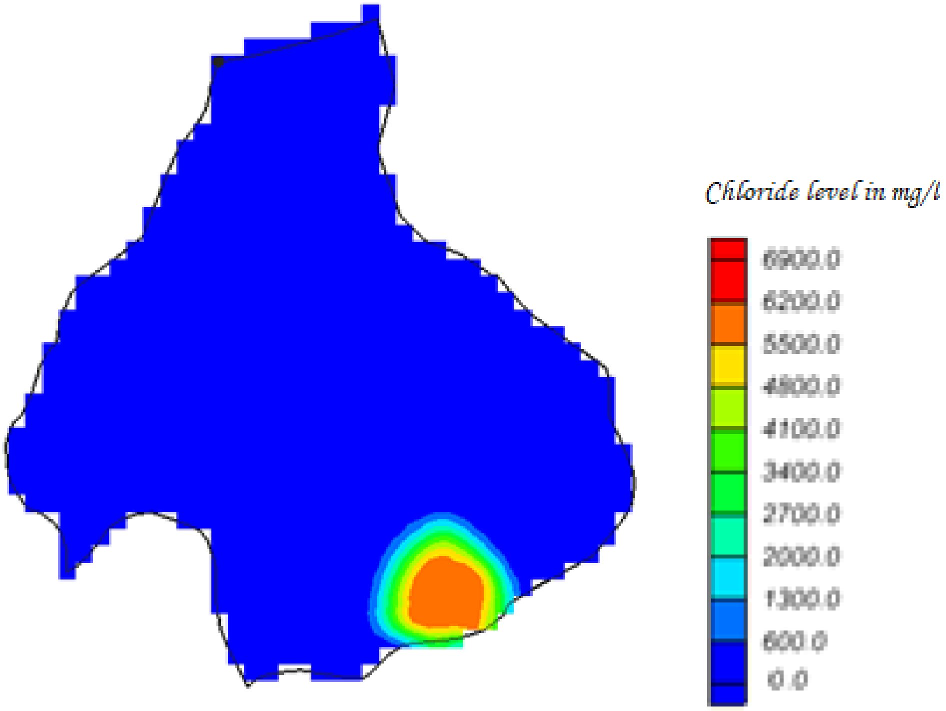


(A) (B)

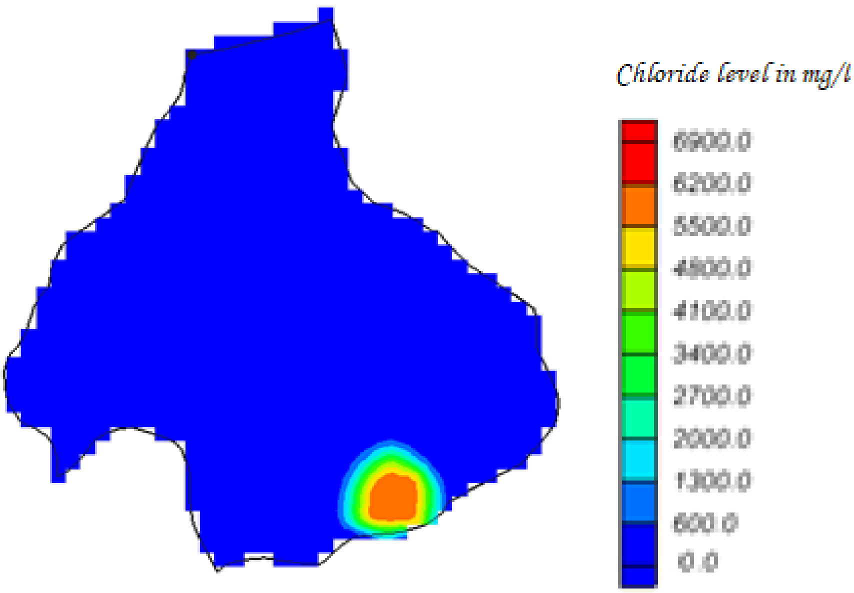


(C)

Figure 6.2 Simulated and observed chloride level during (A) October 2016 (post monsoon), (B) May 2017 (pre monsoon), (C) May 2018 (pre monsoon)


Chloride level in mg/l
6900.0
6200.0
5500.0
4800.0
4100.0
3400.0
2700.0
2000.0
1300.0
600.0
0.0

(A)


Chloride level in mg/l
6900.0
6200.0
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4100.0
3400.0
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2000.0
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600.0
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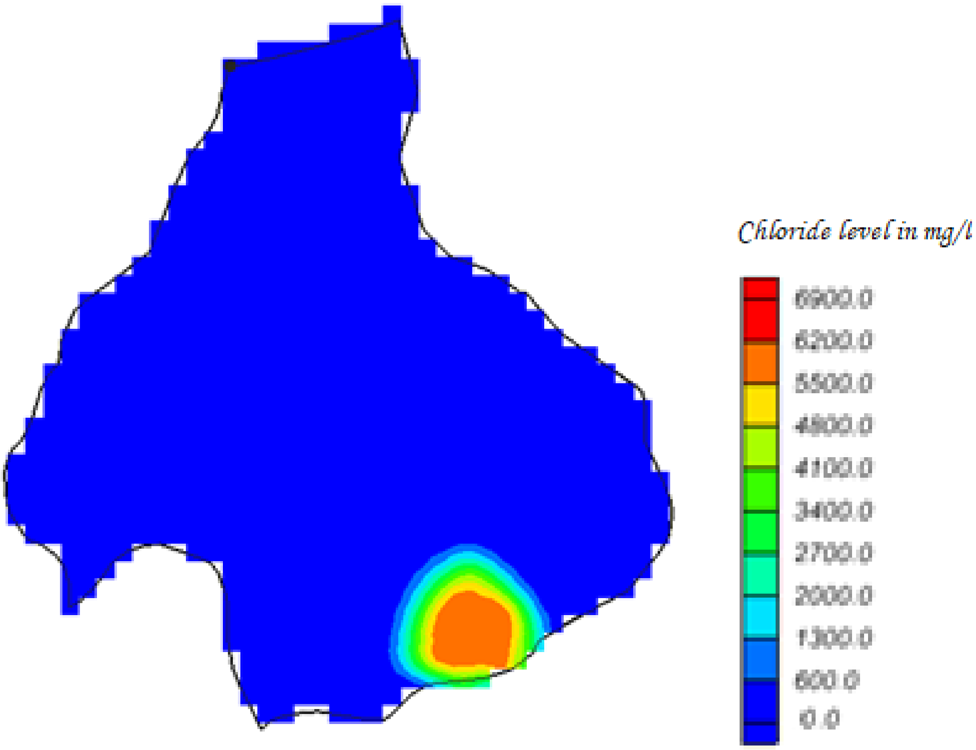
(B)



(C)

Figure 6.3 Plan of simulated chloride distribution during (A) October 2016 (post monsoon), (B) May 2017 (pre monsoon), (C) May 2018 (pre monsoon season)

6.5 MODEL VALIDATION

In order to apply the calibrated solute transport model for future scenario, validation of the model was carried out by taking the data of observation wells obtained from Karnataka State Pollution Control Board which was collected personally during the period 2016 - 2018. As there were only 6 wells falling in the study area, the values of chloride levels of those wells were only taken for validation. The R^2 value of 0.77 was again found to be reliable with that of calibrated results and hence model is considered to be trustworthy for future prediction.

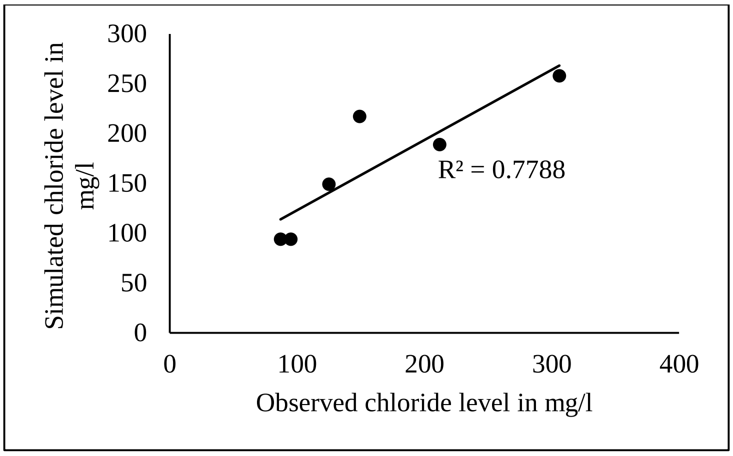


Figure 6.4 Simulated and Observed chloride level during period 2016 -2018

6.6 SENSITIVITY ANALYSIS

The model performance may be analysed through sensitivity analysis of parameter of aquifer. The groundwater investigator gets a better understanding to the responses of the systems to the changes in parameter. Increment and decrement of 25 %, 50% and 75% were applied to the parameters hydrodynamic dispersion coefficient and executed various simulations. In the simulations, the horizontal transverse dispersivity is taken as 1 / 10^{th} of the longitudinal dispersivity. From the graph it can be seen that the maximum variance is about 42 mg / l which show the parameter hydrodynamic dispersion sensitivity is lesser.

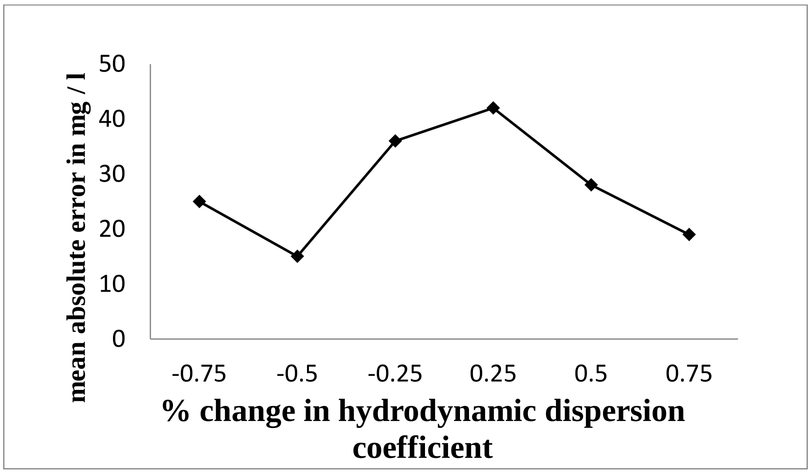


Figure 6.5 Sensitivity analysis conducted for the sub-basin for solute transport model.

6.7 CLOSURE

The solute transport model MT3DMS was successfully applied to simulate the contaminant transport of the study area. Since MT3DMS model involves the model structure involved in MODFLOW, the model domain was not altered. In MT3DMS, the flow and density parameters were introduced and predicted the scenario which could happen in future.

The model was calibrated and validated with reasonable precision coefficient of determination ($R^2 > 0.7$) which shows that the model performance is good. The transport parameters are calibrated and standardized in the study area.

The sensitivity analysis shows that the parameter hydrodynamic dispersion coefficient is negligible.

CHAPTER 7

PREDICTIVE SIMULATIONS

7.1 GENERAL

Environmental degradation due to rise in waste generation because of rapid increase in population as well as economic growth is one among major problems of developing countries like India. As per Central Pollution Control Board, municipal waste generated in India during 2011-2012 was estimated to be 127486 tons per day out of which only 12.45% around 5881 tons per day is treated whereas the rest is unscientifically dumped without treating in open spaces. (Joshi and Ahmed, 2016). Air pollution, water pollution, and soil pollution due to poorly managed landfill leads to risks for many diseases, disability and even death which will hamper growth of economy and development in developing countries. (Dermatas, 2017).

Mangaluru generates 226 tons municipal solid waste per day of which 200 tons is collected and disposed to a landfill located at a distance of 15 km from the city. The landfill at Vamanjoor is a non-engineered one which is having bottom liner but there is no leachate collection and treatment system. Thus, all the leachate formed at the bottom, finds its trails into the neighboring environment .As Vamanjoor is a home for many educational institutes and also a residential area urgent attention needs to be paid to the ground water of this region. The present study has taken up with the objective to find out the trail of contaminant and also possible remedial measures which can be adopted so as to prevent further contamination. In Vamanjoor the complication is mainly due to mixing of leachate with the groundwater. In the present study the ability of nano iron to remediate leachate has been analysed.

7.2 DESCRIPTION OF POSSIBLE SCENARIOS

In the earlier chapters, the calibration and validation of MODFLOW and MT3DMS has been done and has been used to find the groundwater head and also simulated the chloride distribution. In this chapter, MT3DMS is used to predict the solute transport for future anticipated scenarios

SCENARIO 1: REAL TIME SIMULATION OF PRESENT CONDITION

The model was run to find out the current spread of contaminant. Here landfill is assumed as a point source of contaminant which is ejecting pollutant plume continuously and no control measure is adopted to prevent contaminant. The model is run for the present abstraction rate, calibrated recharge rate. Here annual average rainfall of 3810 m is considered. The possible spread of the contaminant is as shown in the figure 7.1. The contaminant plume has reached a distance of 1 km from the landfill in downstream direction. Spread is taking place in the direction of flow. The result is supported by the field data where the wells within 1 km radius are already polluted. Also the model predicts that the pollutant plume is expanding at a rate of 15cm in a day. Here we can see that the pollutant concentration is decreasing as we go away from the landfill. This may be due to the fact that due to the gravitational movement, the leachate movement is hindered by the soil mass. An additional factor can be the adsorption by laterite soil. As time increases, the penetration of leachate increases and it goes deeper and disperses over a longer distance.

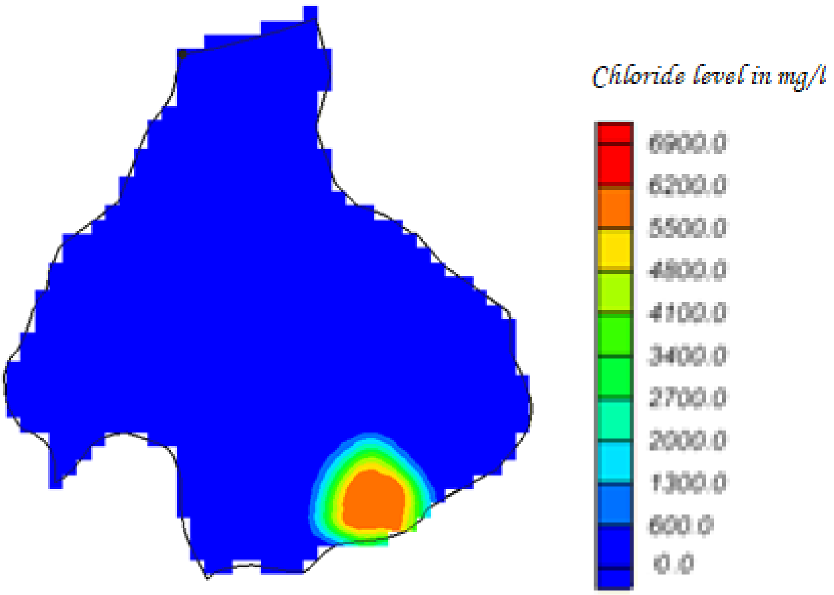
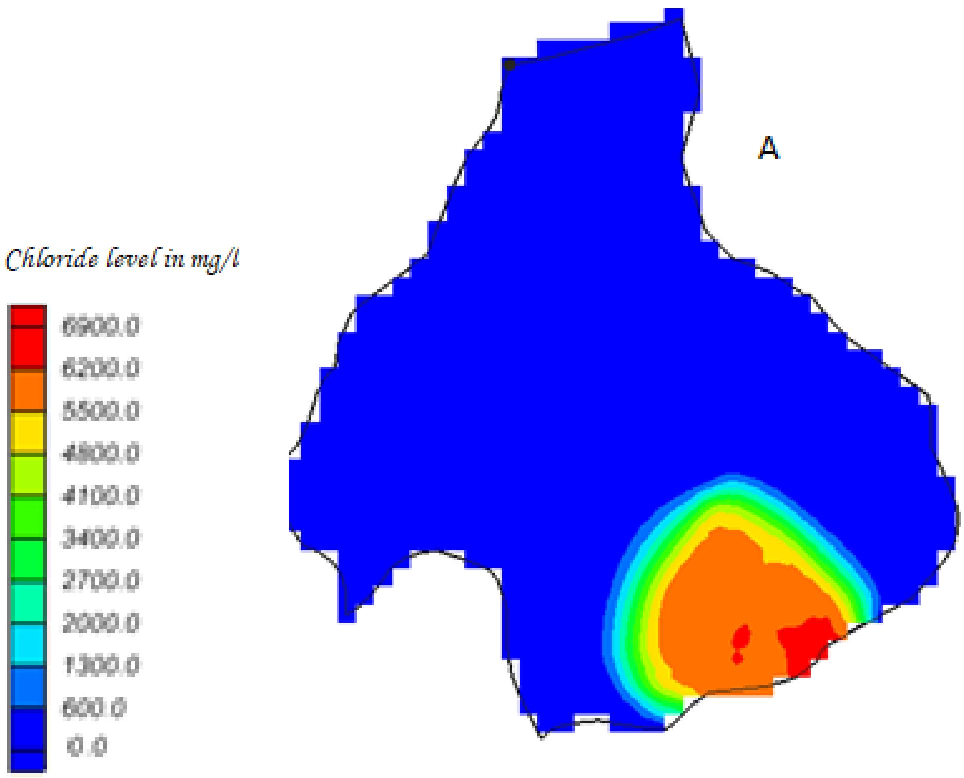


Figure 7.1 Spatial distribution of chloride concentration for the month May 2018

SCENARIO 2: REAL TIME SIMULATION OF PRESENT CONDITION FOR ANOTHER 15 YEARS

The model was then applied for forecasting the spread of contaminant for another 5, 10, 15 years with existing level of emission of chloride from landfill (figure 7.2). The present abstraction rate, calibrated recharge was taken to run the model presuming that the present conditions will prevail for another 15 years. The results of the above study show that trail of contamination is expanding with a velocity of 0.15 m/day and will reach a distance of nearly 1.8 km in another 10 years. The graph (figure 7.3) shows the increase in chloride level in groundwater at end of 5, 10 and 15 years which clearly show that the concentration of pollutant in the observation wells is increasing by more than 50% unless it is treated. But the area of the high concentration of pollutant which is near the landfill is not increasing in the next 5 years which may be due to the phenomenon adsorption by lateritic soil. In this simulation it is assumed that the aquifer is getting recharged with a recharge coefficient of 10% and the no measures has been adopted to prevent the contaminant spread.



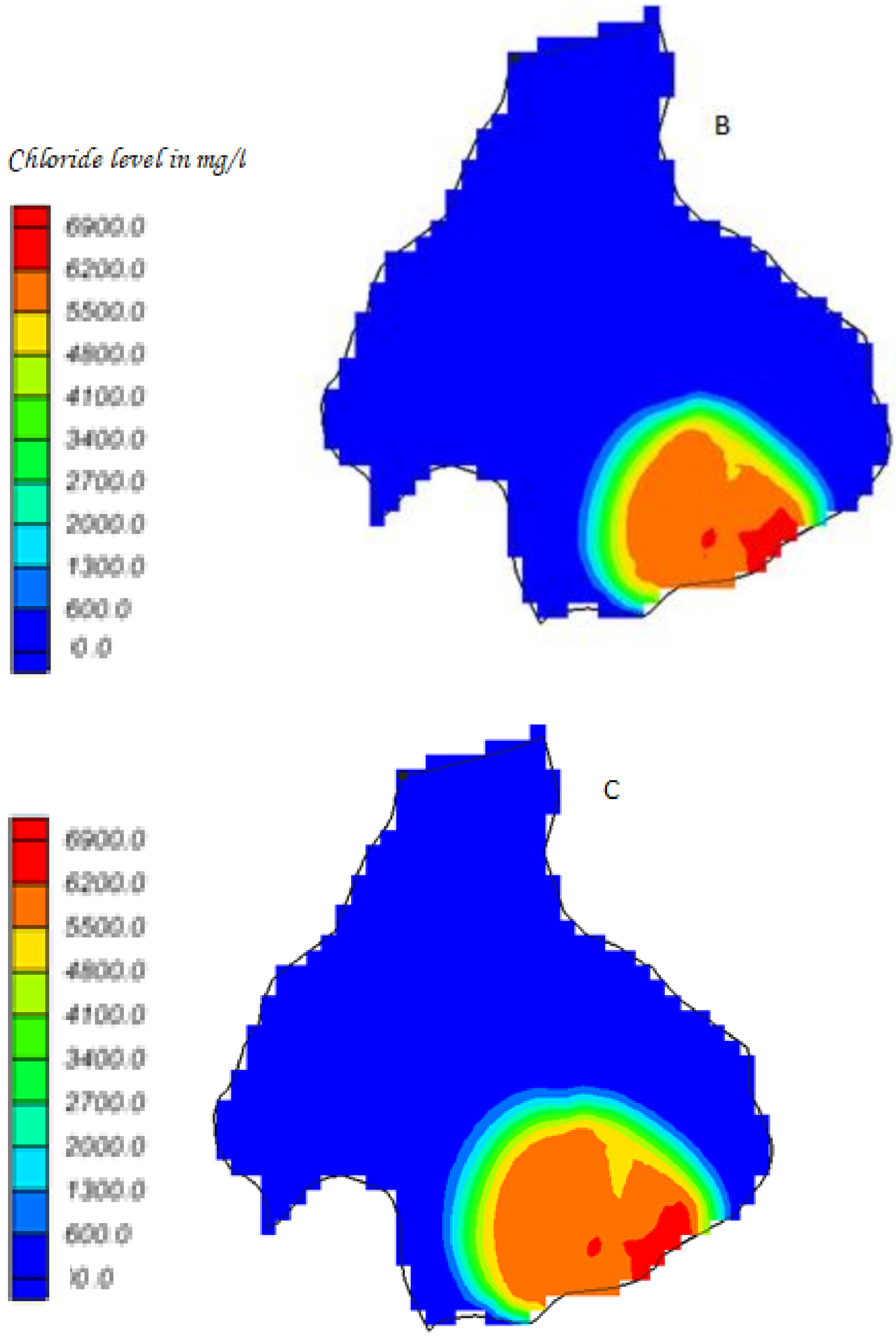


Figure 7.2 Spatial distribution of chloride concentration after (A) 5 years, (B) 10 years, (C) 15 years

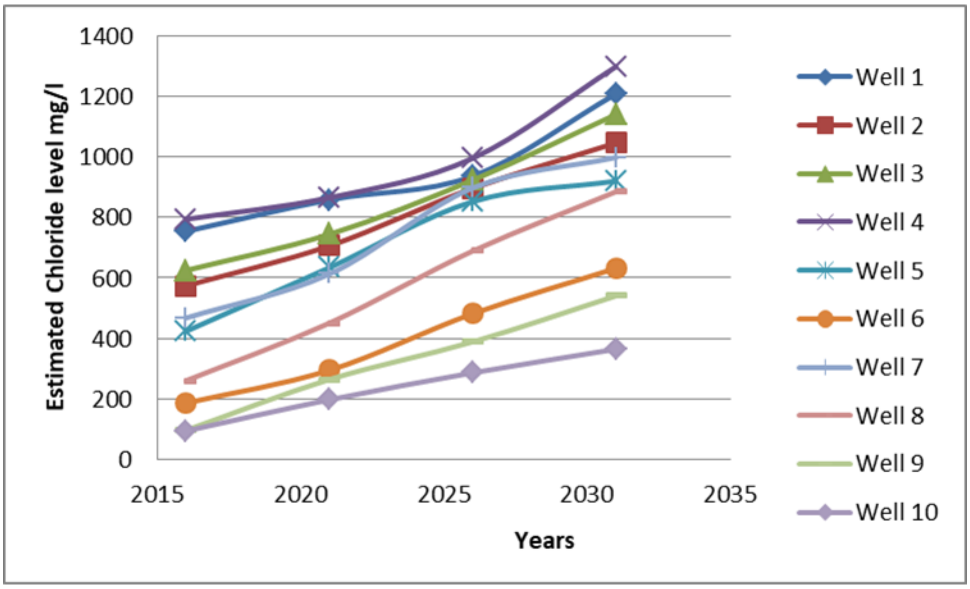


Figure 7.3 Estimated level of chloride in the observation wells at the end of 5 years 10 years and 15 years

SCENARIO 3: SIMULATION FOR MAXIMUM RAINFALL

The figure 7.4 shows the scenario in case of maximum rainfall and for the existing pollutant concentraion is continued to be emitted from landfill. In the last 15 years a maximum annual rainfall of 4810 m had occurred in the year 2010 in the study area. In the recent years Mangaluru is receiving large amount of precipitation during monsoon. It is know that the coefficient of recharge is one among the factors which affect the leachate generation and propogation. Taking into consideration such possibility which can cause an increase in recharge rate this scenario is taken up for simulation. In this scenario the rainfall was taken 4.81 m and run the model so that the resulting simulation shows that the spread of the contaminant is rapid and will reach nearly 1.5 km around the landfill within 5 years. This is because during such heavy rainfall, hydraulic head will be increased, and hence there will be an increase in downward flow of contaminant from the site where landfill is located.The figure. 7.5 gives a comparison of chloride level for the situation of normal rainfall and high rainfall.

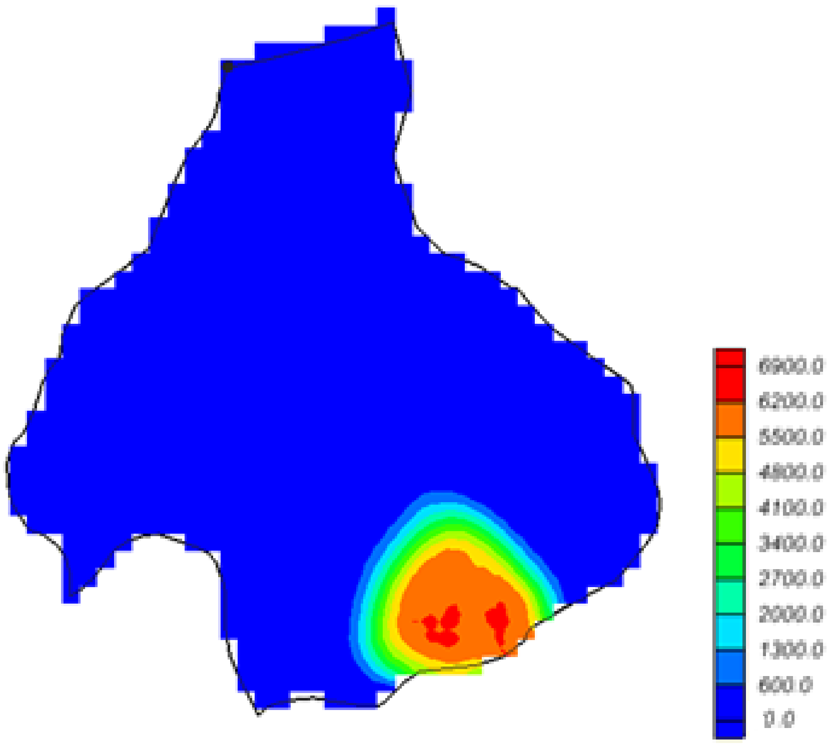


Figure 7.4 Spatial distribution of chloride concentration for maximum rainfall

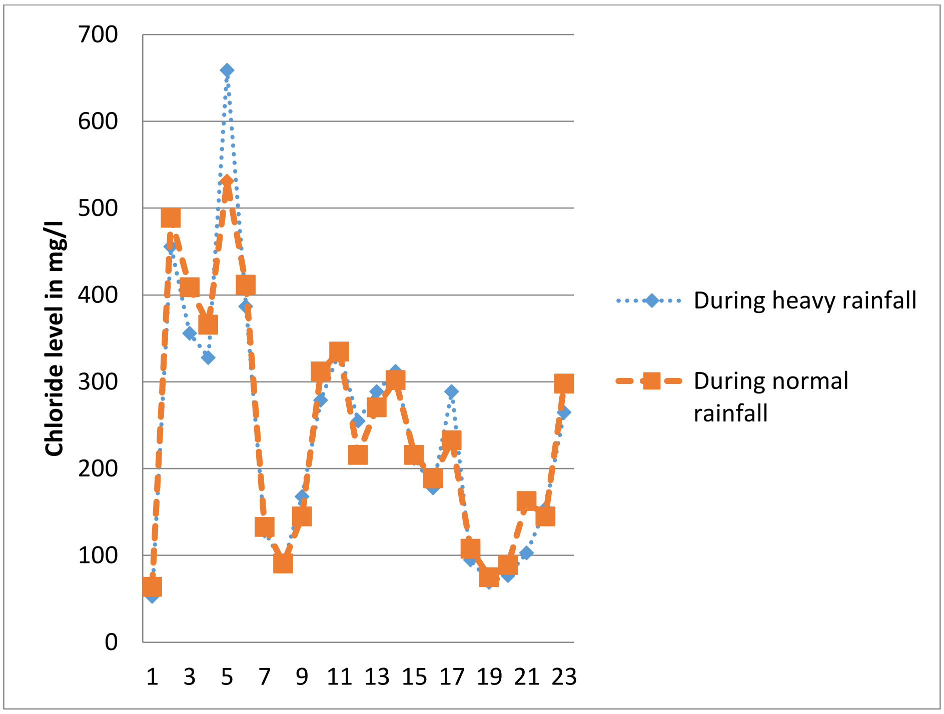


Figure 7.5 Comparison of chloride level during normal and heavy rainfall

SCENARIO 4: WHEN PERMENANT REACTIVE BARRIER OF NANO IRON IS INSTALLED

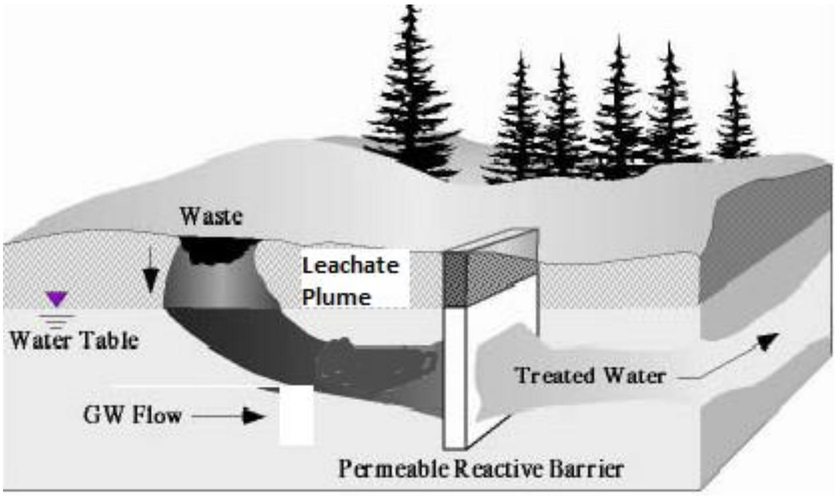


Figure 7.6 Application of permeable reactive barrier for treatment of leachate

The figure 7.6 shows the predictive scenario with and without treatment by permeable reactive barrier using iron nano particle around landfill. From column studies it was proved that iron nano particle coated with starch can reduce the COD concentration by 65%. The COD of leachate from landfill was found to be 14500 mg / l. In this scenario in order to compare the effect of remedial measure which can be adopted at site, COD of 14500 mg / l is given and ran the model to get the present scenario which is when the control measure is not adopted. The resultant COD of observation well simulated by the model is found. Then the model is ran by taking COD of 9500 mg / l (which is after treatment with nano iron) was given to the cells of landfill and ran the model to predict the pollutant concentration at observation wells. The graph (figure 7.7) gives a comparison between the distribution of COD level with and without treatment with permanent reactive barrier of nano iron. It can be seen that the pollutant concentration has been reduced to less than 400 mg / l at 1 km distance from landfill.

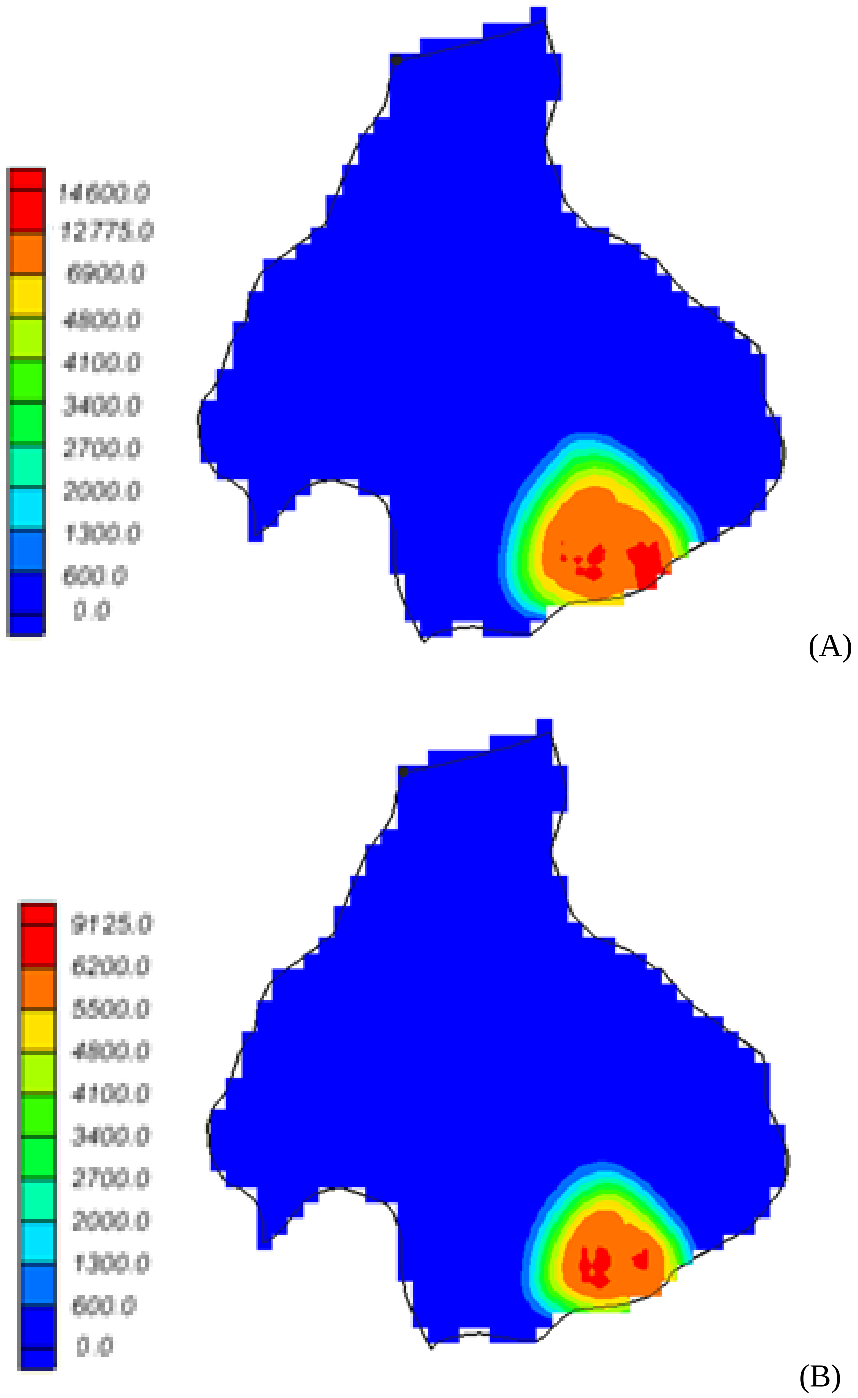


Figure 7.7 Spatial distribution of COD (A) before and (B) after installing permeable reactive barrier around landfill

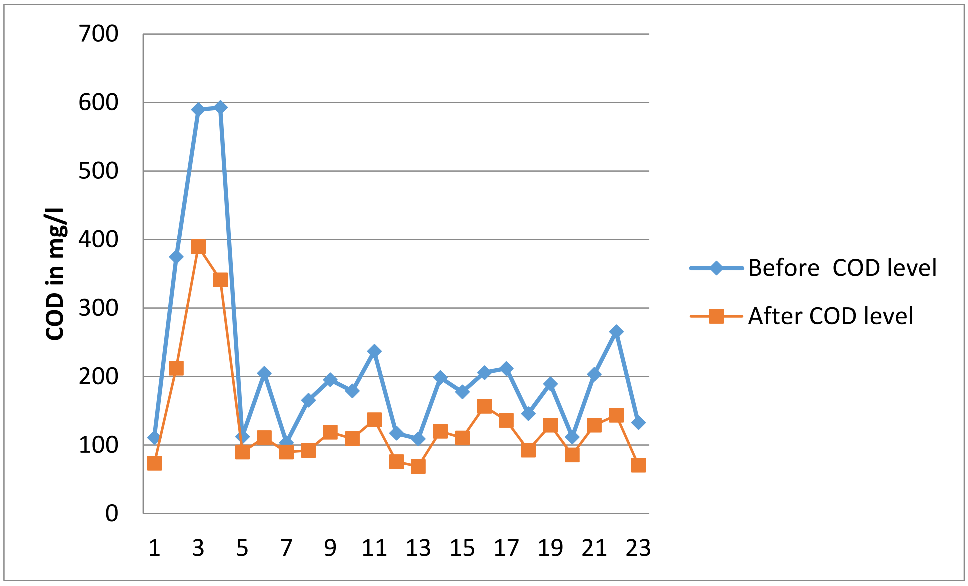


Figure 7.8 COD level before and after installing reactive barrier

7.3 IMPACT OF DIFFERENT SCENARIOS

The model after calibration and validation was used to predict the spatial and temporal impacts of four scenarios of the vulnerability of the aquifer for the contamination of leachate. It was found that if untreated the spread of contaminant will reach to a longer distance.

7.3.1 Temporal impacts of scenario simulation on the aquifer

The reaction of aquifer during 15 years simulation period is shown by presenting graphically. It can be seen that the pollutant plume is continuously expanding if the present emission continues. The longest expansion of plume will reach 2.2 km in 15 years but the area where high concentration of pollutant exist is not expanding in 10 years which may be due to the adsorption of laterite soil and also due to the recharge from the river at downstream. With the increase in recharge we find as the point source is emitting pollutant continuously, during heavy rains, the pollutant plume will expand in a faster way which is evident from the observation wells during monsoon. But after considering the remedial measure of installing permeable reactive barrier it was seen that the concentration of the pollutant in the observation well downstream can be considerably reduced.

7.3.2 Impact on chloride level in observation wells

In the present study chloride is taken as an indicator of the pollution. It can be seen the chloride concentration is increasing as it is continuously ejected from the landfill which is considered as the point source which emit the pollutant. This emission of pollutant has a serious impact on aquifer system. From the graph it can be seen that the pollutant will reach at the well located at a distance of the 2 km radius from the landfill in another 10 years. When the recharge is increased due to increase in precipitation, the pollutant plume will expand in a rapid way. But the high concentration area of chloride is expanding in a comparatively slower way reason may be due to phenomenon like dispersion, the property of sorption of lateritic soil and also the recharge from the river may be the retarding factors.

7.3.3 Spatial impact

It can be seen that the chloride of groundwater in the observation well located near the landfill is more, while the one which is located further is less. This clearly indicates that the landfill is the index of pollution which injects the pollutant continuously to the aquifer. As stated earlier the chloride level in the well located away from landfill is less which can be due to the dispersion of pollutant plume and also due to the adsorption by lateritic soil which can adsorb nearly 12% of pollution which is experimentally proved. If the discharge from landfill continues and no control measures are adopted, then the pollutant plume may reach the wells located further. Also if the precipitation or rainfall if increased, the pollutant plume will move in a faster way and reaches the well located in farther. It is seen that by installing the reactive barrier, the pollutant plume can be effectively prevented by reaching the well located at a distance. Hence it is advisable to install the permeable reactive barrier so that the pollutant plume can be controlled effectively.

7.4 CLOSURE

The model after calibration and validation is applied for the evaluation of general regional impact on the groundwater system for 4 scenarios. The simulations are performed for reasonably a long period which is for 15 years (2018-2033). The scenarios were planned keeping in mind the probable stresses that may be exerted on the aquifer in the coming future. It can be seen that the pollutant plume is expanding in all the cases except for the last scenario that is after the installation of permeable reactive barrier around the landfill. According to the district corporation the city needs around 160 million litres of water per day and the main source of water is from Thumbe vented dam. But during severe summer, the city is facing water crises owing to poor water collection in catchment area due to which the industries in the area has to downside their operations. Vamanjoor landfill has got a bottom liner, but there is no system for the collecting leachate and hence it is getting disposed without treatment. Thus, all the leachate formed at the bottom, finds its trails into the neighbouring environment polluting the underlying aquifer. Hence such a study is of immense importance in the view of prevention of pollution. Groundwater being a precious source of water needs to be conserved without polluting it.

The scenarios which will affect the aquifer was analysed in various aspects considering the time dependent and space dependent variation of chloride level and finally impact of the remedial measure which can be adopted.

The study revealed that the contamination has spread for a distance of nearly 1 km from the landfill and plume is expanding at a rate of 0.15 m /day. By 15 years the plume will reach a distance of 1.8 km from the landfill. If permanent reactive barrier is installed the expansion of plume can be prevented and the pollutant at the observation well located at 1 km from landfill can be reduced to less than 400 mg /l. Hence installation of permeable reactive barrier with nano iron particles can be recommended as a remedial alternative in order to control groundwater pollution due to landfill leachate.

CHAPTER 8

SUMMARY AND CONCLUSIONS

Mangaluru City Corporation is collecting the waste on a daily basis and dumping it into a landfill at Vamanjoor located nearly 8.5 km from city center. The landfill has got a bottom liner, but the system for the collecting leachate is poorly managed and hence it is getting disposed to the neighboring environment without treatment polluting the underlying aquifer.

The current study has been considered with the focus on above matter and simulation of shallow coastal aquifer has been done in order to find out the extent of contamination by the leachate. A local survey was done to find the number of abstraction well of the sub basin. A total number of 68 abstraction well was found of that 23 observation well were chosen for the current study. Water quality analysis was done for the 23 observation well on seasonal basis. The leachate collected was analyzed for various physic-chemical parameters and the results showed that most of the parameters exceeded the IS specified standard for the disposal of waste. As the chemical and physical composition of the leachate changes with time synthetic leachate was prepared in the laboratory for the experiments to be conducted. The removal of chemical oxygen demand from synthetic leachate using nano iron was studied. Batch experiments proved that pH of solution was an important parameter while kinetics coefficients were directly related to pH with correlation coefficients $R^2 > 0.90$. The nano iron dosage of 2 mg/l enhances removal efficiency of COD beyond that dosage the effluent will have traces of iron beyond the limit which is undesirable. The kinetics of the experiments showed that it follows pseudo first order reaction kinetics. Because of the fast reaction kinetics and high removal efficiency, nano iron coated with starch has the fine potential to become an effective remedial agent in treatment of leachate. Furthermore due to its excellent removal efficiency shown during continuous fixed bed column studies, it can be used in permeable reactive barriers. The findings of the study can be further used for applying in the field.

The finite difference model MODFLOW is successfully used in the simulation of groundwater model. After doing successful calibration and validation, the spatial distribution of the water table is simulated. The result of calibration show that a fairly good agreement (R^2 > 0.78) exists between the observed and simulated water levels. After successfully calibrating the model, obtained the parameters as recharge co efficient as 10% of total rainfall, porosity - 30% and river bed conductance - 15m / day. Also the horizontal conductivity was estimated to be 7m / day. The parameters obtained are in agreement with the characterization studies carried out in this area. The validation of model was done with a reasonable precision of (R^2>0.74). The outcomes of sensitivity analysis show the hydraulic conductivity of the aquifer is the most sensitive parameter while significance of the recharge rate is moderate. The simulated model using MODFLOW was incorporated with MT3DMS to simulate contaminant transport of the area. The model was calibrated and validated with reasonable precision (correlation coefficient R^2> 0.7) which shows that the model performance is good. The sensitivity analysis shows that the parameter hydrodynamic dispersion coefficient is of negligible significance. The contaminant transport model MT3DMS was applied for simulating future anticipated scenarios such as finding the current level of contaminant spread, the spread of the contaminant after 15 years, increase in recharge, and when a reactive barrier is installed around the landfill

The main conclusions drawn from the investigation are presented below:

- The physico-chemical analysis of groundwater samples from the observation well reveals that the groundwater in 1 km radius around the landfill is polluted.
- The treatment of synthetic leachate has been performed using starch coated nano iron synthesized in the laboratory. By comparing the results of batch and column studies, it is evident that the starch coated iron nano particles has a good feasibility for in-situ remediation of leachate with a COD removal efficiency of nearly 68% from synthetic leachate. The reaction follows pseudo first order reaction.
- An effort was made for the simulation of response of the unconfined aquifer which receives plenty of monsoon rains with underlying lateritic soil, for future predicted scenarios arising due to the spread of contaminant from landfill. The

groundwater flow was simulated using MODFLOW and solute transport model was simulated using MT3DMS. The sorption of the laterite soil was considered as lateritic soil is a good adsorbent. The specific yield value and the transmissivity were obtained as 7.85 % and 213 m^2 / day respectively and also the horizontal hydraulic conductivity was set as 7 m / day. During the calibration, it was observed that the model performance was satisfactory with co efficient of determination $R^2 = 0.89$.

- The solute transport model MT3DMS was successfully applied to simulate contaminant transport from the landfill. After successful calibration and validation with coefficient of determination $R^2 > 0.7$, the transport parameters such as longitudinal dispersivity 25 m and transverse dispersivity as 2.5 m were obtained.
- The contaminant transport model MT3DMS was applied for simulating future anticipated scenarios and the predictive simulations shows that if the permanent reactive barrier of nano iron is installed the pollutant concentration can be reduced to 400 mg/l at the observation well located at 1 km from landfill.

LIMITATION OF THE STUDY

1. The vertical heterogeneity of the domain is not considered in the current study.
2. The validation of the model was possible at only a few locations because of the non-availability of spatial and temporally spread field observations.
3. The recharge considered here is only due to the precipitation obtained in the area. Any additional recharge is not accounted for the simulation of model.

SCOPE FOR FUTURE STUDIES

1. Effort can be taken so as to refine the three dimensional model which incorporates all relevant details of sub strata.
2. The water quality data from a downstream well could be maintained for a longer period so that the model can be calibrated and validated better.
3. The field study can be conducted to find out the actual removal efficiency of the contaminant using permanent reactive barrier of nano iron.

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LIST OF PUBLICATIONS

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1. Divya Anand, S. Shrihari and H. Ramesh (2018) Comparison of Column and Batch Reactor for Remediation of COD of Leachate Using Iron Nano Particle: *Journal of advanced research in dynamical and control system*,15, 220-223 2.
2. Anand D., Shrihari, S., & Ramesh, H. (2020). Predictive simulation of leachate transport in a coastal lateritic aquifer when remediated with reactive barrier of nano iron. *Groundwater for Sustainable Development,* 100382.

International Conference Papers:

1. Divya Anand, S. Shrihari and Ramesh H. (2016) "A Review Paper on Groundwater Contamination due to Migration of leachate from Landfill". *International Conference on Systems, Energy and Environment 2016, at GEC, Kannur Kerala* ISBN:978-93-8577-85-1
2. A. Divya, S. Shrihari and H Ramesh (2018) *"Modeling of the transport of leachate contaminant in a landfill site: A case study in Mangaluru*" Proceedings of the International Conference in emerging trends in Engineering, Science and Technology (ICETEST 2018) : in Emerging Trends in Engineering , Science and Technology for Society , Energy And Environment Editors : Rajesh Vanchipura, K S Jiji, CRC Press, Taylor and Francis Group
3. Divya Anand, S Shrihari, Ramesh H (2018) "*Study of Groundater Contamination due to landfill leachate in Mangaluru, India*". International Conference on Sustainable Technologies for Intelligent Water Management 2018, IIT Roorkee.