Investigation, Mapping and Treatment Techniques for Fluoride, Nitrate and TDS in Groundwater of Shekhawati Region (Rajasthan, India)

THESIS

Submitted in partial fulfilment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

by

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Pilani | Dubai | Goa | Hyderabad

BIRLA INSTITUTE OF TECHNOLOGY AND SCIENCE, PILANI

2017

Dedication

To my dear parents,

wonderful Sister

for their unconditional support

&

forces of Dark Nights

for

enlightenment over these years.

🜄🜃

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CERTIFICATE

This is to certify that the thesis entitled **“Investigation, Mapping and Treatment Techniques for Fluoride, Nitrate and TDS in Groundwater of Shekhawati Region (Rajasthan, India)”** submitted by **Arun Nihal Singh,** ID No. **2012PHXF025P** for award of Ph.D. of the Institute embodies original work done by him under our supervision.

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Acknowledgement

I would like to take this opportunity to convey my heartfelt gratitude and indebtedness to my Gurus for all their support, guidance and supervision during my research tenure. At the outset, I wish to express the deep sense of gratitude and sincere thanks to my Guru Dr. Anupam Singhal (Associate Professor) and Prof. Rajiv Gupta (Senior Professor), Department of Civil Engineering for their valuable guidance, encouragement, suggestions, and moral support throughout the period of this research work.

I express my deep sense of appreciation to BITS Pilani for providing all the necessary facilities and support to complete the research work. My special thanks to Prof. S. Bhattacharyya, Vice-Chancellor of the University, Prof. A. K. Sarkar, Director, BITS-Pilani, Pilani Campus for allowing me to pursue my research work successfully. I also express my gratitude to Prof. S.K. Verma, Dean, Academic Research and other faculty members of ARD for providing valuable support throughout the programme. I would like to take this opportunity to express my gratefulness to Prof. A. P. Singh and Dr. Shibani K. Jha, who are the members of Doctoral Advisory Committee (DAC), for their kind suggestions, motivation and moral support throughout the program both technically and personally. I would like to thank Prof. R K Mittal, HoD, Civil Engineering for their motivation during difficult times.

I am also thankful to all my professors notably Prof. S. B. Singh, Dr. Manoj K., Dr. Kamalesh Kumar, Dr. D. Bhunia, Dr. S. N. Patel, Prof. Anshuman, Dr. G. Muthukumar, Dr. A. Goel, Dr. Bahurudeen for their support and motivation throughout my studies at BITS-Pilani, Pilani Campus. I am also thankful to all laboratory and secretarial staff for their timely support. I also thank all my friends, especially Anuradha, Nikita, Priya, Amrita, Kanika, Rajesh, Gaurav, Srinivas, Himanshu, Pankaj, Rahul, Jitendra, Satish, Yash, Onkar, Dilawar, Tanmay, Nikhil, Bhakar and all others whose name are not here and have helped me during my Ph.D. Thanks are also due to all faculty and staff members of BITS-Pilani, Pilani Campus for helping me out at various times.

Last but most importantly, I thank my parents and my sister for their care and affection shown towards me to undertake this journey. My thanks are also extended to the universe that has enlightened me with the gift to see the truth beyond the boundaries as a part of the cosmic play. May, I would cherish happy moments spent at BITS Pilani campus for the whole life.

Arun Nihal Singh

Only 3% fresh water is available in the earth surface and rest (97%) is saline water which is present in ocean. Groundwater plays a vital role in our environment and economies as it occupies 30% of fresh water. Being a valuable resource, groundwater need regulations to conserve and protect its quality and quantity. Physico-chemical parameters are a major factor that controls the quality of water and ultimately controls the characterization of water and groundwater.

In this research study, groundwater analysis of Shekhawati region has been carried out. The samples are collected from 163 villages and town in pre and post monsoon season of year 2012. Sixteen physico-chemical parameters such as Temperature, Colour, Odour, Turbidity, pH, Phenolpthalein alkalinity as $CaCO_3$, Methyl orange alkalinity as $CaCO_3$, Total hardness as $CaCO_3$, Ca Hardness as $CaCO_3$, Magnesium hardness as $CaCO_3$, Chloride as Cl^-, Sulphate as SO_4^{-2}, Nitrate as NO_3^-, Nitrite as NO_2^-, Fluoride as F^-, and Total Dissolved Solids (TDS) are determined in the laboratory using the titration and spectroscopy method. The results show that, the concentrations of three parameters (Nitrate, Fluoride and TDS) are higher than the acceptable range and affecting the majority of wells. Hence, Nitrate, Fluoride and TDS have been chosen for detailed studies as many diseases (methemoglobin and fluorosis) are associated with these chosen parameters.

Following observation has been depicted from water testing report.

- 48.5% and 36.2% of wells have shown presence of Nitrate in groundwater within acceptable limit (IS:10500, 2012) during pre and post monsoon respectively.
- 26.4% and 38.0% of wells have shown presence of Fluoride in groundwater within acceptable limit during pre and post monsoon respectively.
- 46.0% and 51.5% of wells have shown TDS in acceptable range in during pre and post monsoon respectively.

The presences of minerals in soil of study area are responsible for higher concentration of Fluoride, Nitrate and TDS in water. The mineral sources are highlighted for these three parameters and 3D modeling depicts their association and distribution. The 3D models are developed by inverse distance (IDW) method. The plot derived from these models between parameter concentration and depth, which indicates the presence of four different layers up to 300 *m* depth.

Knowing the alarming condition of study area, an attempt has been made to find the solution that can reduce the higher values of Fluoride, Nitrate and TDS and make the water potable. Nine different easily available organic materials (Rice Husk, Wheat Husk, Bagasse, Coconut Coir, Amla Seeds, Amla Bark, Banana peel Husk, Aloevera Gel and Potato gel) are tested in laboratory for reducing the Nitrate, Fluoride and TDS concentration. The results showed that only Potato gel has the potential to reduce all these three parameters. Therefore, Potato gel has been selected for further study. The process parameters (time, weight, influent concentration and flow rate) have been optimized for batch study and column study. The experimental results showed that potato gel is efficient enough in reducing the high values of Fluoride, Nitrate and TDS collectively. Remarkably 89%, 92% and 86% reduction in concentration of Fluoride, Nitrate and TDS have been observed during the experiment respectively.

CONTENTS **Page**

List of Figures

List of Tables

3D	Three Dimensional
AL	Above Limit
ASTM	American Society for Testing and Materials
BL	Below Limit
CARIX	Carbon dioxide regenerated ion exchange resins
CD	Chemical Denitrification
CDI	Capacitive deionisation
CSIRO	Commonwealth Scientific and Industrial Research Organisation
CsI	Cesium Iodide
E	East
EC	Electric Conductivity
ED	Electrodialysis
EDR	Electro Dialysis Reversal
EIX	Electrochemical Ion Exchange
EPI	Environment Performance Index
EU	European Union
F^-	Fluoride
GIS	Geographic Information System
HRT	High Retention Time
IAEA	International Atomic Energy Agency
IDW	Inverse Distance Weightage
IRS	Indian Remote Sensing Satellite
IS	Indian Standards
MBR	Membrane Bioreactor
MCL	Maximum Contaminant Level
MIAA	Modified immobilized activated alumina

MIEX	magnetic ion exchange resin
MSF	Multi Stage Flash Process
N	Nitrogen
N	North
NCCMA	North Central Catchment Management Authority
NE	North East
NF	Nano Filteration
NFIS	National Fluoridation Information System
NO_3^-	Nitrate
NRSA	National Remote Sensing Agency
NSF	National Sanitation Foundation
NW	North West
pH	Power of Hydrogen
RO	Reverse Osmosis
RSPCB	Rajasthan State Pollution Control Board
S	South
SBA	strong base anion
SE	South East
SGWB	State Ground Water Board
SL	Safe Limit
SW	South West
TDS	Total Dissolved Solids
UF	Ultra Filteration
UNEP	United Nation Environment Program
UNGEM	United Nations Global Environment Monitoring System
USEPA	United States Environment Protection Agency
W	West

WAC/SAC	Weak Acid Cation / Strong Acid Cation
WFD	Water Framework Directives
WHO	World Health Organization
WQI	Water Quality Index
XO	Ion Exchange Process

1. Introduction

With 66% of the world's surface secured by water and the human body comprising of 75 percent of it, it is apparently clear that water is one of the prime components responsible for life on earth. Water circulates through the land just as it does through the human body, transporting, dissolving, replenishing nutrients and organic matter while diverting waste material. Further in the body, it controls the activities of liquids, cells, tissues, blood, lymph and glandular emissions (WHO, 1996).

This chapter deals with various aspects of water including its characterization, importance and different modeling techniques employed in the treatment of water. The importance of the chosen quality parameters (Nitrate, Fluoride and Total Dissolved Solids) has been discussed and problems associated with these quality parameters are also provided here.

1.1 Purpose of the work

Water, having chemical formula H_2O**,** is a transparent fluid which is available in the world's streams, lakes, oceans and rain, and is the major constituent of the fluids of organisms. As a chemical compound, a water molecule contains one oxygen and two hydrogen atoms that are connected by covalent bonds. Water is a liquid at standard temperature and pressure, but it often co-exists on Earth with its solid state, i.e. ice; and gaseous state: steam (water vapor). It also exists as snow, fog, dew and cloud (Gleick, 1993; Clark et al., 2001).

Water covers 71% of the Earth's surface (Gleick, 1993), and is vital for all known forms of life. On Earth, 96.5% of the planet's water is found in seas and oceans, 1.7% in groundwater, 1.7% in glaciers and the ice caps of Antarctica and Greenland, a small fraction in other large water bodies, and 0.001% in the air as vapor, clouds (formed of solid and liquid water particles suspended in air), and precipitation. Only 2.5% of the Earth's water is freshwater and out of this freshwater 98.8% is in form of icecaps and groundwater. Less than 0.3% of all freshwater is found in rivers, lakes, and the atmosphere, and an even smaller amount of the Earth's freshwater (0.003%) is contained within biological bodies and manufactured products (Gleick, 1993; WHO, 1996; Clark et al., 2001). The global distribution of water is schematically represented in Figure 1.1 (Clark et al., 2001).

Safe drinking water is vital to humans and other life-forms even if it provides no calories or organic nutrients. In almost every part of the world, access to safe drinking water has enhanced over the last decade, but approximately 2 billion people still lack access to safe water (WHO/UNICEF, 2015). A clear correlation exists between access to safe water and gross domestic product per capita (Kulshreshtha, 1998). However, some observers forecast that more than half of the world population will be facing water-based vulnerability by 2025. Work done in last decade (Greenburg, 2005) suggests that by 2030, in some developing parts of the world, water demand will surpass supply by 50% which will present us with a critical condition for sustaining human life. Water plays an important role in the world economy (UNEP, 2015), as it functions as a solvent for a wide range of chemical substances and facilitates industrial cooling and transportation. Approximately 70% of the freshwater used by humans goes to agriculture (Baroni et al., 2007).

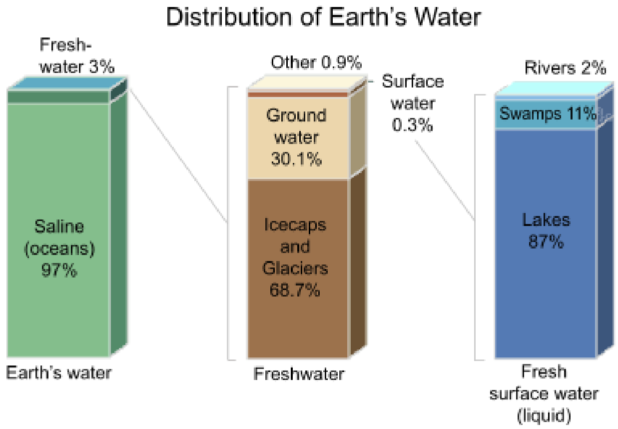

Figure 1.1: A graphical distribution of the water on Earth (Clark et al., 2001)

We all are aware of hydrological cycle for which groundwater is one major constituent. Generally, groundwater flows within aquifers and remain below the water table. Water from very deep source are preserved from a very long time and as these aquifers are formed few million years earlier and this water is stored in these aquifers few million to hundreds years. So the deep aquifer water is some time called fossil water (US EPA, 2015). Groundwater is a major source of water and an integral part of our water supply. At times of low river flow, groundwater enters the rivers, maintaining river flow and few times groundwater flows back to the surface in form of springs or more spectacularly in hot springs and geysers (Ben and Ben, 2011).

The water resources are of major environmental, social and economic value, and if water quality is degraded then this resource will lose its economical value. Water quality is commonly defined by its physical, chemical, biological and aesthetic (appearance and smell) characteristics. Measurements of these indicators can be used to determine and to monitor changes in water quality. It will also help in determining whether it is suitable for the health of the humanity and natural environment. Water quality is the composition of constituents dissolved within the water in the functioning of natural processes and human activities. Chemical parameters are most invoked factor in characterizing water quality (UNEP, 2015). Generally, the water quality indicators can be categorized as (IAEA, 2007):

- **Biological Parameters (**bacteria, algae etc)
- **Physical Parameters** (temperature, turbidity and clarity, color, salinity, suspended solids, dissolved solids)
- **Chemical Parameters** (pH, dissolved oxygen, biochemical oxygen demand, nutrients including nitrogen and phosphorus, organic and inorganic compounds, fluoride, nitrate, toxicants etc.)
- **Aesthetic Parameters** (taints, floating matter)
- **Radioactive Parameters** (alpha, beta and gamma radiation emitters)

Groundwater is always vulnerable to contamination due to water cycle and data on groundwater quality is scarely available. The quality of water isn't dependent on single parameter but depends on multivariable factors (Cheryl et al., 2007). Water quality is closely linked to the surrounding environment and land use (Brien, 2001) and modification of natural stream flows by dams and weirs can also affect water quality. The weather, too, can have a major impact on water quality; particularly in a dry region where drought conditions are always present (Brien, 2001). Water quality frequently declines as rivers flow through regions where land and water use are intense and pollution from intensive agriculture, large towns, industry and recreation areas increases. Korngold et al., (1966); Mohamed et al., (2011); NFIS, (2012) commented that water quality may improve downstream, behind dams and weirs, at points where tributaries or better quality groundwater enter the main stream, and in wetlands.

ASTM, (2010) suggest that groundwater model can have different meaning to different people Groundwater models can provide insight into the complex system behavior and help in developing conceptual understanding. The models are used to establish the past behavior and predict the future behavior of groundwater to some extent. The groundwater model strengthens the support to decision-making and allows the investigation of alternative management approaches (Merz, 2012; BCME, 2012; Anderson and Woessner, 1992) for water policies.

The observation data from about 2500 hydrological sites have been used directly for estimation of water quality on the global scale (Shiklomanov, 1999). Approximately, 35% of the world population will have low fresh water supply and its quality will be very alarming. The global scenario of the water quality is not very appreciable because of contamination of water sources by various means. The various physico-chemical parameters are measured for water quality but they differ by region. From such various parameters i.e. Nitrate, Fluoride and Total Dissolved Solids (TDS) are affecting the world alarmingly. 30% of countries (Zhao, 2015) throughout the globe are affected by higher concentration of Nitrate in groundwater. Around 260 million people in 74 countries worldwide have been drinking water with Fluoride content larger than 1 ppm (WHO, 1996). TDS directly do not affects the human health but changes the taste of groundwater (WHO, 1996). The listing of India in high concentration list (Shiklomanov, 1999; Juntunen et al., 2012) of chemical parameters including Nitrate, Fluoride and TDS encouraged for finding the status of Fluoride, Nitrate and TDS along other parameters in the local study area of Shekhawati.

Table 1.1: Standard limits for chemical parameters under study

Parameter	**Range (mg/l)**	**Standard of country/ Agency**
Nitrate	45 (desirable limit), no relaxation	IS:10500 (in India)
Fluoride	0.6 to 1.2 (desirable limit), if the limit is below 0.6, water should be rejected, max. Limit is extended to 1.5	
TDS	500-2000 (desirable limit), if limit is above 2000, water should be rejected	
Nitrate	10 (max. Contaminant level)	US EPA (USA)
Fluoride	2	
TDS	500	
Nitrate	50	EU EPA (Europe)
Fluoride	1.5	
TDS	NA	
Nitrate	50	WHO (any)
Fluoride	1.5	
TDS	600-1000	

The standards established by Bureau of Indian standard (IS 10500, 2012) is used to characterize the groundwater of study area. The various standards adopted in different countries are given in Table 1.1 (WHO, 1996; IS 10500, 2012; US EPA, 2012; EU, 2014).

Nitrate is the most common chemical contaminant in the world's groundwater aquifers (Shiklomanov, 1999; Peter et al., 2012). According to studies, exposure to higher levels of nitrates or nitrites has been associated with increased incidence of cancer in adults and possible increased incidence of brain tumors, leukemia, and nasopharyngeal (nose and throat) tumors in children. Fluoride is linked with tooth decay, bone fractures and low intelligence in people. Sometimes, fluoride makes toxic compounds when it reacts with other elements (Mary et al., 2005). Alone in India 62 million people are suffering (RSPCB, 2014) from dental and skeletal fluorosis. Rajasthan is one of the 3 states in India, which are highly endemic for fluoride (RSPCB, 2014) and all districts of the state have shown the higher TDS in groundwater. As the study area lies in state Rajasthan, it gives the clear indication of vulnerability of habitants towards the water quality they are using.

The various studies have been carried out (Maithani et al., 1998; Suthar et al., 2007; Batheja et al., 2007; Sabal et al., 2008) at local level indicates the quality of groundwater in northern part of Rajasthan is unfit for drinking and may have health implications due to presence of higher values of total dissolved solids and major ions, e.g. calcium, magnesium, nitrate, fluoride, sodium and potassium. They also suggested to take remedial measures like setting up of large-scale defluoridation & de-nitrification plants, use of simple domestic defluoridation methods and public awareness. It had been found that the water quality had deteriorated in arid and semi-arid regions in last few decades (Batheja et al., 2007; Sabal et al., 2008) and study area lies in the same climatic zone, thus need immediate attention. Due to the higher concentration of minerals and ions in drinking water several cases of dental and skeletal fluorosis, birth defects had appeared at alarming rate in this region. The Table 1.2 (WHO, 1996) shows the common diseases caused by higher concentration of the chosen contaminants.

It is clear that fluoride, nitrate and total dissolved solids concentration in ground water of northern part of Rajasthan, in which Shekhawati region lies, is on higher side and there is a need of developing low cost water treatment schemes for the habitants, which they can sustain. Selective removal of minerals, nitrates, fluoride, calcium and magnesium from tap water that contains relatively high concentrations was carried out with a cation-exchange resin possessing a chelating iminodiacetic acid group (Korngold et al., 1966).

Table 1.2: Health issues associated with parameters under study

Contaminant	**Health issues**
Nitrates and Nitrites	High dose of nitrate and nitrites over a span of time can produce symptoms of following. • Develop Methemoglobinemia • Birth defects • Cancer risk
Fluoride	High dose of fluoride in water can causes: • Dental fluorosis • Crippling skeletal fluorosis • Chronic joint pain • Overt osteoarthritis
TDS	High TDS in water makes water to be corrosive, salty or brackish in taste.

There are many disadvantages displayed by various purification processes and few of them are mentioned here. David, (2015) and Crittenden, (2012) showed that selective salts or ions (eg. calcium and magnesium in the hard water are replaced by sodium ions) replacement take place in ion-exchange and ion- exchange resins have to be backwashed have disposal problems and may cause problems for people's health. Crittenden, (2012) showed that chemical precipitation process requires a lot of operator control for efficient result, which may make this technique too operator-intensive for small treatment plants at household level. It can change the color of water and produces large quantities of sludge which further creates disposal problems (Crittenden, 2012). Reverse osmosis (RO) systems remove most of the minerals from the water leaving it with an acidic pH is major disadvantages (David, 2015) and during the purification process, 90% of water is drained unutilized (eg. 20 gal. of water is flushed down in drain for single gallon of purified water). RO is very slow compared to traditional house hold water filter and needs energy in its operation which makes it costly (David, 2015). Distillation takes large time to purify the water (2 to 5 hour for single gallon of water). It is an energy hungry process and distillation units require regular cleaning of its various compartments. It is again, costly process for household level (NFIS, 2012; Crittenden, 2012).

Thus, many problems and limitations are associated with the various filtration processes (Worku et al., 2007; Sehn, 2008; Shihabudheen et al., 2008; Ramdani et al., 2010; Rani et al., 2008; Peter et al., 2012; Hongyuan et al., 2014; Hichour et al., 2000; Gude and Anand, 2010; Bansiwa et al., 2009). The need of filtration system may change from time to time depending on many factors. But the most important factor to develop the filtration process for household level is its cost, maintenance and durability.

1.2 Research Gaps

Groundwater has been used by humans from the historical period for their daily needs. As the groundwater use is directly related to the population unit, so more people require more water. Water table starts to deplete because of extraction of water and less recharging of aquifer due to reduction in rainfall and concreting of settlement areas.

Meenakshi and Maheshwari, (2006) find that the awareness among the society regarding the quality of drinking water is very limited and confined in much closed loop of environmentalist and water experts. So until the people are ignorant about the water quality and it’s affecting parameters, they are prone to the water borne diseases.

In the selected study area (Shekhawati), bone decay, tumours, leukaemia etc are heavily reported and some studies (WHO, 1996; US EPA, 2012) have shown that these diseases are related with Fluoride & Nitrate. Few times, bacterial activity in surface water leads to odor in water and in some highly mineralised (Iron and Sulfur rich water promote growth of iron and sulfur loving bacteria) regions, leaching of chemicals into water bodies is also a cause of odor in water. These chemical released ions and asthetic and biological particles leads to change in total dissolved solids content in water and their higher amount will cause specific smell. Study on Fluoride, Nitrate and TDS suggested that, deficiency and over dose of these parameters will cause health problems in human (WHO, 1996). The northern part of Rajasthan in which the study area falls is identified as high fluoride, nitrate and total dissolved solids concentration zone along with other parameters (RSPCB, 2014). Thus, the characterization of water quality parameters along their spatial coverage is required for the study area.

Water is contaminated because of natural and anthropogenic activities. Natural pollution occurs due to presence of various minerals in soil strata and rocks. In the process of recharging, groundwater aquifer may get polluted.

There are many techniques and processes (WHO, 1996) to remove the Fluoride, Nitrate and Total Dissolved Solids such as ion exchange method, reverse osmosis and distillation, membrane filtration. Ion exchange method is used to filter out the nitrates. Sand filter, activated carbon, boiling & cooling are generally preferred for TDS removal. But in many part of India conventional treatment method is used for purification of surface water and almost negligible purification is carried for groundwater. Thus, by taking the Fluoride, Nitrate & TDS in consideration, a new material should be identified, which may be affordable by the community at domestic level. In the past, work has been carried out to characterize groundwater on the basis of many physico-chemical parameters (WHO, 1996; Batheja et al., 2007). The gaps identified for this study can be listed as follows:

- In the present thesis, emphasis must be given on determination of water quality index using only Nitrate, Fluoride and Total Dissolved Solids as the study area is highly affected by these 3 quality parameters.
- In the present work, emphasis will be given to treat all three impurities of high concentration (Nitrate, Fluoride and TDS) by a single material.
- Identification of population vulnerable to these three quality parameters .

1.3 Objective of the work

The purpose of this work is to describe the characterization of water quality in Shekhawati region of state Rajasthan, using the data collected during year 2012 for pre and post monsoon seasons. The chemical properties from 163 groundwater samples have been analyzed in the Public Health Engineering Laboratory (PHED), Jhunjhunu, Govt. of Rajasthan. Data from pre and post monsoon seasons of the study is compared with national water quality standards.

The threat from contaminated water towards life is always present in our environment. Higher values of Nitrate, Fluoride and Total Dissolved Solids have shown their ill effect on human life in many forms. Thus, their removal/reduction is necessity of the time. New experiments and materials are evolved which may be used by the people. The objectives of the work are stated below:

- Identification of concentration for Nitrate, Fluoride and TDS in groundwater of Shekhawati region of Rajasthan.

- To carry out the 3D analysis of the chosen water quality parameters (Nitrate, Fluoride and TDS) contamination due to sub surface strata.
- Development / Identification of the low cost material for the treatment of water rich in Nitrate, Fluoride and Total Dissolved Solids.

1.4 Organization of Thesis

The chapter 1 discusses introduction, gap in research and objective. Chapter 2 discusses the research carried out by many scientists and researchers from India and abroad for last 50 years for the groundwater characterization, modeling and treatment of water. Material and methodology for the research is discussed in chapter 3.

Chapter 4 depicts the water quality index and groundwater modeling. Chapter 5 discusses the experimentation of naturally available material in reduction of Nitrate, Fluoride and Total dissolved solids.

Chapter 6 highlights and discusses the main finding of the thesis work. It also gives direction to future work. Various annexures listed, shows the pictures of work during this thesis and includes the results.

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2. Literature Review

This chapter deals with the review of work from other authors globally from year 1973 to year 2015. The review is divided in 3 main component viz. (1) groundwater quality, (2) 3D analysis and (3) removal of Nitrate, Fluoride and Total Dissolved Solids (TDS). The third part is further divided in 3 parts viz. (1) Nitrate, (2) Fluoride and (3) TDS.

2.1 Groundwater quality

Access to safe drinking-water is important as a health and development issue at a national, regional and local level. In some regions, it has been shown that investments in water supply and sanitation can yield a net economic benefit, since the reductions in adverse health effects and health care costs outweigh the costs of undertaking the interventions. Experience has also shown that interventions in improving access to safe water favor the poor in particular, whether in rural or urban areas, and can be an effective part of poverty mitigation strategies.

Studies (Horton 1965; Zoeteman 1973; Harkins 1974; Inhaber 1974; Ott 1978; Dinius 1987; Haire et al., 1991; Nagels et al., 2001; Cude 2002; Hallock 2002;) in many countries showed that available water quality indices (WQI) and their methodology reflect their specific uses and geographical areas of application and most of the methodological approaches include following steps mentioned below:

1. Selection of the water quality parameters.
2. Transformation of the raw parameter data onto a common scale.
3. Decision and allocation of relative weights.
4. Selection of function and formulae.

Caruso, (2001) at regional level showed that water quality generally declines during drought conditions. The Dry climate change scenario is likely to affect surface water quality primarily by reducing surface water flows and increasing water temperatures. Allen et al., (2004); Woldeamlak et al., (2007); Brouyere et al., (2004) and Gleick, (2000) informed that groundwater resources are less susceptible to short term climate variability than surface water. But they are more affected by long-term trends as they are buffered by their sometimes large storage volumes. CSIRO, (2008) told that very little research has been undertaken to determine the sensitivity of aquifers to changes in critical input parameters such as precipitation and runoff despite the fact that groundwater constitutes relatively less water consumption compared with surface water. Surrounding land use and catchment hydrology are two primary drivers (Merz, 2011) of surface water quality and affects groundwater quality as a part of hydrological cycle.

To get the basic understanding of water quality and quantity, characterization, its purpose and effect; the guideline and documents regarding the water characterization, indifferent part of world have been searched and studied. The water framework directive (WFD) (WFD, 2004) by EU is most understandable document. Technical repot (WFD, 2004) on groundwater characterization revels that several countries use the already available data such as inventories and studies, which were used in water management practices for groundwater characterization in their nations. This data comes from geological maps, hydrological & hydrogeological maps, soil profile details (soil map), vulnerability maps, statistic of diffuse pollution source and land cover maps; are used for characterization. This report says that purpose of characterization of water body is to assess it's use and the degree to which these water bodies are at risk of failing to meet the objectives of WFD. It includes the achievement of good status of water quantitatively and chemically in the region. Water bodies may be grouped for the purpose of characterization, which might be based on existing hydrogeological, geological, pedological, land use, discharge, abstraction and other data.

Following above said characterization, it has to be carried out for water body or groups of water bodies, which have been identified for risk (WFD, 2004). A study (CSIRO, 2008) in arid region of continent Australia was carried out which suggested that elevation, water table and anthropogenic process as three main drivers of groundwater quality. Anthropogenic drivers (CSIRO, 2008) include any changes to the quality of recharging water, and changes wrought by anthropogenic-driven processes within the aquifer. The anthropogenic processes related to changes caused by extraction.

Lumb et al., (2009) focused differences in various WQIs which are based on the mannerism of statistical integration and interpretation of parameter values. They observed that approach adopted in the Canadian Water Quality Index which is also known as Canadian Council of Ministers of the Environment Water Quality Index (CCME WQI). CCME WQI is also being endorsed by United Nations Environmental Program (UNEP) in 2007 as a model for Global Drinking Water Quality Index (GDWQI). Dissolved oxygen, pH, turbidity, total dissolved solids, nitrates, phosphates, metals are the most commonly used parameters. Their work also concludes that all indices used for determining the WQI, have limitation and the search for a perfect WQI is still remaining a challenge.

Abdul et al., (2010) advocated that while WQI is used for overall quality assessment of water in some area, still pH play a major role that determines the suitability of water for various purposes and displayed the yearly decline in water quality. Amandi et al., (2010) use WQI in evaluation by elucidating surface water quality in this study. They suggest that WQI is valuable tool in categorizing the pollution sources of surface waters and WQI is attributed to the anthropogenic interference of surface pollutants. Madalina et al., (2010) studied the water quality in Romania and proposed for assessment of water quality for different hydrographical basin separately. Their finding concludes that organic pollution is main indicators of quality of water and water quality doesn't present complex environmental issues. Kavitha and Elangovan, (2010) find the anthropogenetic driver as a soluble constituents in groundwater which comes from soluble minerals in soils and sedimentary rocks.

The concept of indexing water with a numerical value to express its quality, based on physical, chemical and biological measurements, was developed in 1965 by US based National Sanitation Foundation (NSF) (Horton, 1965). Lumb et al., (2009) have used Delphi method to select the parameters in NSF WQI and model was formulated in multiplicative form. This model was implemented across various states in the US while being continually refined. One refined form is known as Oregon Water Quality Index (O WQI). Another model of WQI from Europe (Lumb et al., 2009) is based on the normalization of the concentrations of the water quality parameters and then aggregating them through an additive model with suitable weights attached to the parameters involved. Brunswick, (2011) proposed in his work that water quality can be thought as a measure of the suitability of water for a particular use which would be based on selected physical, chemical and biological characteristics. He showed evidence of global climate change contributing in degradation of water quality in near future.

Despite the paramount importance of water to all human and ecosystem life, there still lacks any good measure to compare how countries perform on water quality (Merz, 2011; GEMS, 2014). Poor data quality and coverage are largely to blame, but there also exist problematic framing issues, which undermine global indexing efforts. Water quality definitions vary depending on the source, location and intended use of the water, and no single definition of water quality exists. Owing perhaps to the difficulties regarding water quality definition and measurement, there is a lack of an international, coordination to mobilize the scientific communities to collaborate on measuring and recording data in a consistent and timely manner. There are challenges of even establishing the relation between the existing WQI (Tanja et al., 2012). Stuyfzand, (1993) and Wong and Batjes, (2007) indicated the increment of anthropogenic activities that have contributed to pollution of the ecosystems and groundwater and had used pollution index POLIN and MANURE to define level of pollution in ecosystem. Hurley et al., (2012) and Ma et al., (2013) suggested alternative in the form of estimation of the water quality index, which is a simple arithmetic tool to assess water quality for determining level of pollution of any ecosystem at given time.

Rubio et al., (2013) have studied the WQI as a function of time and showed that WQI varies monthly and at few points, the good WQI changed to worse from spring to autumn season. Water quality can be used as a significant criterion in matching water demand and supply. Ample (sufficient) degree of freshwater is eminent for biological needs as a vital side of integrated environmental management and sustainable development suggested by Tirkey et al., (2013). Gorde et al., (2013) and Dohare et al., (2014), tells that water quality is dependent on the type of the pollutant added and the nature of mineral found at particular zone of aquifer. Their result of water quality assessment showed that most of the water quality parameters show seasonal variation and slightly higher in the wet season than dry season. Water quality is dependent on the type of pollutant added in water and its nature of self purification.

The Environmental Performance Index (EPI) published by the Yale Center for Environmental Law and Policy (YCELP) and the Center for International Earth Science Information Network (CIESIN) at Columbia University includes a Water Quality Index (WAT QI) (Hsu et al., 2014). WAT QI provides a first global effort at reporting and estimating water quality on the basis of five commonly reported quality parameters: dissolved oxygen, electrical conductivity, pH, total nitrogen and phosphorus concentrations. To this end, a composite index was developed based on data from the United Nation Environment Protection Groundwater Evaluation & Monitoring System (UNEP GEMS) water program and the European Environment Agency (EEA) (GEMS, 2014).

Not only the conventional way of determining WQI passes through changes but computational programs are also used for the purpose. A method based on concept of fuzzy set theory has been used for decision-making for the assessment of physico-chemical quality of groundwater for drinking purposes. Fuzzy synthetic evaluation model gives the certainty levels for the quality class of the water based on the prescribed limit of various regulatory bodies and opinion of the experts from the field of drinking water quality. Singh et al., (2008) used optimization model based on fuzzy rule with groundwater samples physico-chemical parameters were used for the quality assessment using fuzzy synthetic evaluation approach. Deterministic assessment of the drinking water quality on the basis of measurement results according to the prescribed limits by either WHO or BIS will give the results in form of linguistic term like ‘‘desirable’’, ‘‘acceptable’’ and ‘‘not acceptable’’(Singh et al., 2008).

Andre et al., (2009) showed that intrinsic uncertainties and subjectivities of environmental problems could be dealt by using computation methods based on artificial intelligence. A new index, called fuzzy water quality index (FWQI) is developed to correct perceived deficiencies in environmental monitoring, water quality classification and management of water resources in cases where the conventional, deterministic methods can be inaccurate or conceptually limited. Dixon, (2005) improved the methodology for the generation of contamination potential maps by using detailed landuse/pesticide and soil structure information in conjunction with selected parameters using GIS and fuzzy network. A groundwater vulnerability and risk mapping assessment is done by Nobre et al., (2007) which is based on a source pathway receptor approach. A fuzzy hierarchy methodology was adopted to evaluate the potential contaminant source index, including diffusive and point sources. The integration of Modflow and Modpath with numerical modeling for delineating capture zones of wells provided the mechanism to assess groundwater pollution risks have done by him. A systematic calculation of correlation coefficients among different physico-chemical parameters was performed by Meenakshi et al., (2004). The analytical results indicated considerable variations among the analyzed samples with respect to their chemical composition. Majority of the samples do not comply with Indian as well as WHO standards for most of the water quality parameters measured. Ishaku et al.,(2012); Bairu et al., (2013); Asadi et al.,(2007); Noha, (2011); Mouna et al., (2011) indicated that the WQI range is not stable between 0 -100 but must vary beyond 100. This WQI range is dependent on no. of samples and the values of parameters as by their work they have shown that in their cases the range exceed the mark of 300.

Forecasting of groundwater level fluctuations is an important requirement for water quality and modeling in any basin told by Nayak et al., (2006). They investigated the potential of artificial neural network (ANN) technique in forecasting the groundwater level fluctuations in an unconfined coastal aquifer in India. Several ANN models are developed that forecasts the water level of two observation wells. They also told that exclusion of antecedent values of the water level time series may not help the model to capture the recharge time for the aquifer and may result in poorer performance of the models. In general, the results suggest that the ANN models are able to forecast the water levels for short duration only. Yilmaz, (2007) proposed an index for quality evaluation of surface water quality classification using fuzzy logic. In it, traditional quality classes are transformed into continuous form and then the concentration values of the different quality parameters are summed using fuzzy rules, followed by defuzzyfication of summed values develops the index. Patric et al., (2005) used Principal Component Analysis (PCA) for water quality as they proposed that using this method cost of determining WQI could be reduced. They only used four field measurements (pH, temperature, conductivity and Dissolved Oxygen) for the experiment. These parameters are proposed as useful for monitoring global water quality trends.

Nikoo et al., (2011) presents a hybrid probabilistic water quality index by utilizing fuzzy inference systems (FIS), Bayesian networks (BNs), and probabilistic neural networks (PNNs) as available water quality indices have some limitations such as incorporating a limited number of water quality variables and providing deterministic outputs. The FIS, BN and PNN is trained based on the opinions of several water quality experts. The trained BN and PNN can be used for probabilistic water quality assessment using water quality monitoring data. Their results showed that the average relative error in the validation process of the trained BN is 7.8%. Palani et al., (2008) worked on artificial neural networks to predict and forecast quantitative characteristics of water bodies. Authors suggested the true power and advantage of ANNs method lie in its ability to (1) represent both linear and non-linear relationships and (2) learn these relationships directly from the data and provide means to model them. Lee et al., (2002) investigates the effectiveness of artificial neural network models for predicting the Water Quality Index for rivers. They suggested that a significant saving in terms of money and time can be achieved on using the optimized ANN. Gazzaz et al., (2015); Gazzaz et al., (2012) suggested the designing of a ANN model to predict WQI using land use areas as predictors and used the statistical data of previous year of land use and water quality in the area and using three layer perception neural network with feed forward technique. Keka and Saha, (2015) studied computer-simulated artificial neural network model for the evaluation of the relationship between the different parameters of water bodies collected at different stations responsible for water quality measurement. Thus to analyze better, use of self organizing map, WQI and PCA are proposed (Vahideh et al., 2015) to obtain the classification and pollution status in water samples. Numerous physical, chemical, and biological parameters are involved in the environment organism relationship.

Ferreira et al., (2015) aimed to adapt and compare the water quality index of the National Sanitation Foundation (NSF) to the physical, chemical and biological conditions of artificial reservoirs in regions with tropical semiarid climate and its spatio-temporal variability. Water quality attributes that were monitored and used for calculation and adjustment of the index were: pH, temperature, dissolved oxygen, biochemical oxygen demand, total phosphorus, nitrate, total solids, turbidity and fecal coliform. It was observed that the index adapted to semiarid climate regions is statistically different from indices from other regions (Ferreira et al., 2015). Based on the available literature mentioned above, we can say that many contributions have been made to design groundwater quality and monitoring networks during last two decades. Most studies have concentrated on pollution problems caused by point sources and focused on the statistical aspects of the choice of monitoring locations and sample size. Inspite of having new tools available for WQI, classical approach is still chosen above as advance techniques are very complex in nature and data and rigorous training driven for better result limited to small sample size. The schematic view (Figure 2.1) is created for summarising this section.

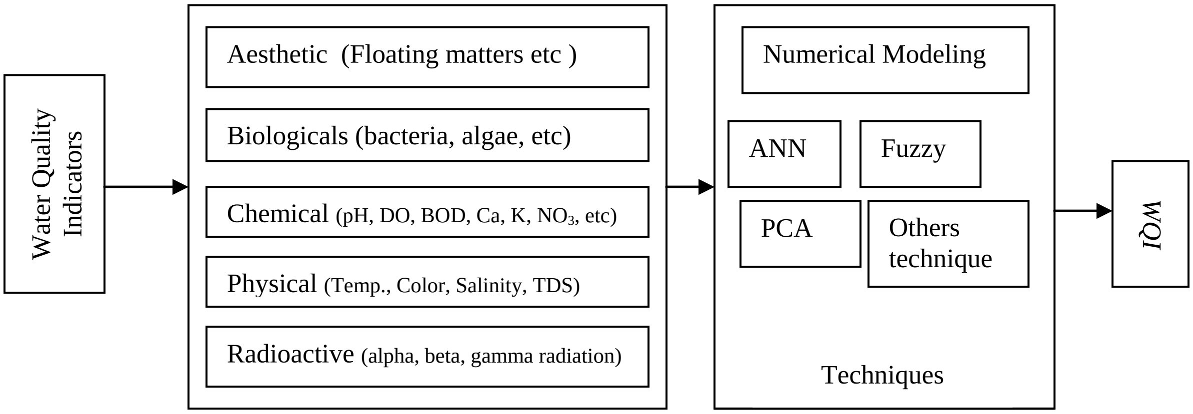

Figure 2.1: Process representation of determination of WQI

2.2 3D Analysis

A model is a tool, designed to represent a simplified version of reality. It is evident that we all use models in our everyday lives. Several type of model has been used to study the groundwater flow system. They are divided in 3 broad categories Sand tank model, Analog model and Mathematical model (Herbert, 1982). Findings of many researchers say that key variable in the hydrological cycle is precipitation, regardless of the climate region (Pilgrim et al., 1988; Wheater et al., 1991). Groundwater in a basin is not at rest but is in a state of continuous movement. The water table is virtually stationary, with mere seasonal fluctuations around the average level. If man interferes in this hydrological equilibrium, undesirable side-effects might be created. Boonstra and Ridder, (1990) suggested that extraction of groundwater from wells will lower the water table which allow the natural recharge to increase, and cause the natural discharge to decrease. If the extraction is kept within certain limits, the increase in recharge and the decrease in discharge will balance it (extraction) and a new hydrological equilibrium will be established. If this level is very deep, it may affect agriculture and the eco-systems in the area indicating the groundwater reserves are being depleted (Boonstra and Ridder, 1990).

Groundwater and the laws that govern its flow has been a subject of interest to many scientists (Herbert and Mary Anderson, 1982; Boonstra and Ridder, 1990) with most of their research focused on finding solutions to specific problems of groundwater flow using Darcy's equation and the equation of continuity for ideal situations. The groundwater model study consists of collecting all existing geological and hydrological data on the groundwater basin. If such data do not exist or are very scanty, a program of field work must first be undertaken to get the data. All the old and newly-found information (Boonstra and Ridder, 1990; BCME, 2012) is then used to develop a conceptual model of the basin, with its various inflow and outflow components. The data used to assess a groundwater balance of the basin is depicted in Table 2.1 below that are used in development of complete groundwater model.

Table 2.1: Data required to develop a groundwater model (BCME, 2012)

<table>
<tr><th colspan="2">Groundwater model</th></tr>
<tr><th>Physical Framework</th><th>Hydrological stress</th></tr>
<tr><td>1.Topography</td><td>1.Watertable elevation</td></tr>
<tr><td>2.Geology</td><td>2.Type and extent of recharge areas</td></tr>
<tr><td>3.Types of aquifers</td><td>3.Rate of recharge</td></tr>
<tr><td>4.Aquifers thickness and lateral boundaries</td><td>4.Type and extent of discharge areas</td></tr>
<tr><td>5.Aquifer boundaries</td><td>5. Rate of discharge</td></tr>
<tr><td>6.Lithological variations within the aquifer</td><td rowspan="2"></td></tr>
<tr><td>7. Aquifer characteristics</td></tr>
<tr><th colspan="2">Groundwater balance</th></tr>
</table>

A conceptual model is based on a number of assumptions that must be verified in a later phase of the study. In an early phase, however, it should provide an answer to the important question: does the groundwater basin consist of one single aquifer (or any lateral combination of aquifers) bounded below by an impermeable base (Boonstra and Ridder, 1990). Developing and testing the numerical model requires a quantitative hydrogeological data. It is common practice to present the results of hydrogeological investigations in the form of maps, geological sections and tables upon developing the numerical model. Some of these maps cannot be prepared without first making a number of auxiliary maps. The complexity of the hydrological processes seen in semi-arid regions is observed by Singh, (1995) and he indicated the difficulty in predicting the spatial and temporal variation of the processes that might occur within these regions. Therefore, the use of hydrological models has been of interest for integrated water resources management and flood prediction some times.

Ye et al., (1997); Hernandez et al., (200); Lazaro et al., (2001) found lack of resources for data collection for the purposes of hydrological and groundwater models for complex geological regions. In semi arid regions rainfall events are in general of short duration and high intensity and often characterized by a large degree of spatial heterogeneity (Pilgrim et al., 1988; Wheater et al., 1991; Martinez-Mena et al., 1998; Lázaro et al., 2001). The characteristics of high intensity of rain and short duration are even more pronounced in regions with complex topography such as mountain ranges etc (John and Guan, 2004). In semi arid regions, the density of rain gauges are very low and spatial estimation of precipitation is usually computed from well established spatial interpolation technique from point measurement (Lazaro et al., 2001; John and Guan, 2004). Walker et al., (2002) worked on groundwater yield and sensitivity analysis for the Ordovician time aquifer. They only worked on conceptual model and the parameters whose uncertainties may affect the estimation of sustainable yield. The scaling down of routine hydrological and hydrogeological monitoring in many jurisdictions has further exacerbated (intensify) this problem. Many natural resource management policy makers and managers tend to consider process models as “silver bullets” without fully understanding that any model is only as good as the data upon which it is based and has been tested (Silberstein, 2003). The complexity of the hydrological processes seen in semi-arid regions is observed by many researchers which makes it difficult to predict the spatial and temporal variation of the processes that might occur within these regions. Singh, (1995); Wagener et al., (2004); Wheater, (2008) indicates that hydrological models are simplified representation of a real-world system and consist of a set of equations that may be empirically founded or based on physical laws or a set of conceptual operations and hydrological models have been developed of great variety. Groundwater models (conceptual and mathematical) vary in complexity based on the potential impacts, modelling objectives, hydrogeological framework, and data availability. Complexity of modeling can be considered to be the degree to which a model application resembles, or is designed to resemble, the physical hydrogeological system (Murray Darling Basin, 2001). The Figure 2.2 describes the iterative process of modeling for groundwater system.

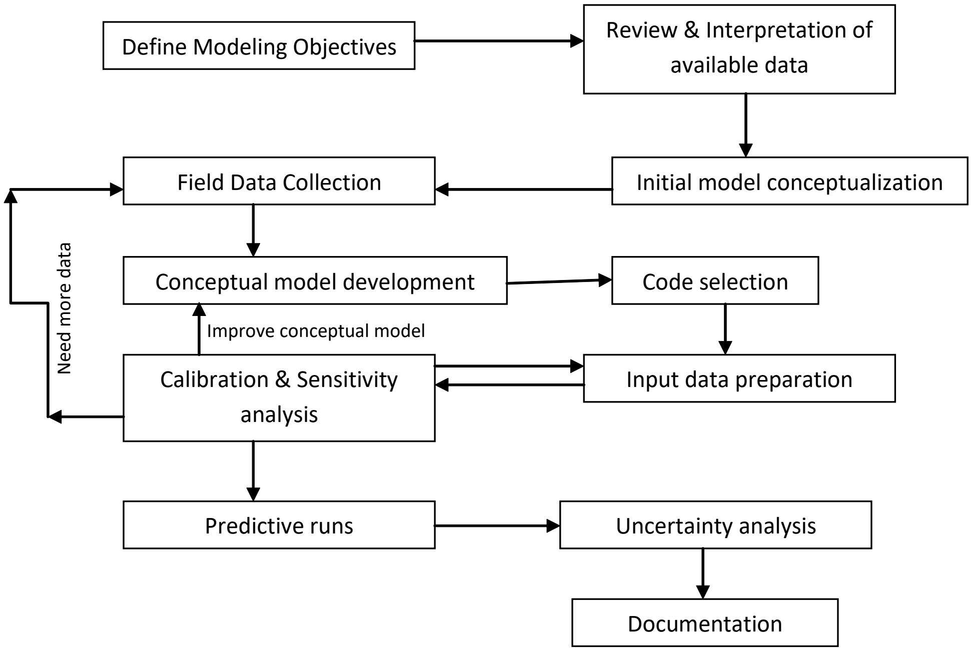

Figure 2.2: Iterative process of modeling (BCM, 2012)

Grube et al., (2004) worked on delineation and interpretation of origin & patterns of salinized water in the Lubeck area of NW Germany. They prepared separate models for various parameters under consideration as geology and groundwater flow. They also suggested based on groundwater flow model that 7000 year were taken to infiltrate more than 1000 m in an aquifer. They also concluded that the data structure will define the type of model to be created. Hammersmark et al., (2008); Doble et al., (2006) found that little attention had been given to arid and semi arid areas that have particular challenges. The researchers tried to bring together world-wide experience and some of the world’s leading experts to provide state-of-the-art guidance for modelers of arid and semiarid systems. A comprehensive data is required to develop a model. Funds and time are required to collect the data and this is the main reason for lack of data. They have also proposed that calibration has been possible for small (sub-reach scale) study areas for a very detailed process models but success has been very less at catchment and regional scales.

Overton et al., (2006); Rassam et al., (2009) incorporated publically available (i.e. inexpensive non-proprietary) Geographical Information Systems (GIS) and other software frameworks for detailed models that will be usable for management as forecasting or as scenario prediction models unless they have been thoroughly calibrated and validated for each point and process. Flemming, (2008) suggested that in semi-arid regions, hydrological regime is extreme and highly variable mainly due to rainfall patterns characterized by events of short duration and high intensities and large heterogeneity of the landscape. He also suggested that mechanisms and driving forces behind each component of the hydrological cycle should be considered for reliable estimates of the overall water resources. Wheater, (2008) showed the models might differ in their degree of determination (deterministic – stochastic models) such as (a) in their type of process representation (conceptual – empirical models), (b) in the extent and resolution of temporal and spatial scales they cover (lumped – distributed models), (c) in the hydrological processes they consider, and (d) in the dimensionality of the component descriptions.

Jolly et al., (2009) and Rassam et al., (2009) have found that there had been very significant advances over the last 15 years in the modeling of groundwater-surface water-floodplain interactions. They suggested that sophisticated numerical models are only valid under rich data situations. In addition to the studies described in their work, there are many published studies focusing on temperate and tropical regions. Modeling has progressed from relatively simple 1D and 2D analytical and empirical approaches to highly sophisticated 3D spatially distributed integrated modeling systems, with advances mirroring the vast increases in desktop computing power over that time. A groundwater numerical model for Minqin oasis, an arid area of northwest China, was developed using FEFLOW software to simulate regional groundwater changes under transient conditions by Feng et al., (2010). They highlighted the vertical recharge and discharge (source/sink terms) for the groundwater models could be determined from land-use data and irrigation systems for the different crops in the different sub-areas. The results from calibration of the model show reasonable agreement between observed and calculated water for the observation wells.

Three Dimensional (3D) applications have been expanded worldwide in the last decade. Traditional (historical) technological and data handling limitations typically resulted in Two Dimensional (2D) mapping products, and analysis of geological data using cross sections. In response to geological agencies desire to map and communicate the value of natural systems to modern society (outside of the industries of natural resource exploration and extraction), 3D methods have become prevalent (Thorleifson et al., 2010; Berg and Leetaru, 2011). Recent transitions to 3D mapping are possible due to technology advances in digital cartography, GIS, data storage, analysis, and visualization tools. While not a replacement for traditional 2D methods, 3D methods can just improve subsurface depictions of materials and structures and fasten the process of creating a model, which is useful in resource and engineering projects (ASTM, 2010; Berg and Leetaru, 2011). Barnett et al., (2012) said that understanding and communicating concepts and results can be enhanced by data visualization. Three-dimensional analysis of the data (as in interpolation of stratigraphy and water level data for visualization purposes) can be a component of a hydrogeological conceptualisation in areas where a complex model is required or the groundwater system is itself complex. ASTM, (2010); Berg and Leetaru, (2011); Barnett et al., (2012) come across that groundwater models are used to answer specific questions or to achieve a specific objective. Modeling objectives and methods vary depending on the nature of the question being asked and the characteristics of the site or system. The necessary level of detail or accuracy of results can vary, depending on the objective. In terms of environmental effects, models are used for environmental assessments, sentivity analysis, understanding the dynamics or other permitting requirements (ASTM, 2010; BCM, 2012; Berg and Leetaru, 2011; Barnett et al., 2012). Further, groundwater models that can be used to address problems related to dimensionality of visualization, analytical to numerical and flow model etc.

The literature helps in understanding that hydrological modeling of semi arid regions is more difficult than in other hydrological regimes due to more extreme hydrological conditions in combination with a large spatial variability of landscape characteristics. In such region, scarcity of data hampers reliable model predictions. More than fourty years had been passed using the modeling tools and modeling methods but almost all modeling tools have been primarily developed or tested for humid area applications. The generalized summary of model development is represented in Figure 2.3

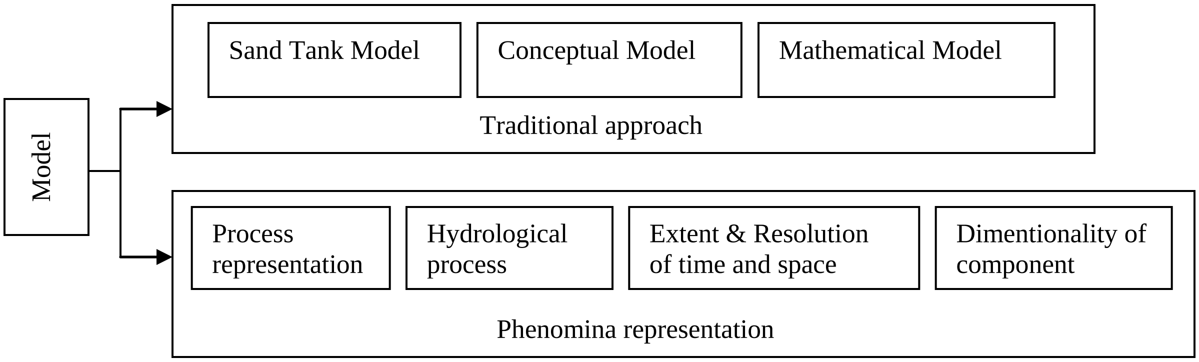

Figure 2.3: Catagerization of Models

2.3 Health issues due to Nitrate, Fluoride and Total Dissolved Solids

The study has been focused on Nitrate, Fluoride and TDS and problem and their remedies have been discussed in the same sequence. The quality of groundwater and surface water bodies have been analyzed globally by many international agencies (Montgomery, 1985) and showed that 23% of primary drinking water source violates standard of human health due to excessive concentrations of pollutants found in water. Elevated Nitrate, Fluoride and TDS concentrations in drinking water sources present a potential risk to public health and found to be present in drinking water supplies in the European Economic Community, United States, Canada, Africa, the Middle East, Australia, New Zealand and Asia (Croll and Hayes, 1988; Fried, 1991; Nixon, 1992). A survey conducted by the U.S. Environmental Protection Agency (EPA) (Briskin, 1991) indicated that up to 1,130 public and approximately 250,000 private domestic water supply wells may have been exceeding the maximum contaminant level (MCL) for nitrate. The similar situation have been discussed by WHO (WHO, 2005) with higher concentration of Fluoride and TDS in water, globally. Thus, it is found that availability of potable water will be one of the major concerns in developing countries in near future and severe shortage of water would lead to a number of individuals being affected due to bad health (Miller, 2003; WHO, 2005).

Nitrite is absorbed in the blood and hemoglobin (the oxygen-carrying component of blood) is converted to methemoglobin. Methemoglobin does not carry oxygen efficiently and resulted in a reduced oxygen supply to vital tissues such as the brain. Methemoglobin in infant blood cannot change back to hemoglobin, which normally occurs in adults. Severe methemoglobinemia can result in brain damage and death. Other symptoms include headache, dizziness, weakness or difficulty in breathing. Prolonged intake of nitrate is linked to gastric problems due to the formations of nitrosamines. N-nitrosamine compounds have been shown to cause cancer in test animals. The blue-baby syndrome (where a large portion of the infant’s blood bypasses the lungs) is also associated with high nitrate intake (Fraser et al., 1980).

Mirvish, (1995) reflected pro-carcinogenic nature of nitrate i.e. it reacts with other chemicals (amines and amides) to form carcinogenic compounds (N-nitroso) compounds. The physiological studies provide strong support indicating the association between nitrate contamination of drinking water and increased cancer rates. N-nitroso compounds has been associated with 15 different types of cancers, including tumors in the bladder, stomach, brain, esophagus, bone & skin, kidney, liver, lung, oral & nasal cavities, pancreas, peripheral nervous system, thyroid, trachea, acute myeleocytic leukemia and T & B cell lymphoma (Mirvish, 1995).

Dental fluorosis is a tooth enamel defect characterised by opaque white areas in the enamel, caused by excess exposure to fluoride while the teeth are forming in the jaw and before they erupt into the mouth. Tooth development occurs during the first 8 years of life; beyond this age children are no longer susceptible to fluorosis. Dental fluorosis reflects overall fluoride absorption from all sources at a young age, and is a known effect of drinking water containing naturally very high concentrations of fluoride (ATSDR, 2003; Public Health England, 2014). Recently, the main issues in question are whether fluoride in drinking water has an impact on cancer rates (particularly the bone cancer osteosarcoma) or on the intellectual development (IQ) of children. Because fluoride accumulates in bones, the risk of bone defects or fractures has also been extensively analysed. While, there are published studies suggesting that such associations exist (Health effects of water fluoridation, 2014).

A report of World Health Organization contained an annexure of reviewing work that had been reported in Russian literature. This annexure (Rozelle, 1993; Rozelle 1997; Guyton, 2006) concludes that consumption of water with less TDS than 100 *mg/l* disturbs the body's water and salt balance, promoting the release of sodium, potassium, chloride, and calcium ions from the body of animals or humans, imposing a stress on the mechanism of homeostasis, promoting changes in the gastrointestinal muscles and mucosa, and reducing the thirst quenching capacity of the water (Rozelle, 1993; Rozelle 1997; Guyton, 2006).

The other reported problem with TDS with respect to drinking water quality is its effect on taste. The palatability of drinking water with a TDS level less than 600 *mg/l* is generally considered to be good. Drinking water supplies with TDS levels greater than 1200 *mg/l* are unpalatable to most consumers. An aesthetic objective of upto 500 *mg/l* should ensure palatability and prevent excessive scaling. However, it should be noted that at low levels of TDS contributes to the palatability (sweetness) of drinking water (WHO, 2005).

2.4 Methods for water purification

There are many processes available to remove and reduce the higher concentration of elements present in water. The general classification (Punmia et al., 2012; ENAM, 2009; Luo et al., 2011) follows as (Figure 2.4) for the water purification and Table 2.2 illustrates the disadvantage (Al-Subaie, 2007; Della et al., 2007; Brown and Aaron, 1991) of these processes.

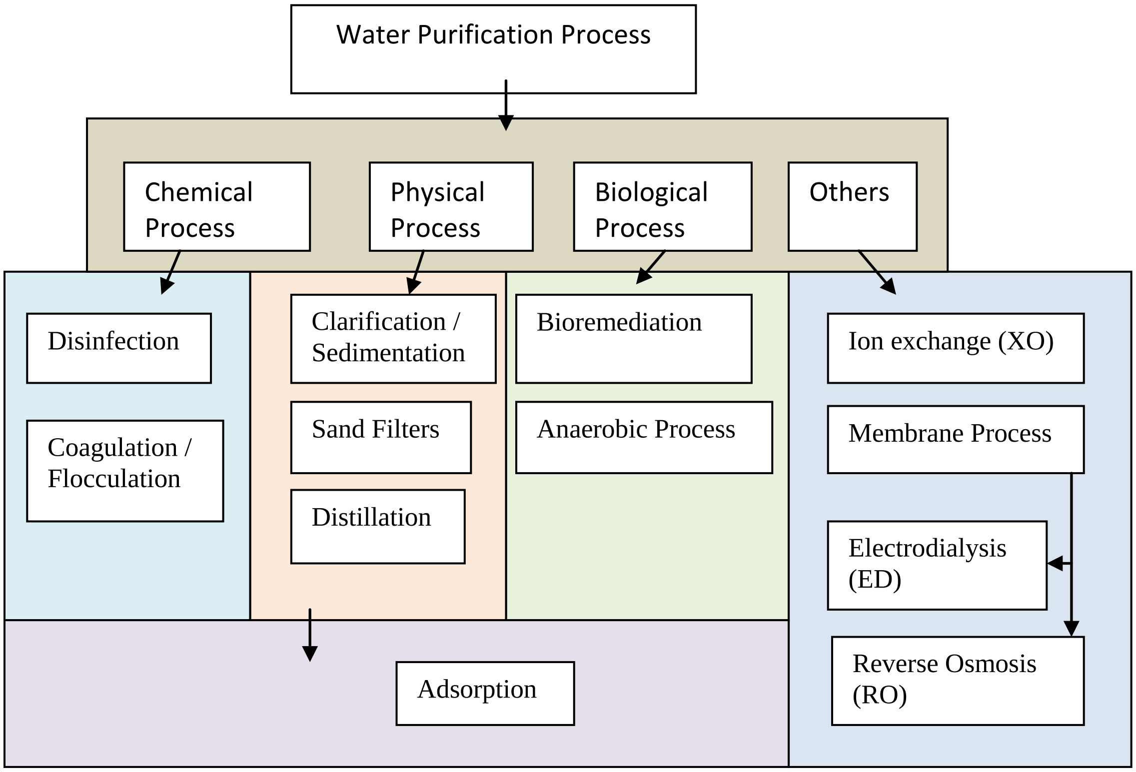

Figure 2.4: Classification of water treatment process

Table 2.2: Disadvantages of the water treatment processes

Water treatment process	**End products**	**Disadvantages**
Chemical Process	Change in characteristics of water, deposition of salts, sludge generation	Odour, Unfit for direct consumption, costly
Physical Process	Non selective in removal, improve physical characteristic of water	Need large space, not handy, energy consumption,
Biological Process	Treated pickling liquor free from heavy metals	Disposal problem of metal contaminated exhausted biosorbents
Others	Deposition of metal and ions	Costly and not easy to operate, backwashing, wastage of water
Membrane separation	Deposition of metal and ions	Expensive , fouling of the membranes

Thus, every process has its advantage and disadvantage. It is need that in water purification water should not get wasted and its characteristic should remain unchanged and should be easy to operate.

2.4.1 Nitrate

The effective work on reduction of nitrate from drinking water had been started in end of seventh decade of last century. Clifford and Weber, (1978) had showed the selectivity of ions play important role in removal of specific ion in water. They observed that sulfate selectivity was reduced by increasing the distance between ion-exchange sites and nitrate selectivity can be increased by increasing the matrix and functional group hydrophobicity (Clifford and Weber, 1978; Lauch and Guter, 1986). Sova, (1986) showed that under basic pH conditions, nitrate reduction can be induced according to the following reaction (1):

$$3NO_3^- + 8Fe(OH)_2 + 6H_2O \longrightarrow NH_3 + 8Fe(OH)_3 + OH^- \qquad (1)$$

Rautenbach et al., (1986) showed the nitrates could be removed by reverse osmosis cells under pressures ranging from 300 to 1,500 *psi* to reverse the normal osmotic flow of water. Cellulose acetate, polyamides and composite materials were used to prepare the membrane. A pilot plant using spiral wound modules with composite membranes was operated with a 2 m^3/h capacity, at an operating pressure of 203 *psi*. Influent pretreatment consisted of passing the water through 5 μm cartridge filters and acid dosing to avoid scaling. The results showed high levels of denitrification (Rautenbach et al., 1986).

An electrodialysis system required a supply of pressurized water (50-75 psi) with pretreatment. In the electrodialysis reversal (EDR) process, the polarity of the electrodes was reversed two to four times and an hour is needed to alter the direction of ion movement. The EDR process reduced scaling and chemical usage compared with conventional ED and was used for the production of drinking water from nitrate rich water (Rautenbach et al., 1987). They also showed that nitrate removal efficiency of ED and RO processes was almost the same.

The enzymes associated with denitrification are synthesized under anaerobic or partially aerobic conditions (Synder et al., 1987; Ritter and Eastburn, 1988). Many bacteria belonging to different genera can grow anaerobically by reducing ionic nitrogenous oxides to gaseous products. Nitrates or nitrites served as the terminal electron acceptors instead of oxygen and resulted in generation of ATP (Ritter and Eastburn, 1988). Such denitrification was dissimilatory nitrate reduction. When electrons are transferred from the donor to the acceptor, the organism gains energy which was applied for the synthesis of a new cell mass and the maintenance of the existing cellmass. Biological denitrification exploits the ability of certain naturally-occurring bacteria to use nitrate for respiration under anoxic conditions (absence of oxygen). The overall process is the reduction of nitrate to nitrogen gas and proceeds as reaction (2):

$$NO_3^- \longrightarrow NO_2^- \longrightarrow NO \longrightarrow N_2O \longrightarrow N_2 \qquad (2)$$

Synder et al., (1987); Rautenbach et al., (1987); Ritter and Eastburn, (1988) suggested that denitrification can be achieved using both heterotrophic and autotrophic bacteria. An organic carbon substrate, such as methanol, ethanol or acetic acid, is required as a food source for the bacteria in heterotrophic denitrification. An inorganic energy source such as sulphur, reduced sulphur species (e.g. thiosulphate) or hydrogen is required in autotrophic denitrification. The carbon needed for bacterial growth is obtained from bicarbonate in the water. Various unit processes have been developed for biological denitrification, using different substrates and different reactor configurations to support bacterial growth. Heterotrophic denitrification systems are applied more widely than autotrophic processes.

In some cases biological denitrification may need to be coupled with an ion exchange resin process in order to optimize the overall efficiency of the nitrate removal (Hoek and Ven, 1988). In this process nitrate is removed by an ion exchange process. Regeneration of the rich nitrate load resin is carried out in a closed circuit by biological denitrification.

Philpot et al., (1988) showed that nitrate removal capacity of ion exchange resin is reduced by sulphate ions during ion exchange process. A process was developed in which regeneration and exhaustion were performed in the same direction and reduced nitrate concentrations from 15.8 to 5.7 *mg/l*. The Carbon dioxide regenerated ion exchange resins (CARIX) (Holl and Kretzschmar, 1988) process for removing nitrate, sulfate, and hardness from water was based on ion exchange principles. The exhausted exchange resins were regenerated through contact with a concentrated carbon dioxide solution. Ion exchange removes anions including nitrate from the water, exchanging them for equivalent amounts of chloride or any other cation. Once the exchange capacity of the resin is reached, the resin bed is taken out of service and the resin is regenerated using sodium chloride solution (brine), which returns the resin to the chloride form. After rinsing with clean water the bed is returned to service. The spent regenerant contains a high concentration of sodium chloride together with the anions (nitrate and sulphate) removed from the resin bed.

Kokufuta et al., (1988) studied the passage of nitrate water through a polyelectrolyte complex resin bed containing strong base anion (SBA) exchange resins on which nitrate ions were exchanged for chloride or bicarbonate ions until the resin exhausted. The exhausted resin was regenerated using a concentrated solution of sodium chloride or sodium bicarbonate. Viraraghavan, (1990) illustrated that nitrate removal capacity of the resins was reduced by Silica and iron precipitates. Horold et al., (1993) developed catalytic process for the removal of nitrite and nitrate from water. Their work showed that Palladium-alumina catalysts were effective in reducing nitrite to nitrogen (98%) and ammonia in the presence of hydrogen. The presence of lead (5%), copper (1.25%) and $A1_2O_3$ as catalyst were found to completely remove nitrate from water having an initial nitrate concentration of 100 *mg/l* in influent. The reaction time was 50 *min* and this process operated effectively at a temperature of 10°C and pH range of 6 to 8.

A CARIX pilot plant (Wenli et al., 1994) having flowrate of 0.047 m^3/s was constructed in Germany which was effective in reducing nitrate concentrations from 90 *mg/l* to less than 5.7 *mg/l*. The consumption of carbon dioxide amounted to 0.35 kg/m^3 of treated water. Adham et al., (1996); Rautenbach et al., (1987) illustrated that the costs of EDR and RO were about the same for nitrate reduction from 100 to 50 mg NO_3^-/l. It was expected that capital and maintenance cost of membrane filtration would reduce with time. Ion exchange process was found to be five times more economical in comparison to RO process (Lauch and Guter, 1986).

Volokita et al., (1996) used shredded newspaper for denitrification of water in a column study. Newspaper is a good source of carbon and provide colony support for microbial populations. The team found that this system could remove 77.78% of nitrate after 30 days and 38.9% after 120 days. This longer time was necessary to accommodate the growth of sufficient denitrifying bacteria in the system. This study also reveals that temperature and retention time have marked effect on cellulose based denitrification. The retention time can be increased by decreasing the flow or by increasing the length of column. The ink on newspaper also affected microbial growth in system, but not a limiting factor. It was also observed that highest denitrification was occurred with clean newspaper at temperature of 25° to 32° C.

Biological process has been applied during the end of last century in the field of drinking water treatment due to efficient performance and problems associated with other nitrate removing processes. Physical and chemical methods such as ion exchange, reverse osmosis, nanofiltration and electrodialysis all show poor selectivity for nitrate removal (Hell et al., 1998; Choi et al., 2009). Studies done by Bi et al., (2001); Dong, (2001) shows that fertilizers or excessive usage of nitrogen based fertilizers are main source of nitrate contaminants in groundwater. When fertilizer is applied to crops, excess nitrogen leaches as nitrate to groundwater causing degradation in water quality and increasing agriculture production. Animal waste from livestock operations and defected septic systems may also increase nitrate concentration in groundwater.

Darbi et al., (2002) assessed sulfur and limestone for nitrate removal through autotrophic denitrification from water in a batch study. In this study sulfur was used as electron donor and limestone to maintain the pH. The optimum mixing ratio of sulfur and limestone was 1:1, yielding about 98% nitrate removal and minimizing sulfate production at pH 7. Sulfate production was decreased when nitrate removal increased in batch study.

Jokela et al., (2002) conducted an experiment to eliminate nitrogen from municipal landfill leachate by a biological process. Nitrification was tested in 3 types of reactors: (1) UF nitrification filter with crushed bricks as a filter medium, (2) down flow nitrification filter with wood chips, and (3) nitrification in suspended carrier biofilm process (SCBP). All the nitrification reactors were inoculated by nitryfying activated sludge collected from sewage treatment plant. in the UF filter nitrification efficiency was 60-68% in 60 days. In down flow filter efficiency was 90% in 70 days with SCBP, efficiency was 75-99% after 112 days. They suggest UF mode was more efficient because of its higher HRT.

Luk et al., (2002); Chen et al., (2003) experimented on hydrogen over palladium copper on Y-Al_2O_3 as tubular catalytic membrane to reduce nitrate ions in water. Their work showed that Pd-Cu (4:1) combined catalyst removed the nitrate effectively. The study was carried in batch form and less nitrate concentration was removed very effectivly but higher values of nitrate causes difficulty and form ammonium which reduce the nitrate removal efficiency of catalyst. The use of hydrogen diffusion in controlled condition lead to minimize the ammonium formation at higher concentration of nitrate ions.

Experimental results of Zhang et al., (2003) showed that Fe: NO_3^- ratio of about 15: 1 was required in the presence of copper catalyst for the reaction to proceed. This process generated a large quantity of iron sludge and formed ammonia that requires removal by air stripping. The process was associated with high costs. In chemical denitrification by powdered aluminum ammonia was found to be the principal reaction product (60-95%) at pH of 10.25, which was removed by air stripping (Zhang et al., 2003; Murphy, 1991; Luk et al., 2002). The denitrification was explained by researchers on the basis of the following reactions (3), (4) & (5) (Murphy, 1991):

$$3NO_3^- + 2A1^{+++} + 3H_2O \longrightarrow 3NO_2^- + 2Al(OH)_3 \tag{3}$$

$$NO_2^- + 2A1^{+++} + 5H_2O \longrightarrow NH_3 + 2Al(OH)_3 + OH^- \tag{4}$$

$$2NO_2^- + 2A1^{+++} + 4H_2O \longrightarrow N_2 + 2Al(OH)_3 + 2OH^- \tag{5}$$

Lisi et al., (2004) used granulated tires for the removal of nitrate. They found that 48kg tires crumb can remove 16.2 *g* of NO_3^- to N by adsorption. A membrane bioreactor (MBR) was investigated for denitrification of nitrate contaminated drinking water by many researchers (Sarina and David, 2004; Ergas et al., 2004). Kietlinska and Renman, (2005) applied sand, BFS (blast furnace slag) and Polonite (siliceous sedimentary rock) to remove nitrogen species and heavy metals from landfill leachate in a column study. Total inorganic nitrogen could be removed by sand is 4%, polonite is 18% and BFS is 8%.

Schipper et al., (2005), performed an experiment with a sawdust denitrification wall to remove nitrate in shallow groundwater with an HRT of 5 days. They filled a trench (35 *m* long, 1.5 *m* deep and 1.5 *m* wide) with monterey pine sawdust (30% by volume) mixed with excavated soil. Authors suggested that the nitrate concentration was the limiting factor to denitrification, rather than carbon, because denitrification rate increased when additional nitrate was added to the soil. Because of the higher nitrate level, denitrifier could grow easily and subsquently increased the denitrification rate. They found a nitrate to nitrogen removal rate of 1.4 *g* N/*cu. m*. of per day which was 97.2% of the nitrate removal. Kumar and Chakraborty, (2006) had shown that 1.16 *g* of aluminum was required for the reduction of 1 *g* of nitrate. Aluminum reacted with water as per the following reaction (6):

$$2A1 + 6H_2O \longrightarrow 2Al(OH)_3 + 3H_2 \tag{6}$$

Chen et al., (2003) found that Pd-Cu combined catalysts at a ratio of 1:4 can maximize the nitrate reduction into nitrogen; above 80% total nitrate removal efficiency was realized. Kumar and

Chakraborty, (2006) told that 84% denitrification efficiency might be achieved at ambient temperature and pressure using zero-valent magnesium $(Mg(O))_{14}$ at pH of 2.

Mc Adam and Simon, (2007) showed that immersed heterotrophic membrane bioreactor (MBR) produced high quality product water when NO_3^- contaminated water was made to flow through the lumen of tubular microporous membranes. NO_3^- diffused through the membrane pores. Denitrification took place on the shell side of the membranes (Sarina and David, 2004). The MBR achieved over 99% NO_3^- removal at an influent concentration of 200 mg NO_3^- /*l*.

The mulch biowall system, a passive treatment and inexpensive method in removal of atrazine and nitrate from groundwater had been studied by Cole Allison, (2012). His studies includes three types of organic mulch: cedar, cypress and hardwood and they are used to prepare biowall. Cedar mulch biowall had highest organic carbon content and showed the most effectiveness in reduction of nitrate among 3 material chosen. The results of his studies showed the co-removal of nitrate and atrazine depending on electron acceptor conditions, presence of a carbon source and presence of other competing bacteria.

Zazouli et al., (2013) reviewed heterotrophic and autotrophic processes for removal of nitrate from water. In heterptrophic denitrification, methanol, ethanol and acetic acid are used as carbon source. Autotrophic nitrate removal has advantage of not requiring of carbon source while it has slow growth rate of autotrophic bacteria and low nitrate removal rate. They further concluded that while heterotrophic denitrification requires post treatment to eliminate residual carbon source from water and to remove organic matter which can sustain the regrowth of microorganism. Autotrophic denitrification also needs post treatment for degasification and for removal of biomass. Autotrophic process is more complex than hetrotrophic because of the three phase (gas, liquid and solid) process.

David et al., (2014) worked on mechanical wetland of 400 *sq m* to experiment the nitrate removal efficiency of open system. This experimented land was lined with impermeable geptextile fabric to prevent growth of emergent macrophytes. 2-10 *cm* layer of algae and diffuse biomat comprised of algae, associated heterotrophic microbes and detritus was present on top of liner. This wetland receive nitrified, non-disinfected water effluent from municipal treatment plant. The resulting hydraulic retention time varied from 1-3 (+/-0.3) days. Nitrogen species were monitored throughout pilot scale open water wetland to determine removal efficiencies. On the annual basis, approx 60% of the nitrate was removed in wetland. 50% of nitite and ammonia also removed in the system. The potential NO_3^- removal mechanism in open water wetland includes denitrification, assimilatory uptake and anammox. NH_4^+ produced at wetland bottom was assimilated converted to nitrogen gas via anammox or oxidized to NO_3^- at biomat-water interface. Microbial denitrification in anoxic regions of biomat, fueled by algal derived organic carbon, was predominated NO_3^- loss mechanism. One more possiblity is that nitrate may also have been lost by autotrophic denitrification driven by the oxidation of sulfides which was formed by SO_2^- reduction at bottom of the biomat (David et al., 2014).

Motta et al., (2015) had used the bacteria Azospira sp. OGA 24 for denitrification of water and wastewater in a bioreactor. The bioreactor was sparged with argon in order to obtain anaerobic conditions, so that bacteria could use nitrare as the only final electron acceptors for their respiratory functions. 90% efficiency is shown by this bacteria in denitrification. Motta et al., (2015) proposed that in the presence of an excess of the organic substrate and at a relatively high nitrate, the stages with maximum rate of nitrates consumption can be described by both zero- and a first order kinetics.

2.4.2 Fluoride

Several new technologies (Hanemaaijer et al., 2007; NFIS, 2012) have been introduced in recent years for the removal of fluoride includes

- Crystalactor
- Memstill technology
- The WaterPyramid solution
- The Solar Dew Collector system
- Boiling with brushite and calcite

But most common technologies (Giesen, 1998; NFIS, 2012) still used for fluoride removal are as:

- Nalgonda process (high dosage of alum and lime are used in a coagulation/sedimentation process, where the precipitation of aluminium hydroxide instantly binds a part of the water fluoride.)
- Contact precipitation (Contact-precipitation is a process where the water is mixed with the precipitating chemicals, being calcium and phosphate ions, flowing into a catalytic filter column. So far this process is only known to operate in a fluoride-saturated bone char, being the catalyst, dosed with calcium chloride and sodium di-hydrogen phosphate.)

- Bone Charcoal (Bone charcoal work as a adsorption process)
- Activated Alumina (adsorption process)
- Clay (membrane filtration)

The prevalence (occurrences) of fluoride induced diseases are mainly due to the consumption of more fluoride through drinking water. It is necessary to find out the fluoride contamination areas to adopt remedial measures to the people on the risk of fluorosis. Sujana, (2011) demonstrated the adsorption efficiency of bauxite for fluoride ions removal from systhethic as well as groundwater samples. Fluoride adsorption is dependent on pH, temperature, initial adsorbate and other anion concentration in solutions. The kinetic study revels fluoride ions adsorption on bauxite surface followed first order. The presence of competing anions (sulphate, phosphate, carbonate) have shown adverse effect and bauxite has shown the encouraging results in groundwater samples.

In recent years many naturally occurring geomaterials have been tested to find out cost effective alternative for removing high fluoride content from water. Bauxite is one of the abundantly available mineral, mainly consists of oxides of alumina, iron, silica and titania (Yanxin et al., 2001; Mohapatra et al., 2004; Hiemstra et al., 2000; Sujana et al., 2009). Das et al., (2005) says that thermally activated titania rich bauxite could used for fluoride removal from aqueous solutions. Modified immobilized activated alumina (MIAA) was used by Aneeza et al., (2013) for reducing the fluoride from drinking water. They also showed that efficiency of MIAA was 1.35 times is more as compared to normal immobilized activated alumina. They applied the sol-gel method to prepare MIAA. Their work also claimed that the MIAA was ten percent more efficient than activated charcoal in fluoride removal.

Tang et al., (2009); Emmanuel et al., (2008); Sun et al., (2011); Kamble et al., (2007); Kumar et al., (2011); Tembhurkar et al., (2006); Maliyekkal et al., (2006) have worked with many adsorbent materials and tested for fluoride removal consists activated alumina, activated charcoal, zeolite, biosorbent and nanosorbents. Activated charcoal is considered as universal adsorbant because of its application and viability. Activated alumina is also effective adsorbant for fluoride removal from water but it has limited regeneration capacity and slow rate of adsorption.

He and Cao, (1996) had tried various combinations of tricalcium phosphate (TCP), bone char (BC), hydroxyapatite (HAP) and for removal of high fluoride (10-12 *ppm*) water. The combination of bone char and monocalcium phosphate in ratio of 300:23 has shown most efficiency in fluoride reduction within 24 hour in pH range of 6.5-8.5. The defluoridation efficiency of relatively insoluble calcium phosphate was TCP (87%) > HAP(68%) > BC(66.4%), when they were used singly in a batch procedure for 24 hour under routine conditions. When optimal amount of free phosphate were added together with BC or HAP to high fluoride water, the removal of fluoride reached 95%.

Ayamsegna et al., (2008) explored the geomaterials to remove fluoride from water for rural area. The batch experiments were performed on laterite and bauxite tailing (geomaterial) with high fluoridated water to determine potentiality of material in fluoride removal from rural water supplies. The raw bauxite tailing showed the higher removal capacity. Few experiments with heat treated bauxite tailing were also performed and at 600 ^{o}C the tailing gives best result in reduction of fluoride. In these two geomaterial the fluoride removal is more in bauxite tailing than laterite tailing.

Adsorption involves passage of water through a contact bed where fluoride is removed by ion exchange or surface chemical reaction with the solid bed matrix (Srivastava et al., 2009; Wang et al., 2001). After a period of operation, a saturated column must be refilled or regenerated. The different adsorbents used for fluoride removal include activated alumina, carbon, bone charcoal, activated alumina coated silica gel, calcite, activated saw dust, magnesia, serpentine, tricalcium phosphate, activated soil sorbents, carbion, defluoron, and other synthetic ion exchange resins (Srivastava et al., 2009; Wang et al., 2001; Singh et al., 2001; Raichur et al., 2001; Bulusu et al., 1980). Adsorption with activated carbon is another efficient technique, however, high cost and challenges with the spent carbon limit its large scale application (Ong et al., 2010). Granular activated carbon is often employed in adsorption columns because of its non-specific nature of adsorption on its surface (Ko et al., 2002). Powdered activated carbon has also been employed successfully in water defluoridation despite that the process is highly pH dependent with optimum results below pH 3 (Meenakshi et al., 2006).

NFIS, (2012) had proposed to use activated alumina to reduce fluoride at household level. Alumina is aluminum oxide which is manufactured to produce highly porous and adsorbent material. As water passes through it, fluoride gets adsorbed onto the alumina. Sometimes activated carbon filter is used after activated alumina treatment unit to remove tastes from water caused by alumina treatment (NFIS, 2012). Ayoob et al., (2008) have demonstrated the use of alumina in removal of fluoride at pH 5. At this pH level 85-95% of fluoride may be removed in water. Reduction in pH of drinking water could lead to development of acidic characteristic in water and activated alumina does not have an endless capacity to adsorb fluoride. Also alumina in water is increased sometimes while using activated alumina for fluoride removal.

Lee et al., (2001); McKay et al., (1990) had used high temperature treated bone char that provides a rich surface of heterogeneous componenets which allows physisorption, chemisorption or ion exchange to occur. Physisorption (i.e. physical adsorption) is adsorption that involves van der Waals forces (intermolecular forces) and there are no significant changes in the electronic orbital patterns of the species involved. Chemisorption on the other hand, involves valence forces of the same kind that result in the formation of chemical compounds. The combination of physisorption, chemisorption and ion exchange processes renders bone char a better sorbent, in terms of ion uptake capacity, among other carbon based adsorbents such as activated carbon and peat (Lee et al., 2001; McKay et al., 1990).

Alagumuthu et al., (2010) explored the ability of cynodon dactylon based thermally activated carbon to remove fluoride from aqueous solution. With optimised parameters, it reduces 83.77% fluoride in water at neutral pH. They also find that bicarbonates present in solution interferes the removal of fluoride.

2.4.3 Total Dissolved Solids

Total Dissolved Solids (TDS) refers to the total amount of all inorganic and organic substances including minerals, salts, metals, cations and anions that are dispersed within a volume of water. By definition, the solids must be small enough to be filtered through a sieve measuring 2 micrometers. TDS concentrations are used to evaluate the quality of freshwater systems. TDS concentrations are equal to the sum of positively charged ions (cations) and negatively charged ions (anions) in the water. Sources for TDS include agricultural run-off, urban run-off, industrial wastewater, sewage, and natural sources such as leaves, silt, plankton, and rocks. Piping or plumbing may also release metals into the water. Treatment options depend on the nature of the cations and anions present in the water. For example, a water softener can reduce problems associated with calcium, magnesium, and iron. A reverse osmosis system or distillation unit may be recommended to treat elevated TDS levels associated with high levels of sodium or potassium (WHO, 2005). The side effects (WHO, 2005) of higher total dissolved solids are found in the form of water hardness and change in taste of water.

Total dissolved solids are not appreciably removed using conventional water treatment processes. In fact, the addition of chemicals during conventional water treatment generally increases the TDS concentration (CCREM, 1987 and DNHW, 1993). Certain treatment processes, such as lime–soda ash softening and sodium exchange zeolite softening, may slightly decrease or increase the TDS concentration, respectively. Demineralization processes are required for significant TDS removal. Although the technology is available to reduce TDS levels significantly, the economic cost may be a major constraint (CCREM, 1987; Andelman, 1998).

Brown et al., (2002) had used a novel ion exchange process called "Recoflo" which has made it possible to utilize either strong or weak acid cation resin to produce soften waters at TDS levels up to 7000 *mg/l*. By utilizing large dosages of high purity brine it is possible to eliminate the use of acid and caustic, even for regeneration of weak acid cation (WAC) resins. The softener equipment is extremely compact, utilizing resins bed heights of only 15 *cm* that operate at flow rates up to 180 *l/min*.

Ryoo et al., (2003) indicated that multi-stage flash (MSF) process produces 43.5% of desalinated water of world production but requires a significant amount of energy to vaporize the water. The water quality from electrodialysis treatment is comparable to RO, and may require post-treatment stabilization. The process tends to be most economical for source water with TDS levels in excess of 4,000 *mg/l*. It is established that RO and electrodialysis have very high defluoridation capacity (85–95 %) and functions effectively in any pH range. However the water loss is high (20-30 % for electrodialysis, 40–60 % for RO), have high capital cost and are energy intensive (Zakia et al., 2001).

Capacitive deionisation (CDI) consists of the process of removing ions through their adsorption on the surface of two oppositely charged porous electrodes. This electrochemical process is conducted at low voltage (typically 0.8–1.5 V) without high-pressure pumps and acts as a flow-through capacitor (Andelman, 1998); Ryoo et al., 2003; Kuran et al., 2003; Al-Subaie, 2007). The work of Priya and Palanivelu, (2006) showed application of electrodialysis processs in combination with bipolar membrane (EDBPM) for the treatment of RO rejected effluent. This method removed 99% of TDS along with recovery of salts in form of acids and bases. Energy consumption can hinder its applicability. Kitis et al., (2007) worked on magnetic ion exchange resin (MIEX) and showed removal of organic matter from drinking water which is a part of TDS. Lab results indicate that MIEX resin can reduce organic matter at low dose and short contact time, very effectively.

Eric et al., (2007) worked on reducing TDS present in water. Reverse osmosis, nanofiltration (NF) in conjunction with ultrafiltration (UF) pretreatment have evaluated for reduction of TDS. Pilot scale test showed that RO and NF membrane can successfully remove TDS from effluent when paired with coagulation enhanced UF pre-tretment at high flow rate also. Synthetic effluent is prepared by the addition of required amount of salts into deionized water by Basha et al., (2008) and performance on removal of Cl^-, SO_4^{2-}, PO_4^{3-}, Ca^{2+}, Fe^{2+} and Mg^{2+} in laboratory scale plate and frame type electrochemical ion exchange (EIX) cells, were evaluated under varying operating conditions. Ruthenium dioxide coated titanium plates (RuO_2/Ti) were used as anode and stainless steel plates as cathode in present investigation.

Xiaoyu et al., (2009) performed an electrodialysis operation to remove TDS from polymer-flooding water. The influence of flow rate and electrical potential on rate of TDS removal was studied during electrodialysis operation. Removal rate of the main ions in polymer-flooding water is: $Ca^{2+} > Cl^- > Na^+ > HCO_3^-$. From the economical viewpoint, energy consumption increases greatly, and electrical potential increased for the same flow rate, but the influence of flow rate on energy consumption was not evident. The researchers (Xiaoyu et al., 2009) studied electrodialysis technology to remove TDS of oily wasterwater and achieved closed circulation of polymer-flooding water in crude oil extraction.

Romain et al., (2009) demonstrated the good results in removal of TDS, nitrate and ammonium ions from water using charged barrier capacitive deionisation system. It showed the 80-94% effectiveness in removing TDS. One advantage of this system is that no chemical is used for regeneration of electrods used in it. Nkwonta and Ochieng, (2010) studied the application of roughing filters in TDS removal from water. In roughing filter they used gravel and charcoal separately and their result showed that both have same efficiency in removal of TDS. They also recommend that charcoal could be used in places where gravel could not be available. Roughing filters should be used as pretreatment process for water as they efficiently separate fine solid particles over prolonged periods without addition of chemicals. The performance of charcoal is better than gravel due to slightly higher specific surface area and porosity that might enhanced sedimentation and other filtration process like adsorption, when compared with gravels.

Rima et al., (2010) used unmodified bagasse and ethylenediaminetetraacetic acid (EDTA) salts modified bagasse fibers to remove the TDS in colling tower water. The EDTA modified bagasse showed the best result in TDS removal. The efficiency of TDS removal is maximum at pH of 6.5 and it increased with decrease in particle size. The adsorption parameters were determined by Langmuir and Freundlich isotherms. FTIR is used to show the changes on surface of bagasse fibre. They concluded that removal mechanism involves either complexation by chemical functions of fibers or adsorption by electrostastic van der walls interactions. Vannela et al., (2013) work with photobioreactor where high TDS water is associated with nutrients and not dominated by Na^+ and Cl^- but by HCO_3^- and NO_3^- could be used to grow Synechocystis sp. PCC 6803, which gives good response in photobioreactor. This process could also be used in reduction of TDS from water.

Elshikhipy et al., (2014) had used different dose of alum and with dose of 200 *mg/l* alum applied in aeration tank that improved the TDS reduce by 50% while treating the activated sludge. They further concluded that optimized time was needed for sedimentation and flocculation of mineral salts.
Devlina et al., (2015) investigated the role of a nano bio-composite for the removal of total dissolved solids from tap water. In the present case, two forms viz., bead and membrane is tested for their TDS removal efficiency in native, cyclodextrinated, sulfonated and aminated forms. Under batch conditions, various pretreated forms of bead and membranes are tested separately at varying pH, bead dosage, membrane dosage, time and dilutions. Among the various pre-treated samples, the aminated forms of both bead and membrane were found to exhibit the maximum efficiency at a pH value of 6.0, bead and membrane dosage values of 6 *g*, time of 6 *h* and dilution of 75%. Maximum TDS removal (bead type: 93.4.8%; membrane type: 99.8%) was noted in case of aminated matrix followed by sulfonated matrix (bead type: 87.9%; membrane type: 83.2%), cyclodextrinated matrix (bead type: 72.3%; membrane type: 79.8%) and control matrix (bead type: 62.1%; membrane type: 74.5%). This nano bio-composite was prepared using a blend of chitosan, plant gum and carbon nanotubes.

Casey et al., (2015) characterized the performance of new microbial capacitive technology for simultaneous removal of organic pollutants and salts. The microbial capacitive desalination cell (MCDC) was able to remove total dissolved solids (TDS) at a rate of 2760 *mg/l/h* and chemical oxygen demand (COD) at a combined rate of 170 *mg/l/h*, which was 18 times and 5 times faster than the traditional microbial desalination cell (MDC), respectively. One advantage of MCDC is that all three chambers could be used to remove both organic and inorganic contaminants. The reactor removed 65% of the TDS and 85% of the COD in 4 hours of operation in the desalination chamber, and 98% of the salts while 75% of the organics were recovered during the regeneration process.

Contamination of groundwater is reduced by several methods as mentioned in Chen (2003). They are (1) sealing of contaminant sources; (2) catchments drain or tube well to prevent the contaminated water from merging into groundwater systems; (3) blending of fresh water (low in value) for dilution. But all these measures can't go into effect in a short time and they can't keep the pace with the increasing need of drinking water due to the increasing of the population.

Membrane filtration processes are among advanced water treatment technologies that have been mainly employed in treatment of pure and ultra pure water. The US EPA recommended reverse osmosis, as one of the best available technologies (US EPA, 2003) for removing high nitrate, fluoride, total dissolved solids, salinity, magnesium and many more. Reverse osmosis and nano-filtration (NF) are the well known membrane technologies that can remove a large spectrum of contaminants from water such as pathogens, turbidity, heavy metals, salinity, natural and synthetic organics, and hardness (Dysart, 2008). Water does not physically pass through the membrane in the electrodialysis process as such particulate matter is not removed and therefore not technically considered filters.

There is wide range of contamination removal techniques and materials available to employ when their levels in potable water are likely to result in a state of causing any disease. Choices of technology will depend on appropriateness where factors such as availability of materials, cost, level of contaminant treatment required and technical expertise availability to the community.

2.5 Conclusion

Characterization of water quality should be linked with human health as higher values of chemical parameters will affect the humans directly or through food chain. The modeling helps in selecting the vulnerable zones for groundwater recharge and discharge along with the possibility to look beneath the subsurface for some natural cause of bad health of groundwater.

Wide range of contamination removal techniques and materials are available to treat the potable water when contaminants concentration is beyond limit. Choices of technology will depend on appropriateness and the factors such as availability of materials, cost, level of contamination and availability of technical expertise to the community should be considered.

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3. Methodology and Experimentation

Shekhawati region of Rajasthan has been selected as study area. It includes Churu, Sikar and Jhunjhunu districts. Separate methodologies are formulated for groundwater quality, 3D analysis and removal of Fluoride, Nitrate and Total Dissolved Solids (TDS). The material or data required for each objective is mentioned in respective sections. Formulas and their notations have been described in this chapter which are used for calculation and described in chapter 4 and 5. The specification of instruments and software used in the work are also discussed in this chapter.

3.1 Study Area

The area of study, Shekhawati, which is a part of Thar desert in Rajasthan lies in west of Delhi and north of Jaipur and extends between Lat. 27° 15'N to 29° 00' N and Long. 73° 45'E to 76° 5'E (Figure 3.1). It is covered in path/row 105/92, 104/92, 106/91, 106/92 of satellite IRS P6 (NRSA, 2006). It covers an area of 30,653 km^2. It includes 3 district viz. Jhunjhunu, Sikar and Churu. The topography of the study area is not very complex. The area falls in Semi Arid to Arid climatic type with seasonal (June-September) rainfall during monsoons and shows extreme weather conditions during summer and winter (GSI, 2011).

In over 90% of the cases, groundwater is the only source for domestic, industrial and irrigation in the State of Rajasthan, India (Kachwaha, 1981). Since physico-chemical quality of the groundwater determines its use so, an intensive physico-chemical quality survey of the groundwater for the entire Shekhawati was carried out. 163 water samples were collected from the different locations. Field parameters viz. Temperature, Colour, Odour, Turbidity, pH, Phenolpthalein alkalinity as $CaCO_3$, Methyl orange alkalinity as $CaCO_3$, Total hardness as $CaCO_3$, Ca Hardness as $CaCO_3$, Magnesium hardness $CaCO_3$, Chloride as Cl^-, Sulphate as SO_4^{-2}, Nitrate as NO_3^-, Nitrite as NO_2^-, Fluoride as F^-, and TDS were determined. The three parameters viz. Nitrate, Fluoride and TDS are selected for the detailed study in the chosen study area because very high concentration of these parameters (Batheja et al., 2007; RSPCB, 2014a) have been reported and many diseases (Fluorosis, Methemoglobinemia) in humans (WHO, 1996) are associated with chosen parameters. The rapid growth of industries and population has resulted in indiscriminate discharge of waste water, giving rise to deterioration of the quality of groundwater (Kachwaha, 1981). The data is obtained through intensive sampling & lab analysis for Nitrate, Fluoride and TDS have used for characterization of groundwater in Shekhawati region.

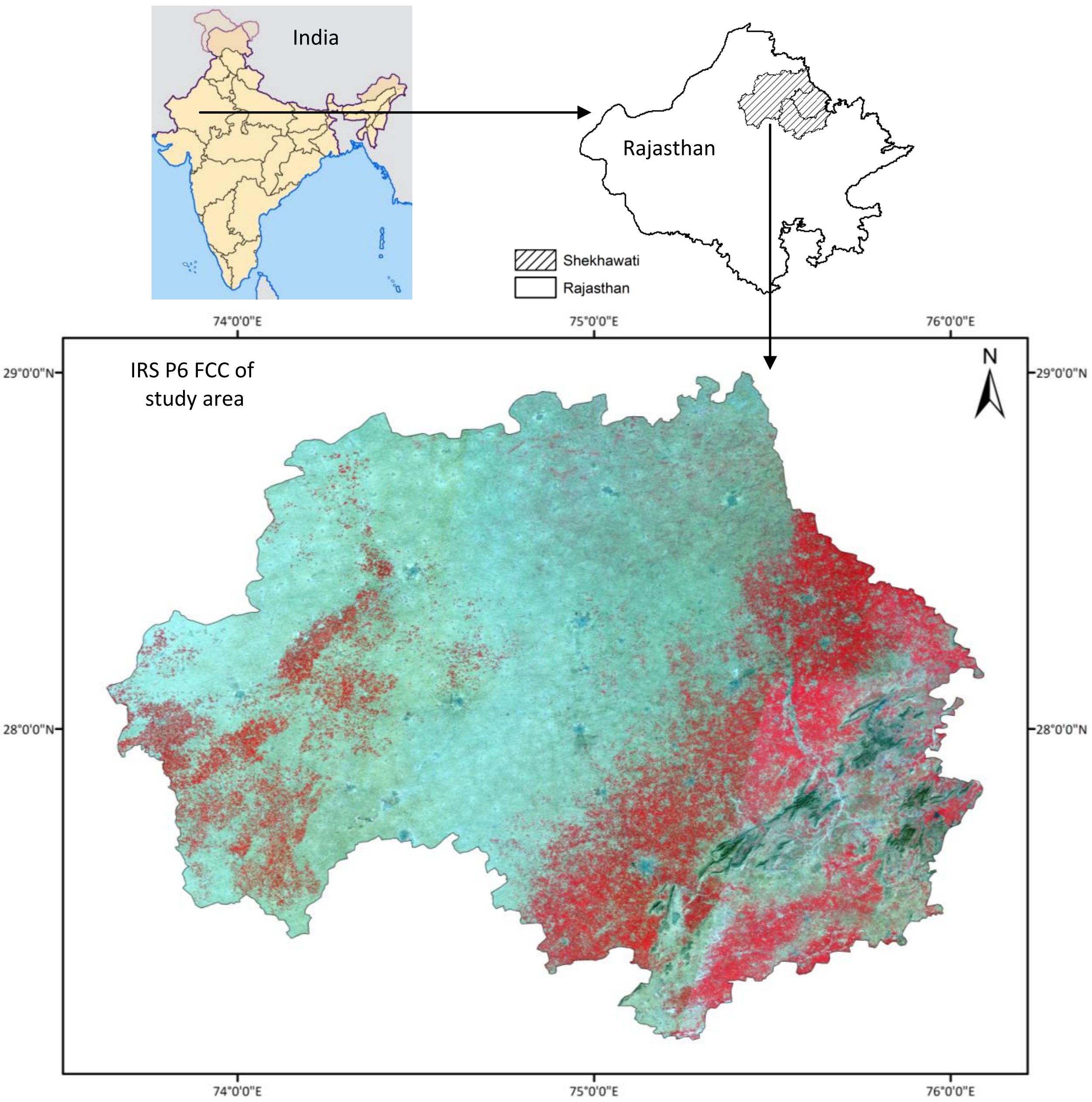

Figure 3.1: Map of Study Area.

Rajasthan state pollution control board has dataset of electric conductivity (EC) from year 1986 to 2014 (RSPCB, 2014a; RSPCB, 2014b) which is used as base data for electric conductivity. We have used this dataset to represent our sampling time in Figure 3.2 for Shekhawati region. As the individual dataset of parameters understudy are unavailable and ionic concentration is directly related with electric conductivity, thus to represent overall ionic concentration and its trend Figure 3.2 is plotted.

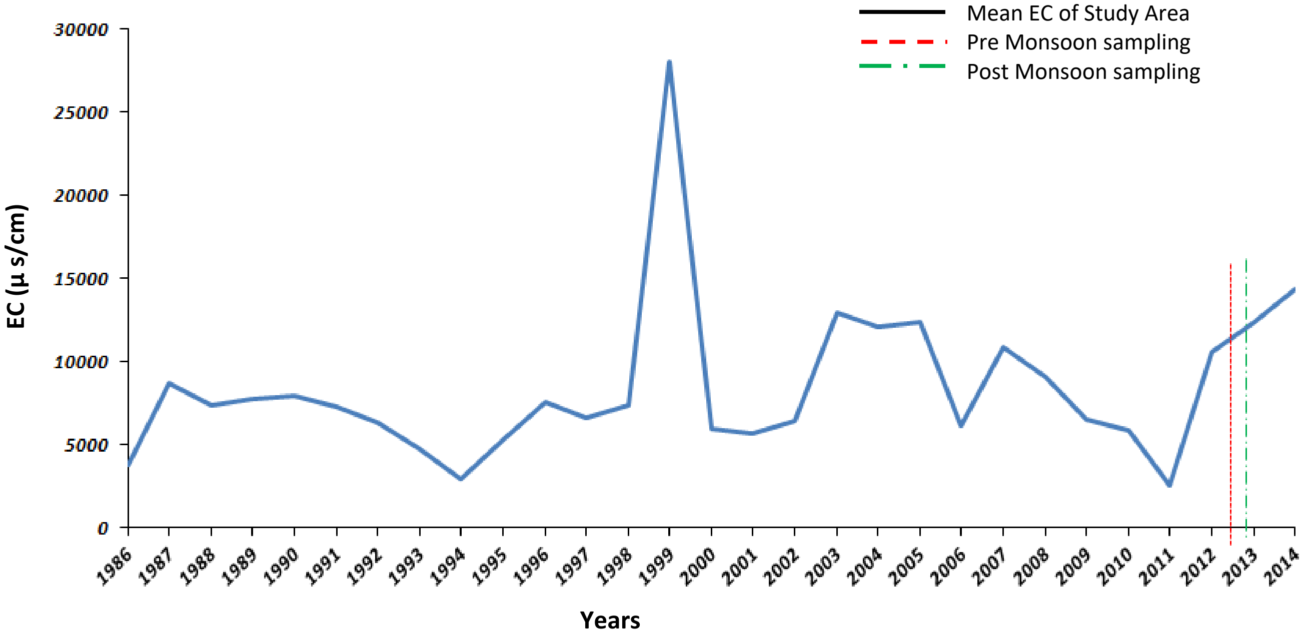

Figure 3.2: Sampling time indicated on EC trend in study area (RSPCB, 2014a; RSPCB, 2014b)

Samples are collected in pre monsoon and post monsoon seasons of year 2012. 163 samples in each season are collected. This thesis also aims to increase our understanding of the quality of water within desert and arid climatic zone. Chemical properties are determined in the Public Health Engineering Department (PHED) laboratory at Jhunjhunu, Rajasthan. The sampling schedule during pre monsoon, and post monsoon helped to determine seasonal characteristics of the groundwater. Water-quality results are compared to applicable water-quality standards mentioned in IS: 10500 (IS 10500, 2012).

3.2 Methodology

The following methodology has been adopted to characterize the groundwater:

- Physico-chemical analysis of sample for identification of Nitrate, Fluoride and Total Dissolved Solids in groundwater of Shekhawati region of Rajasthan.
- 3D analysis of the chosen water quality parameters to present the distribution of concentration in sub surface strata.
- Development or identification of the material for the treatment of Nitrate, Fluoride and TDS present in groundwater.

To achieve the objectives of study, following steps have been considered viz. (1) Groundwater characterization, (2) 3D analysis and (3) Removal of Nitrate, Fluoride and Total Dissolved Solids.

3.2.1 Groundwater quality

The methodology followed for groundwater quality estimation in Shekhawati region is shown in Figure 3.3.

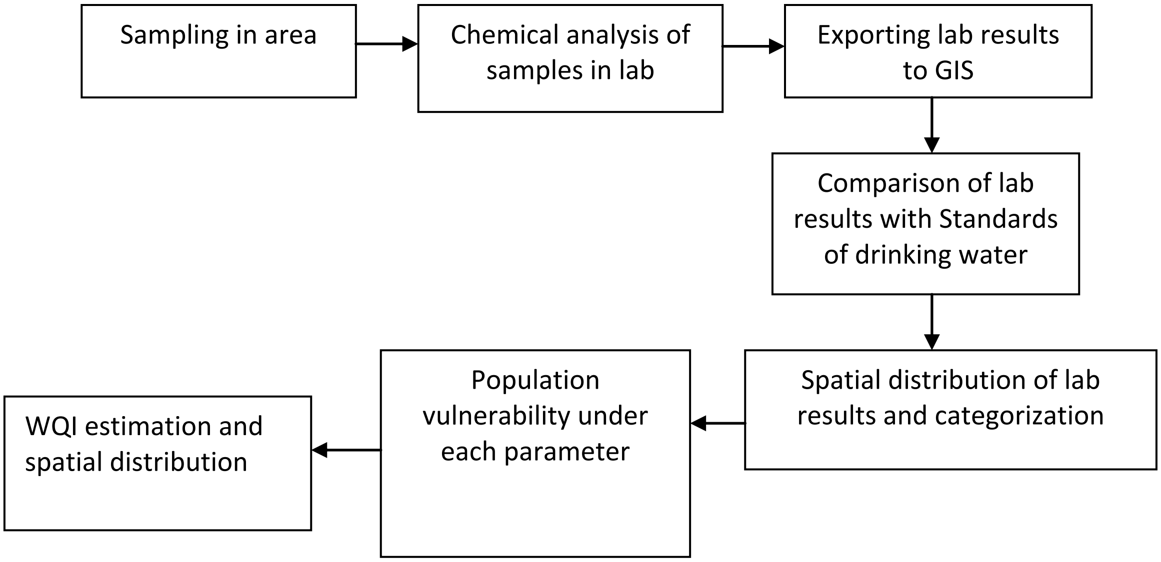

Figure 3.3: Flowchart showing procedure followed for WQI determination in study area.

3.2.2 3D Analysis

The methodology followed for performing 3D analysis for showing the variations in chosen parameters in Shekhawati region is shown in Figure 3.4.

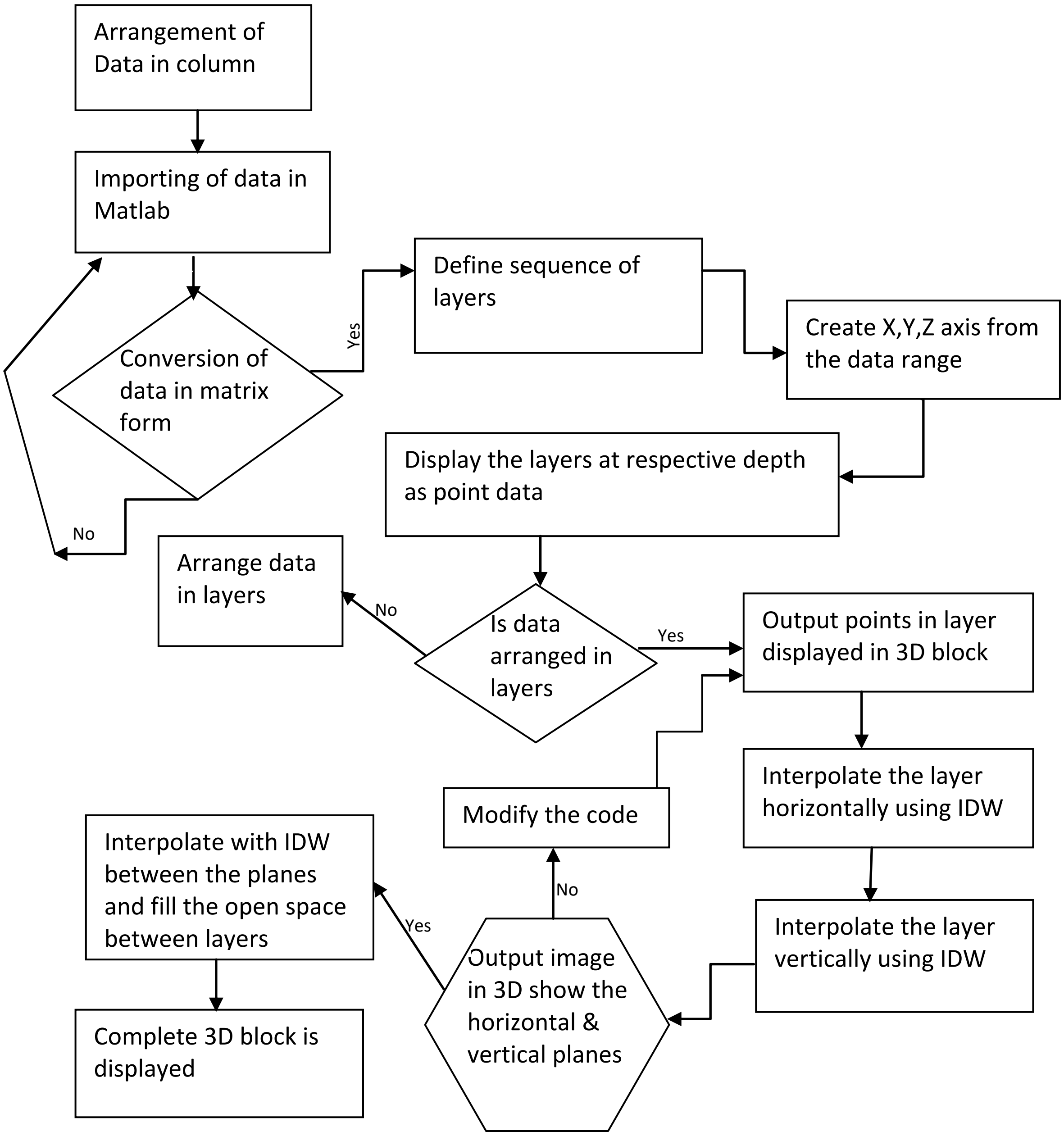

Figure 3.4: Methodology adopted to show distribution of parameters in 3D.

3.2.3 Removal of Nitrate, Fluoride and Total Dissolved Solids

The methodology followed for removal of Nitrate, Fluoride and Total Dissolved Solids is shown in Figure 3.5.

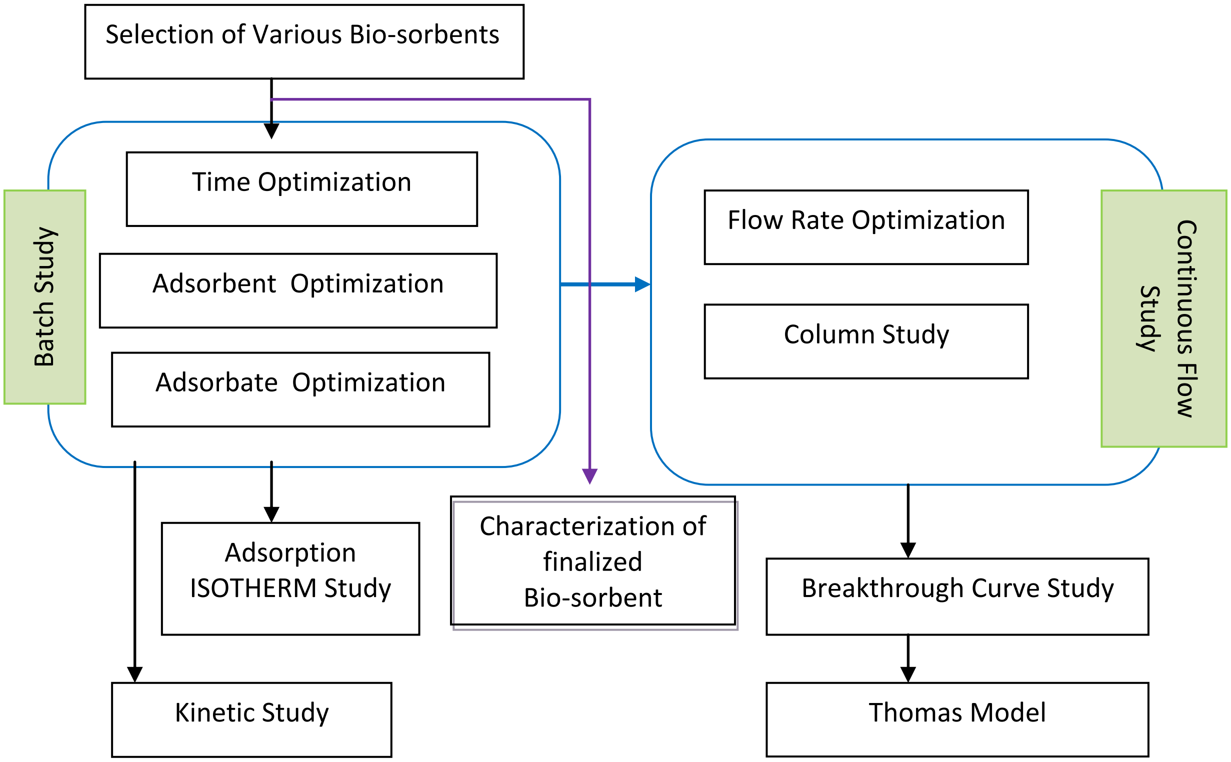

Figure 3.5: Methodology adopted for Nitrate, Fluoride and TDS removal

3.3 Experimental data

Based on objectives, data and material chosen and details of resources utilized are specified here.

3.3.1 Groundwater quality

The data used for investigation of the chemical parameters and characterization of groundwater have been discussed below.

- 163 samples of groundwater for pre monsoon and post monsoon duration are used to investigate Nitrate, Fluoride and Total Dissolved Solids. The locations of samples are shown in Figure 3.6. The Pictures of sampling duration are shown in Annexure 1A and details of sampling location are provided in Annexure 2A.

- The sampling plan for collecting water sample has been developed in Geographic Information System (GIS) based on equi-interval grid where two sampling location were 15 *km* apart. A good coverage of the study area can be more easily achieved with equi-interval grid. As the locations are generated through GIS, thus the nearest well is approached from these points for samples. The samples are collected from the tube wells in two litre water bottles.
- The specific values of chemical parameters (Nitrate, Fluoride and TDS) have been determined at PHED, Jhunjhunu, Rajasthan for all the samples.

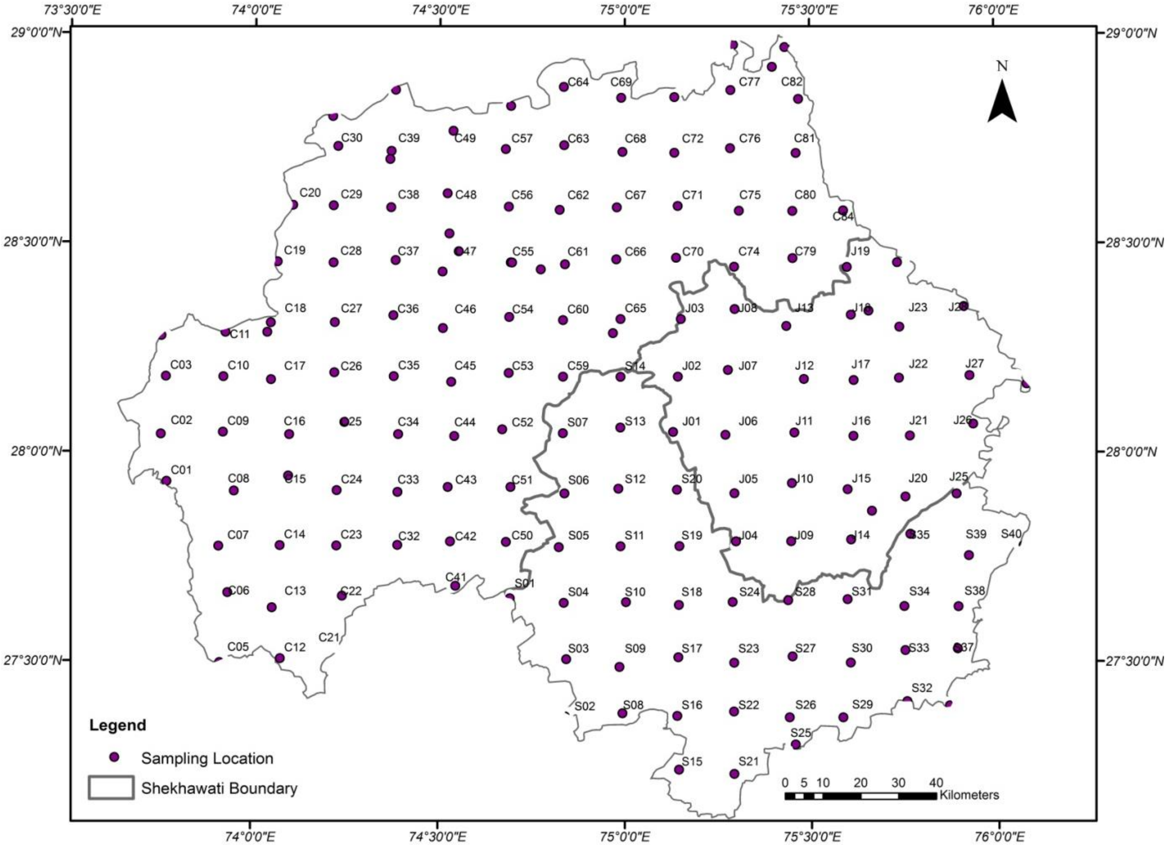

Figure 3.6: Map showing the sampling location in study area

- The details of the testing procedure are provided in section 3.4. The photographs showing the sample collection, chemical testing of samples and instruments used are illustrated in Annexure 1B.
- Further, these obtained values of above said parameters are compared with Indian standards (IS 10500, 2012).
- Arc GIS (ver 10.2) is used to create various maps used in the study to show spatial distribution of these parameters.

- Population from census data of Survey of India (Census of India, 2011) has been used. As our sample collection year is 2012, so population is forecasted for year 2012. The forecasting is done by Arithmetical increase method whose formula is mentioned below in eq. (equation) 3.1. This Arithmetic formula is used because of on verification of other population forecasting methods for previous decades; it gives more nearer population values.

  Population after nth decade will be $P_n = P + n.C$ (3.1)

  Where, P_n is the population after 'n' decades and 'P' is present population. C represents the population growth rate.
- The water quality index is determined by formulas mentioned here. At first, quality rating Q_i, for the ith water quality parameter can be obtained by the following relation mentioned from equation 3.2 to equation 3.4 (Tiwari and Ali, 1988).

  $$Q_i = \frac{V_i}{S_i} \times 100 \tag{3.2}$$

  The overall water quality index was calculated by aggregating these quality ratings linearly as follows,

  $$WQI = \sum_{i=1}^{n} Q_i \tag{3.3}$$

  The average water quality index (AWQI) for n parameters was calculated using equation

  $$AWQI = \frac{\sum_{i=1}^{n} Q_i}{n} = \frac{WQI}{n} \tag{3.4}$$

  Where, Q_i = Quality rating of the ith parameter at a given sampling site, V_i = observed value of the ith parameter at a given sampling site, S_i = water quality standard for ith parameter and n = number of parameters.

3.3.2 3D Analysis

- For the 3D distribution, the water quality parameters determined at 163 locations for both pre and post monsoon seasons have been used.
- For generating the 3D views, Matlab (ver. R2012b) is applied.
- Inverse Distance Weightage (IDW) technique of interpolation is used as it uses distance and parameter value to predict the new value for the space considered for interpolation.

- For verifying the results of 3D analysis, the location of state ground water board (SGWB) wells have been used and they are illustrated in Figure 3.7. Out of 163 sampling location and state ground water board location, only four locations are in close proximity. Soil log (SGWB, 2014) is discussed for these four locations and deviation between real data and simulated data for subsurface depth is used to verify the accuracy of the presented 3D analysis.

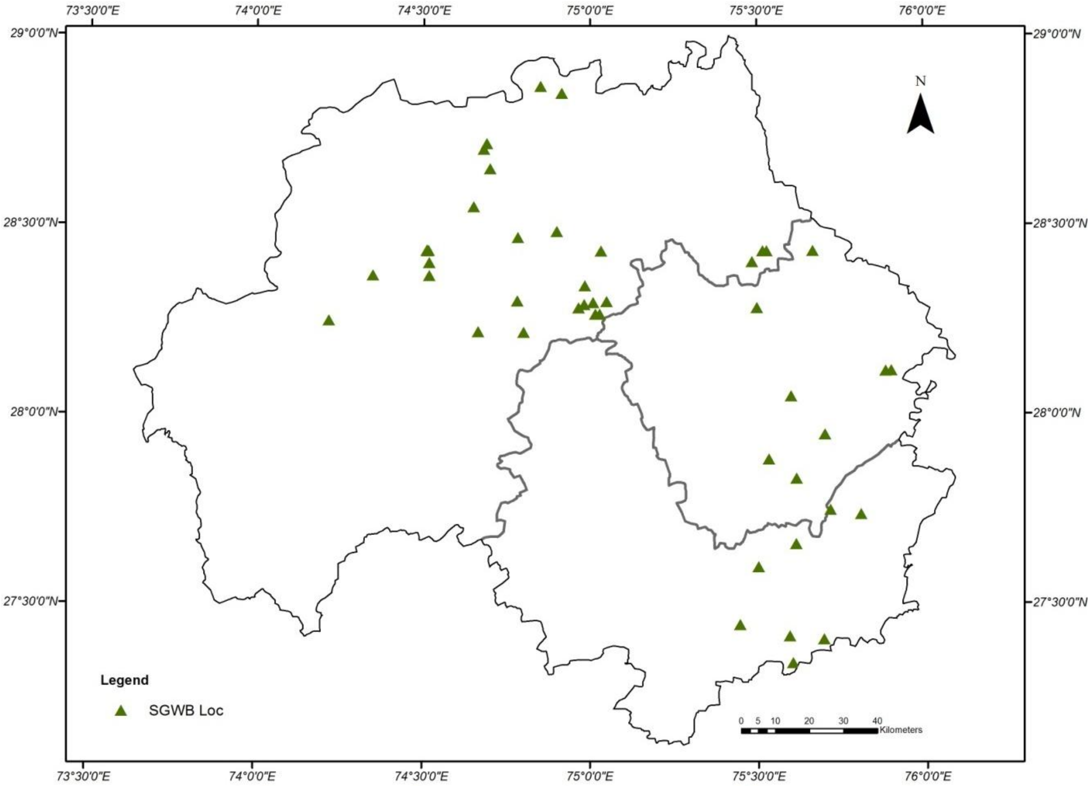

Figure 3.7: Groundwater monitoring wells locations in Shekhawati (SGWB, 2014)

3.3.3 Removal of Nitrate, Fluoride and Total dissolved solids

For achieving the last and important objective of this study, ie. removal of Nitrate, Fluoride and TDS present in groundwater; nine natural materials have been used. The list of these materials is provided in Table 3.1 below and their photographs are shown in Annexure 1C.

Table 3.1: List of material used in study

Sr.	Material Name	Scientific Name	Material Code	Form of material
1	Wheat Husk	*Triticum*	WH	Powder
2	Rice Husk	*Oryza sativa*	RH	Powder
3	Banana peel Husk	*Musa*	BH	Powder

4	Bagasse	*Saccharum officinarum*	SH	Powder
5	Coconut Coir	*Cocos nucifera*	CC	Chopped fiber
6	Amla Seed	*Phyllanthus emblica*	AS	Powder
7	Aloevara Gel	*Aloe Barbadensis Miller*	AG	Gel
8	Amla Bark	*Phyllanthus emblica*	AB	Powder
9	Potato	*Solanum tuberosum*	PG	Gel

These materials are prepared for the experimentation by following steps.

a) Washing of the material at room temperature for removal of dust particles.

b) Materials are oven dried at Temp. 103 ± 3 °C to remove moisture content (Reeb and Milota, 1999).

c) Oven dried samples are grinded and meshed to the size of 10 *µm*.

d) Coconut coir and Aloevera gel have not been grinded and used as such.

e) Potato gel is prepared by suspending potato slurry in distilled water in beakers followed by gentle heating and holding at 55-60 °C for 24 hour (Hans et al., 2004).

The groundwater used for experimentation and collection of groundwater is based on lab results of sampling. The samples C50 and C51 is recollected due to presence of high concentration of Nitrate (304 *mg/l*) and Fluoride (21 *mg/l*) in them respectively, while sample C60 is recollected for high TDS (2240 *mg/l*). These samples are analyzed in environmental engineering laboratory of BITS- Pilani, Rajasthan.

3.3.3.1 *Batch study*

The batch study is carried out to optimize the various parameters (Time, Weight and Concentration) for removal of nitrate, fluoride and total dissolved solids, separately. In the study, collected samples are used as influent for high concentration of nitrate, fluoride and total dissolved solids and details are provided in section 3.4.1. The samples are prepared based on description provided in standard methods, 1995 (APHA, 1995) for chemical analysis. Under batch study, these three parameters are optimized:

i. Contact Time
ii. Weight of Adsorbent
iii. Concentration of adsorbate

3.3.3.2 *Isotherms*

In general, an adsorption isotherm is an invaluable curve describing the phenomenon governing the retention (or release) or mobility of a substance from the aqueous porous media or aquatic environments to a solid-phase at a constant temperature and pH. Adsorption equilibrium (the ratio between the adsorbed amount with the remaining in the solution) is established when an adsorbate containing phase has been contacted with the adsorbent for sufficient time, with its adsorbate concentration in the bulk solution in a dynamic balance with the interface concentration. Its physicochemical parameters together with the underlying thermodynamic assumptions provide an insight into the adsorption mechanism, surface properties as well as the degree of affinity of the adsorbents (Foo and Hameed, 2010). There are many isotherms available to identify the adsorption mechanism and here we are using following two isotherms due to their universal acceptance.

Freundlich isotherm (Reynolds and Richard, 2009) is the mathematical relationship that describes the non-ideal and reversible adsorption and it is not restricted to the formation of monolayer. This empirical model can be applied to multilayer adsorption with non-uniform distribution of adsorption heat and affinities over the heterogeneous surface. The amount adsorbed is the summation of adsorption on all active sites (each having bond energy). In multilayer adsorption, the stronger binding sites are occupied first, until adsorption energy is exponentially decreased upon the completion of adsorption process (Foo and Hameed, 2010). Graph between $\frac{x}{m}$ and C_e is developed for Freundlich isotherm. The standard form of this isotherm is expressed by equation 3.5 and its linear form by equation 3.6.

$$\frac{x}{m} = X = KC_e^{1/n} \tag{3.5}$$

$$\log\left(\frac{x}{m}\right) = \log X = \log K + \frac{1}{n}\log C_e \tag{3.6}$$

where, x = mass of solute adsorbed (*mg*), m = mass of adsorbed (*mg*),

X = mass ratio of the solid phase- that is, the mass of adsorbed solute per mass of adsorbent,

C_e = equilibrium concentration of solute, mass/volume (*mg/l*)

K and n = experiment constants (Reynolds and Richard, 2009)

Langmuir empirical model (Langmuir, 1918) assumes monolayer adsorption (the adsorbed layer is one molecule in thickness), with adsorption can only occur at a finite (fixed) number of definite localized sites, that are identical and equivalent, with no lateral interaction and steric hindrance between the adsorbed molecules, even on adjacent sites. Homogeneous adsorption is referred in Langmuir isotherm which suggests that each molecule possesses constant enthalpies and sorption activation energy (all sites possess equal affinity for the adsorbate) and no transmigration of the adsorbate in the plane of the surface occurs (Foo and Hameed, 2010). Graph between $\frac{1}{x/m}$ and $\frac{1}{C_e}$ is developed for plotting Langmuir isotherm. The standard form of this isotherm is expressed by equation 3.7 and its linear form by equation 3.8.

$$Q = \frac{Q_{\max} K C_e}{1 + K C_e} \tag{3.7}$$

$$\frac{1}{Q} = \frac{1}{K Q_{\max} C_e} + \frac{1}{Q_{\max}} \tag{3.8}$$

where,

K= experiment constant or relative energy of adsorption (*L/mg*),

C_e= equilibrium concentration of solute, mass/volume (*mg/l*),

$Q=(x/m)$, mass ratio of the solid phase, i.e., the mass of adsorbed solute per mass of adsorbent,

x= mass of solute adsorbed (*mg*), m= mass of adsorbed (*mg*),

and, Q_{max} = ultimate adsorption capacity (*mg/g*)

3.3.3.3 *Kinetics*

To know the order of reaction (Averill and Eldredge, 2006; Bures, 2016), 3 graphs viz., (1) time vs concentration difference (T vs ΔC), (2) time vs log of concentration difference (T vs log ΔC) and (3) time vs inverse of concentration difference (T vs 1/ ΔC) are plotted. The order of reaction would be determined as,

(a) If T vs ΔC is straight line then, it is of Zeroth order reaction.

(b) If T vs log ΔC is straight line, then it is of First order reaction.

(c) If T vs 1/ ΔC is straight line, then it is of Second order reaction.

3.3.3.4 *Continuous study*

Further, with the finalized material based on batch study, continuous study is performed. Under continuous study, one parameter, i.e. flow rate is optimized after the optimization of Adsorbate, Adsorbent and Time. The peristaltic pump (model RH-P-110S-50) from Ravel has been used and it has the flowrate capacity between 0.1 *ml/min.* to 50 *ml/min.* and specification shown in Annexure 1D. After optimization of these four parameters (time, adsorbent, adsorbate and flowrate), column test is carried out. During column run, influent containing optimized concentration of Nitrate, Fluoride and TDS is continuously passed separately for 144 hours. The effluent sample is collected at regular intervals and analyzed for values of Nitrate, Fluoride and TDS. The value of Nitrate and Fluoride in water sample and effluent is analyzed using UV Spectroscopy (Evolution 201 from Thermo Scientific) method and TDS is determined by method mentioned in section 3.4.4. The parameters of column study are mentioned in Table 3.2

Table 3.2: Parameters of column study

Parameter	**Value**
Height of column	37.5 *cm.*
Height of packed material in column	34 *cm.*
Diameter of column	3 *cm.*
Mass of Material used in column	30 *g.*
Flow Rate	6 *ml/min.*
Concentration of Nitrate, Fluoride and TDS	Optimized values

3.3.3.5 *Breakthrough curve*

Breakthrough curve (Basmadjian, 1997; Warren et al., 2005) helps in identifying the breakthrough time and breakthrough volume. The adsorbent behaviour is studied through this curve. The graph developed between normalized concentration (C_e/C_o) and time (T) or volume (V) is termed as breakthrough curve where C_e & C_o are effluent & influent concentration respectively. The breakthrough curve (BC) is also termed as frontal chromatogram. It represents the evolution of the solution concentration as function of adsorption parameters like contact time between liquid and solid phase, solvent concentration and temperature (Figure 3.8).

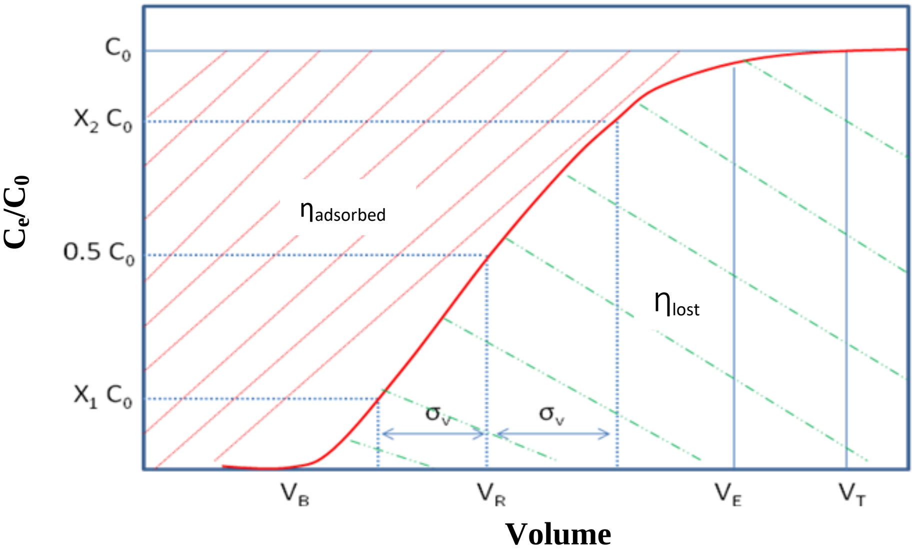

Figure 3.8: Breakthrough curve

The total amount of the analyte originally present in the sample is the product of the analyte concentration and sample volume, C_0V_0. The amount lost (η_{lost}) due to breakthrough is graphically represented by the area under the frontal chromatogram (Reynolds et al., 2009). Thus, the amount retained in the column ($\eta_{adsorbed}$) equals the difference between the total amount and the amount lost, graphically corresponding to the area above the frontal chromatogram. The breakthrough curve can give precious information regarding the cartridge and the solid phase inside, like the number of theoretical plates, the linear capacity or the recovery factor. The breakthrough volume V_B, the equilibrium volume V_E, the retention volume V_R and total volume V_T are fundamental parameters that characterize this curve. These parameters are determined using standard deviation method over this curve (Gelencser et al., 1995).

The retention time of the analyte (V_R) can be determined as given in equation 3.9:

$$V_R = 0.5C_0 \qquad (3.9)$$

The breakthrough volume (V_B) is usually defined as in equation 3.10:

$$V_B = V_R - 2\sigma_v \qquad (3.10)$$

where σ_v is the standard deviation of the derivative curve and determined from curve

Number of theoretical plates (N) of efficiency of the column can be determined by equation 3.11:

$$N = \frac{V_R(V_R - \sigma_v)}{(\sigma_v)^2} \qquad (3.11)$$

The equilibrium volume (V_E) can be defined as equation 3.12:

$$V_E = V_R + 2\sigma_v \tag{3.12}$$

where σ_v can be determined from curve.

3.3.3.6 *Thomas Model*

Rigorous fixed bed models, usually cast in the form of partial differential equations, allow a realistic mathematical description of the sorption column dynamics. When the equilibrium relationship is linear, an analytical solution for the fixed bed dynamic behavior can always be obtained. For nonlinear systems the governing equations are usually solved numerically. Thomas model gives a general analytical solution for these equations and the assumption of non linear equilibrium relationship of Langmuir isotherm. Thomas model neglects the axial dispersion. Thomas model is employed by many researchers to predict the breakthrough curves for adsorption (Yasmen and Shahlaa, 2010).

Thomas model (Thomas, 1944) provides a general analytical solution with help of a graph between volume and log of neutralized concentration. Its standard equation is given below in equation 3.13 and linear form of it is represented by equation 3.14.

$$\frac{C_e}{C_o} = \frac{1}{1+\exp\left[\frac{K_t}{Q}\left(q_o M - C_o V\right)\right]} \tag{3.13}$$

$$ln\left(\frac{C_e}{C_o} - 1\right) = \frac{K_t q_o M}{Q} - \frac{K_t C_o}{Q} V \tag{3.14}$$

where C_e, C_o = the effluent and influent concentrations of adsorbate in water (*mg/l*),

q_o = the maximum adsorption capacity (*mg/g*),

M = the total mass of the adsorbent (*g*),

Q = volumetric flow rate (*ml/min*),

V= the throughput volume (*ml*)

K_t = the Thomas rate constant (*ml/min/mg*)

3.4 Sample preparation, storage and analytical procedure

Following section defines the process for sample preparation, storage and analytical procedure.

3.4.1 Sample preparation and storage

The groundwater is used for experimentation and sample C50 and sample C51 have been used for Nitrate (304 *mg/l*) and Fluoride (21 *mg/l*) testing and sample C60 for TDS (2240 *mg/l*) is used in study. They have been re-collected in 100 *l* container during pre monsoon sampling and diluted with distilled water for experiments as required. The samples are stored at 4 °C in deep freezer (APHA, 1995).

3.4.2 Analytical procedure for determination of Nitrate

Principle: Determination of nitrate (NO_3^-) (APHA, 1995) is difficult because of the relatively complex procedures required, the high probability that interfering constituents will be present, and the limited concentration ranges of the various techniques. An ultraviolet (UV) technique (method B) that measure the adsorbance of NO_3^- at 220 *nm* is suitable for screening uncontaminated water (low in organic matter).

Procedure:

(a) 50 *ml* clear sample is filtered if necessary and added 1 *ml* HCl solution and mix thoroughly.

(b) Prepare NO_3^- calibration standards in the range 0 to 7 *mg* NO_3^- N/*l* by diluting the 50 *ml* the following volumes of intermediate nitrate solution: 0, 1, 2, 4, 7, 35 *ml*. Treat NO_3^- standards in same manner as samples.

(c) Read absorbance or transmittance against redistilled water set at zero absorbance or 100% transmittance. Use a wavelength of 220 *nm* to obtain NO_3^- reading and a wavelength of 275 *nm* to determine interference due to dissolved organic matter.

(d) In a dry test tube add first reagent NO_3^- in 4 *ml*. add 0.50 ml amount of sample in it. Again second reagent NO_3^- in 0.50 *ml* and leave the mixture in test tube for 10 *min* to complete the reaction. After 10 *min*, fill the cuboid cell from the test tube and measure the nitrate value in spectrophotometer.

Calculation: For samples and standards, subtract two times the absorbance reading at 275 *nm* from the reading at 220 *nm* to obtain absorbance due to NO_3^-. Construct a standard curve by plotting absorbance due to NO_3^- against nitrate - nitrogen concentration of standards. Using corrected samples absorbance, obtain sample concentration directly from standard curve. If correction value is more than 10% of the reading at 220 *nm*, then this method cann't be used (APHA, 1995).

Reactions: In sulfuric and phosphoric solution, nitrate ions react with 2,6-dimethylphenol (DMP) to form 4-nitro-2,6-dimethylphenol that is determined photometrically (APHA, 1995).

3.4.3 Analytical procedure for determination of Fluoride

Principle: The (sodium 2-(parasulphophenylazo-)-1,8-dihydroxy-3,6-naphthalene disulphonate) SPADNS colorimetric method (APHA, 1995) is based on the reaction between fluoride and a zirconium dye. Fluoride reacts with the dye lake, dissociating a portion of it into a colorless complex anion (ZrF_6^{2-}) and dye. As the amount of fluoride increases, color produced becomes progressively lighter. Spectrophotometer, is used at 570 *nm*, providing a light path of at least 1 *cm* and also it have attached greenish yellow filter having maximum transmittance at 550 to 580 *nm*.

Procedure:

(a) Add reagent F^- in 0.5 *ml* into a dry test tube and then add 5 *ml* of sample in it.

(b) Next mix second reagent 1 *g* in this test tube and leave for 15 *min* for completing the reaction.

(c) Fill the cuboid cell from the test tube and measure the value in spectrophotometer.

(d) Prepare fluoride standards in the range of 0 to 2 *mg* F^-/l by diluting appropriate quantities of standard fluoride solution to 50 *ml* with distilled water. Pipet 5 *ml* each of SPANDNS solution and zirconyl acid reagent to each standard and mix well. Set photometer to zero absorbance with the reference solution and obtain absorbance reading of standards. Plot a curve of the milligrams fluoride adsorbance relationship. Prepare a new standard curve whenever a fresh reagent is made or a different standard temperature is desired. As an alternative to using a reference, set photometer at some convenient point (0.300 or 0.500 absorbance) with the prepared 0 *mg* F^-/l standard. If the absorbance falls beyond the range of the standard curve, repeat using a diluted sample.

Calculation: The following relation is used for determination of fluoride as shown in equation 3.15 (APHA, 1995).

$$. \ F^-(mg/l) = \frac{A.B}{V.C} \tag{3.15}$$

where, A=μg F^- determined from plotted curve,

B= final volume of diluted sample (in *ml*),

C= volume of diluted sample used for color development (in *ml*)

V= volume of sample (in *ml*)

When the prepared 0 *mg* F^-/l standard is used to set the photometer, alternatively fluoride concentration can be calculated by equation 3.16 as:

$$F^{-}(mg/l) = \frac{A_0 - A_x}{A_0 - A_1} \qquad (3.16)$$

Where, A_0= absorbance of the prepared 0 mg F^-/l standard,

A_1=absorbance of a prepared 1 mg/ F^-/l standard and

A_x= absorbance of the prepared sample

Reaction: In a buffered, weakly acidic solution, fluoride ions react with alizarin complexone and lanthanum (III) to form a violet complex that is determined photometrically (APHA, 1995).

3.4.4 Analytical procedure for determination of Total Dissolved Solids

Principle: A well mixed sample is filtered through a standard glass fibre filter and the filtrate is evaporated to dryness in a weighed dish and dried to constant weight at 180 °C (APHA, 1995). The increase in dish weight represents the total dissolved solids. This procedure may be used for drying at other temperatures.

Procedure:

(a) Insert disk with wrinkled side up into filtration apparatus. Apply vacuum and wash disk with three successive 20 *ml* volume of reagent grade water. Continue suction to remove all trace of water.

(b) If volatile solids are to be measured, ignite cleaned evaporating dish at 550 °C for 1 *h* in a muffle furnace. If only TDS are to be measured, heat clean dish to 180 ± 2 °C for 1 *h* in an oven. Weight immediately before use.

(c) Choose sample volume to yield between 10 to 200 *mg* dried residue. If more than 10 *min* is required to complete filtration, increase filter size or decrease sample volume.

(d) Stir sample with a magnetic stirrer and pipet a measured volume onto a glass-fibre filter with applied vacuum. Wash with three successive 10 *ml* of reagent grade water, allowing complete drainage between washing, and continue suction for about 3 *min* after filtration is complete. Transfer total filtrate to a weighed evaporating dish and evaporate to dryness on a steam bath or in a drying oven. If necessary, add successive portions to the same dish after evaporation. Dry evaporated sample for at least 1 *h* in an oven at 180 ± 2 °C, cool in a desiccator to balance temperature and weigh. Repeat drying cycle of drying, cooling, desiccating and weighing until a constant weight is obtained or until weight change is less than 4% of the previous weight or 0.5 *mg*, whichever is less. Duplicate determinations should agree within 5% of their average.

Calculation: The following relation is used in determination of TDS as shown in equation 3.17 (APHA, 1995).

$$\text{TDS } (mg/l) = \frac{(A-B)100}{V(ml)} \tag{3.17}$$

where, *A*= weight of dried residue + dish (in *mg*),

B= weight of dish (in *mg*) and

V= volume of sample (in *ml*)

3.5. Instruments

For the analytical work, the samples were analyzed in UV spectrophotometry (Evolution 201 from Thermo Scientific) (Annexure 1E) and pump used for upflowing the water in column study is peristaltic pump (RH-P-110S-50) (Annexure 1F) from Ravel. The specification of reagents used in analysis is provided in Annexure 1G. The Fourier transform infrared spectroscopy (FTIR) is carried out with PerkinElmer Spectrum Version 10.03.09, (Frontier FT-IR) (Annexure 1H) for the purpose of detecting changes in transmittance of adsorbent. The pictures of UV Spectrophotometer and FTIR is shown in Annexure 1D.

3.5.1 Ultraviolet–visible spectroscopy

In Ultraviolet-visible spectroscopy, light in the visible (380-780 *nm*) and adjacent ultraviolet (190-380 *nm*) (near-UV) ranges are used. The absorption or reflectance in the visible range directly affects the perceived color of the chemicals involved. In this region of the electromagnetic spectrum, molecules undergo electronic transitions. Molecules containing π-electrons or non-bonding electrons (n-electrons) can absorb the energy in the form of ultraviolet or visible light to excite these electrons to higher anti-bonding molecular orbitals (Skoog et al., 2007). The more easily excited the electrons, the longer the wavelength of light it can absorb. The Beer-Lambert law states that the absorbance of a solution is directly proportional to the concentration of the absorbing species in the solution and the path length. Thus, for a fixed path length, UV-Vis spectroscopy can be used to determine the concentration of the absorber in a solution (Skoog et al., 2007).

Ultraviolet-visible (UV-Vis) spectroscopy is a widely accepted technique to achieve knowledge about the ground state absorption characteristics of any particular system, in terms of absorption bands and extinction coefficients at different wavelengths. Major shifts in the absorption spectrum are often induced by change in either hydrogen bonding characteristics, solvent polarity or polarizability (Skoog et al., 2007; Lackowicz, 2006). Spectral shifts are also caused by environmental effects, which alter the relative energy of ground and excited states. The absorbance (A) of an absorbing species is the difference between the intensity of light incident (I_0) to the intensity of light transmitted (I) in a solution. It is also directly proportional to the concentration (C) of the species and its molar extinction coefficient (ε_λ) at the measuring wavelength λ and is given by the equation 3.18.

$$A = \log\left(\frac{I_0}{I}\right) = \varepsilon_\lambda Cl \tag{3.18}$$

where, l is the path length for the light beam passing through the sample.

3.5.2 Fourier transform infrared spectroscopy

Fourier transform infrared (FTIR) spectroscopy (Stuart Barbara, 2010) is based on the idea of the interference of radiation between two beams to yield an interferogram. The latter is a signal produced as a function of the change of pathlength between the two beams. The two domains of distance and frequency are inter convertible by the mathematical method of Fourier-transformation.

FTIR stands for Fourier Transform Infra Red, the preferred method of infrared spectroscopy. In infrared (IR) spectroscopy, IR radiation is passed through a sample. Some of the infrared radiation is absorbed by the sample and some of it is passed through (transmitted). The resulting spectrum represents the molecular absorption and transmission, creating a molecular fingerprint of the sample (Smith, 1996). Like a fingerprint no two unique molecular structures produce the same infrared spectrum. Therefore, infrared spectroscopy can result in a positive identification (qualitative analysis) of every different kind of material. In addition, the size of the peaks in the spectrum is a direct indication of the amount of material present.

The range of Infrared region (700 *nm* – 1 *mm)* lies between wavenumbers from about 12800 ~ 10 cm^{-1} (Stuart Barbara, 2010) and can be divided into near-infrared region (12800 ~ 4000 cm^{-1}), mid-infrared region (4000 ~ 200 cm^{-1}) and far-infrared region (50 ~ 1000 cm^{-1}). Infrared spectrum is molecular vibrational spectrum. When exposed to infrared radiation, sample molecules selectively absorb radiation of specific wavelengths which causes the change of dipole moment of sample molecules. Consequently, the vibrational energy levels of sample molecules transfer from ground state to excited state. The frequency of the absorption peak is determined by the vibrational energy gap. The number of absorption peaks is related to the number of vibrational freedom of the molecule. The intensity of absorption peaks is related to the change of dipole moment and the possibility of the transition of energy levels. Therefore, by analyzing the infrared spectrum, one can readily obtain abundant structure information of a molecule. The common used region for infrared absorption spectroscopy is 4000 ~ 400 cm^{-1} because the absorption radiation of most organic compounds and inorganic ions is within this region (Stuart Barbara, 2010).

3.6 Characterization of material

The adsorbent (i.e. potato gel) is characterized by FTIR (Stuart Barbara, 2010), before and after adsorption. The analysis is shown in Chapter 5.

3.7 Conclusions

The study area defines the boundary of region taken for study. It gives information of its climatic condition. The methodology and experimental setup used for groundwater characterization, 3D analysis and removal of Nitrate, Fluoride and TDS are discussed. Characterization study is fulfilled only if the population vulnerability is known. 3D analysis is done to know the vertical variation of the parameters under study for decision making for future groundwater extraction. The nine natural materials are considered for the study of reduction in Nitrate, Fluoride & TDS. The procedure (Batch & Column study) of conducting this study is also mentioned here. It defines the data, resources and equipment utilized in this study and help in producing the result and analysis provided in chapter 4 and chapter 5.

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4. Groundwater quality and 3D Analysis

This chapter initially deals with quality of groundwater. The spatial extent is shown for the water quality parameters (Nitrate, Fluoride and TDS). The water quality index (WQI) is determined for various data and its spatial extend with population vulnerability is measured. Secondly, the 3D analysis of the chosen parameters used in visualization of vertical and horizontal variation of their quality in slice form. The concentration vs. depth plots are developed to extract the information how the groundwater quality is changing beneath the surface.

4.1 Groundwater quality

The Shekhawati region lies in the state of Rajasthan. It includes three districts viz. Jhunjhunu, Sikar and Churu and their area is given in Table 4.1. The region lies under semi-arid to arid climatic condition as it is an extension of Thar Desert in NE & E direction. The vegetation cover is negligible and the surface water is absent. The groundwater is very deep in the region. Its area is 30,623 square kilometers.

Table 4.1: Area of districts

Jhunjhunu	Sikar	Churu	Total
5909 km²	7676 km²	17038 km²	30,623 km²

163 locations have been identified in Shekhawati region for the groundwater sampling with the help of Geographic information system (GIS). The Equal-interval grid is chosen for sampling as it gives more systematic information in understanding of spatial distribution pattern of different parameters. The adjacent sampling locations are 15 km apart and nearest well is approached from this point for sampling. The sampling location map is shown in chapter 3 (Figure 3.6). The sampling has been carried out during the month of June 2012 and October 2012 for pre monsoon & post monsoon seasons respectively. The groundwater samples have been collected in a row pattern and sample bottles are kept in ice box to avoid any change in physical and chemical characteristics (Sundaram et al., 2009). The groundwater samples have been delivered at PHED lab, Jhunjhunu, Rajasthan for analysis within 48 hours of their collection. The nomenclature of locations has been given in Annexure 2A for the collected samples.

31, 40 and 92 samples have been collected from Jhunjhunu, Sikar and Churu districts respectively, during pre monsoon and post monsoon season of year 2012. Total 163 samples are used to classify the study area for each single season. The samples are analyzed in PHED Lab and the analysis method is mentioned in chapter 3. The results for the samples are given in Annexure 2B for pre and post monsoon seasons respectively.

Table 4.2 provides the summary of the chemical characteristics of the groundwater samples for pre & post Monsoon seasons. The average value of Nitrate during pre & post monsoon is 114.55 *mg/l* & 150.86 *mg/l* respectively and indicates that the value of contaminant is above the maximum permissible limit. The average values of Fluoride during pre & post monsoon is 1.29 *mg/l* & 1.11 *mg/l* respectively and indicates that value of contaminant is in range of permissible limit. The average value of Total Dissolved Solids (TDS) during pre & post monsoon is 1681.04 *mg/l* & 1607.27 *mg/l* respectively and indicates that the value of contaminant is in range of permissible limit.

Table 4.2: Statistical summary of samples for pre and post monsoon season

	Range of values (*unit in mg/l*) Pre Monsoon			**Range of values (*unit in mg/l*) Post Monsoon**		
Parameter	***Minimum***	***Maximum***	***Average***	***Minimum***	***Maximum***	***Average***
Nitrate	2.00	790.00	114.55	2.00	1803.00	150.86
Fluoride	0.10	27.70	1.29	0.10	21.00	1.11
TDS	90.00	11,400.00	1681.04	80.00	13,600.00	1607.27

The standards (Table 4.3) mentioned by Govt. of India in IS: 10500 is used to categorize the groundwater in the study area. The three categories are defined, based on the standards prescribed as follows:

(1) Category 1: The values are lower than desirable limit (known as Below Limit- BL)

(2) Category 2: The values falls between desirable and maximum permissible limit (known as Safe Limit-SL)

(3) Category 3: The values are higher than permissible limit (known as Above Limit- AL)

Table 4.3: Indian Standards Specification (IS:10500, 2012)

Parameter Requirement	**IS: 10500 Desirable limit ($S_{i,min}$)**	**Remarks**	**Permissible limit in the absence of alternate source, ($S_{i,max}$)**
Nitrates *(mg/l)*	45	No relaxation/ Beyond this methanemoglobinemia takes place	-

Fluoride *(mg/l)*	0.6 to 1.2	If the limit is below 0.6 water should be rejected. High fluoride may cause fluorosis	1.5
Dissolved solids, *(mg/l)*	500	Beyond this palatability decreases and may cause gastro intentional irritation	2000

Table 4.4: Range used to categorize the sample data

Para\Range	**BL**	**SL**	**AL**
Fluoride *(mg/l)*	<0.6	0.60-1.5	>1.5
Nitrate *(mg/l)*	-	<45	>45
TDS *(mg/l)*	<500	500-2000	>2000

We have differentiated the total number of well samples into three group viz. Below Limit (BL), Safe Limit (SL) & Above Limit (AL) based on the categorization procedure mentioned in Table 4.4. Out of 163 wells, 48.47% and 36.19% wells lie under safe limit for pre and post monsoon season respectively for Nitrate. Out of 163 wells, 26.38% & 38.04% wells lie under safe limit for pre and post monsoon season respectively for Fluoride. Out of 163 wells, 46.01% and 51.53% wells lies under safe limit for pre and post monsoon season respectively for TDS. This indicates the severity of the problem in the study area for potable water for its habitants.

For potable purposes the three categories are reduced to two categories, namely (1) Safe (includes the values of safe limit category only) and (2) Rejected (includes the values of below limit and above limit categories). Table 4.5 and 4.6 shows the number of wells in three categories respectively, for pre and post monsoon season respectively.

Table 4.5: Wells under various categories for pre monsoon season

Numbers of Wells under 3 categories				**Parameter**
Safe	**Rejected**			
Safe limit	***Below limit***	***Above limit***	***Total***	
79	-	84	163	Nitrate
43	82	38	163	Fluoride
75	*44*	*44*	*163*	TDS

Table 4.6: Wells under various categories for post monsoon season

Numbers of Wells under 3 categories				**Parameter**
Safe	**Rejected**			
Safe limit	***Below limit***	***Above limit***	***Total***	
59	-	104	163	Nitrate
62	81	20	163	Fluoride
84	*40*	*39*	*163*	TDS

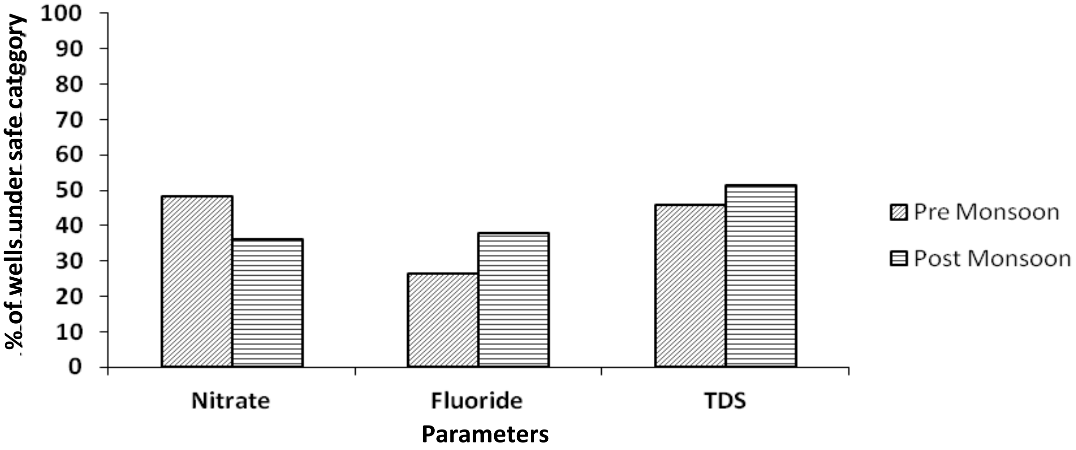

Figure 4.1: Changes in wells during pre to post monsoon under safe category

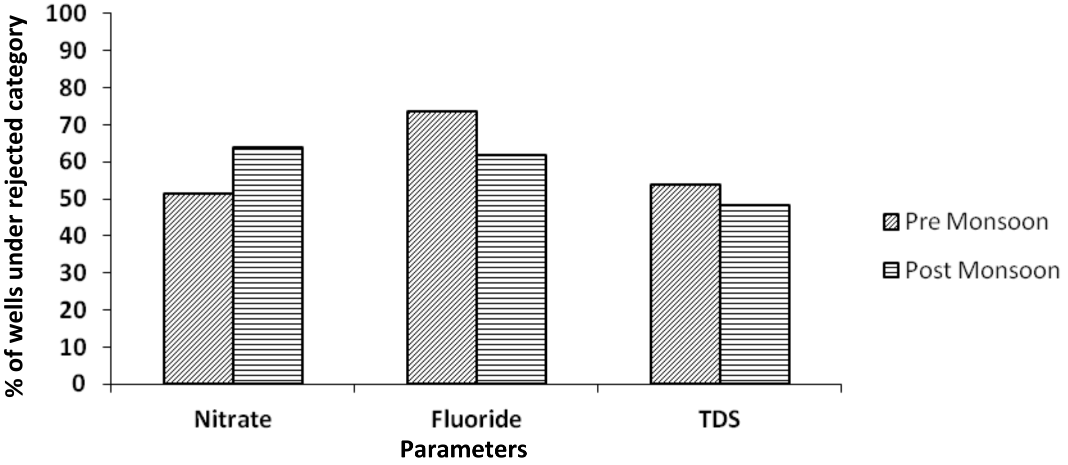

Figure 4.2: Changes in wells during pre to post monsoon under rejected category

Figure 4.1 & 4.2 sharply indicates the rise in number of wells under safe limit for Fluoride and TDS, from pre monsoon to post monsoon season in study area. While decline in number of wells under safe limit for Nitrate, from pre monsoon to post monsoon season is observed. The increase in number of wells in safe category of Fluoride and TDS may indicate the dilution of minerals (Biotite and Mica) in water that results due to good rainfall during the monsoon time of the sampling year (2012). While the decline in wells in safe category of Nitrate might be linked with leaching of nitrate compounds from agricultural area in few pockets. The concentration of Nitrate in the wells may be increased due to increase in agricultural activities from pre monsoon to post monsoon season.

4.2 Spatial distribution

The spatial distribution is used to show the extend of any category over the geographic surface. It helps in identifying the region under various categories and their vulnerability. It also helps in locating the affected population by individual category.

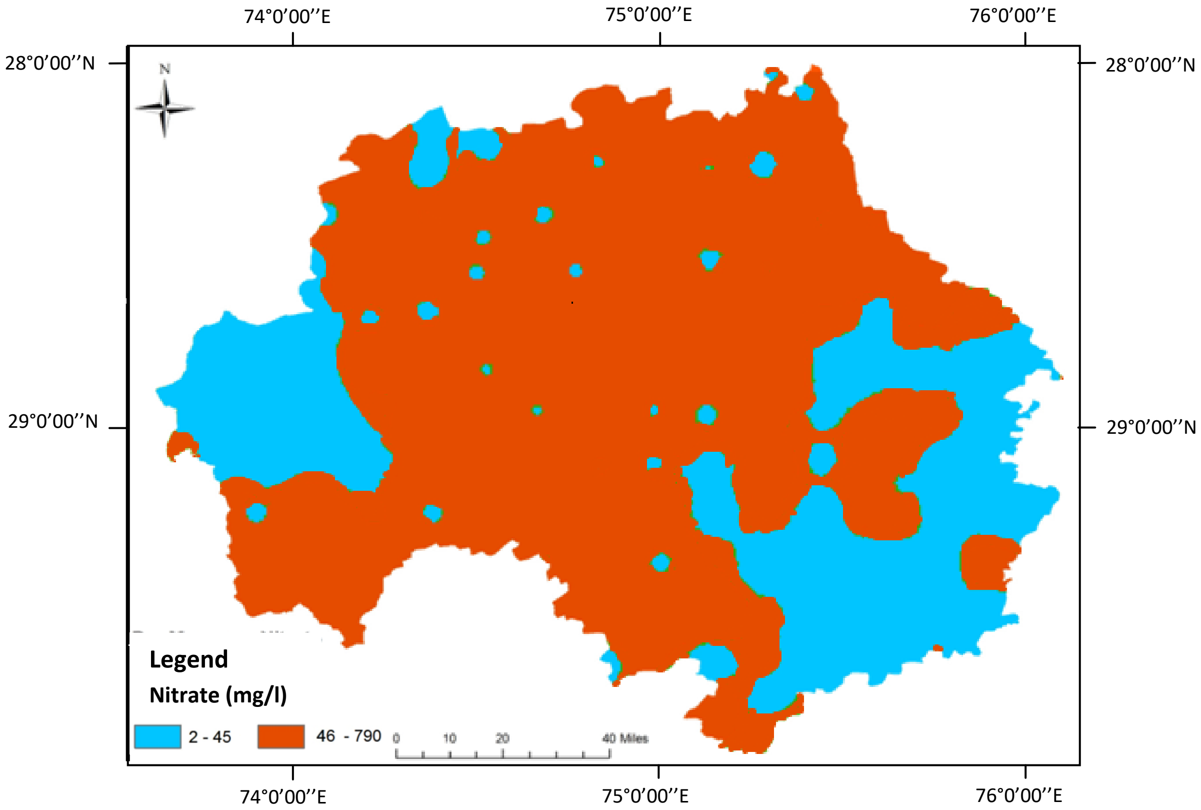

Figure 4.3: Spatial distribution of Nitrate in study area during pre monsoon

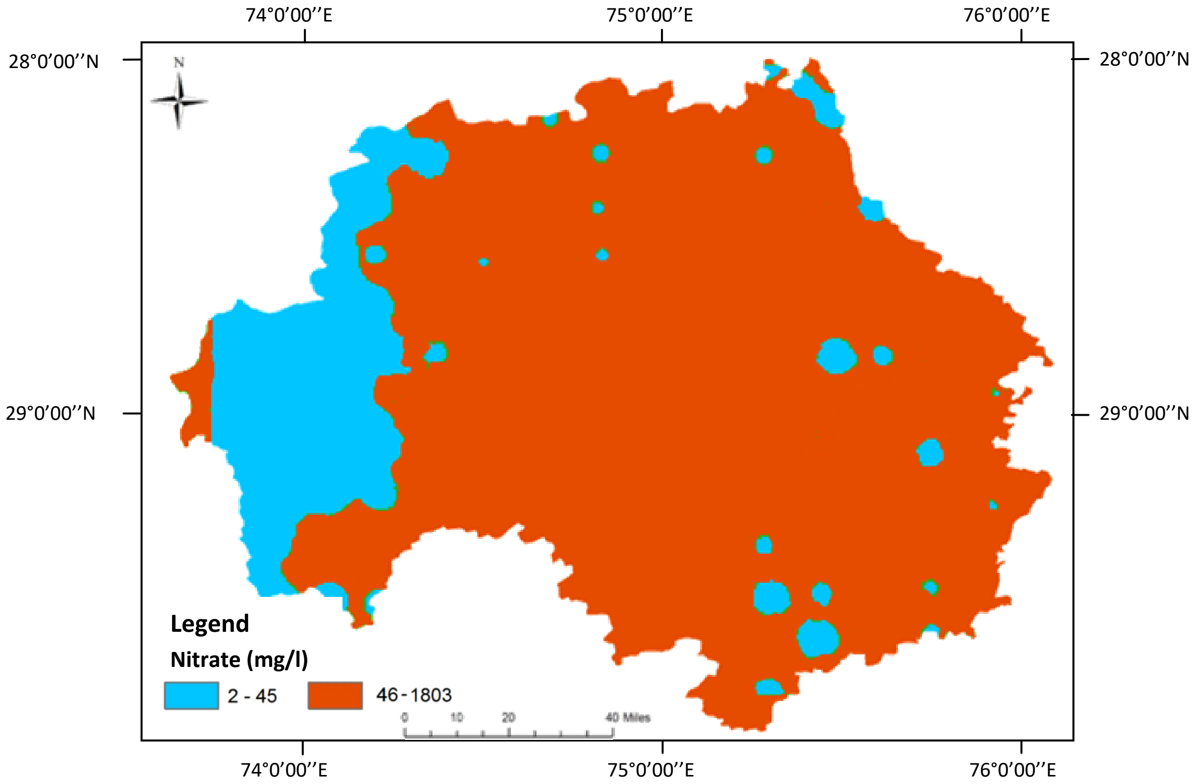

Figure 4.4: Spatial distribution of Nitrate in study area during post monsoon

Figure 4.3 & Figure 4.4 shows the spatial distribution of Nitrate in the study area for pre & post monsoon respectively. The two categories are used to show the distribution of Nitrate in the area. The first category has the range less than 45 *mg/l* of Nitrate, second category shows the range more than 46 *mg/l* of Nitrate.

Figure 4.5 & Figure 4.6 shows the spatial distribution of Fluoride in the study area for pre & post monsoon respectively. The three categories are used to show the distribution of Fluoride in the area. The first category has the range 0-0.60 *mg/l* of Fluoride, second category shows the range from 0.61-1.5 *mg/l* of Fluoride and third category shows the range more than 1.5 *mg/l* of Fluoride.

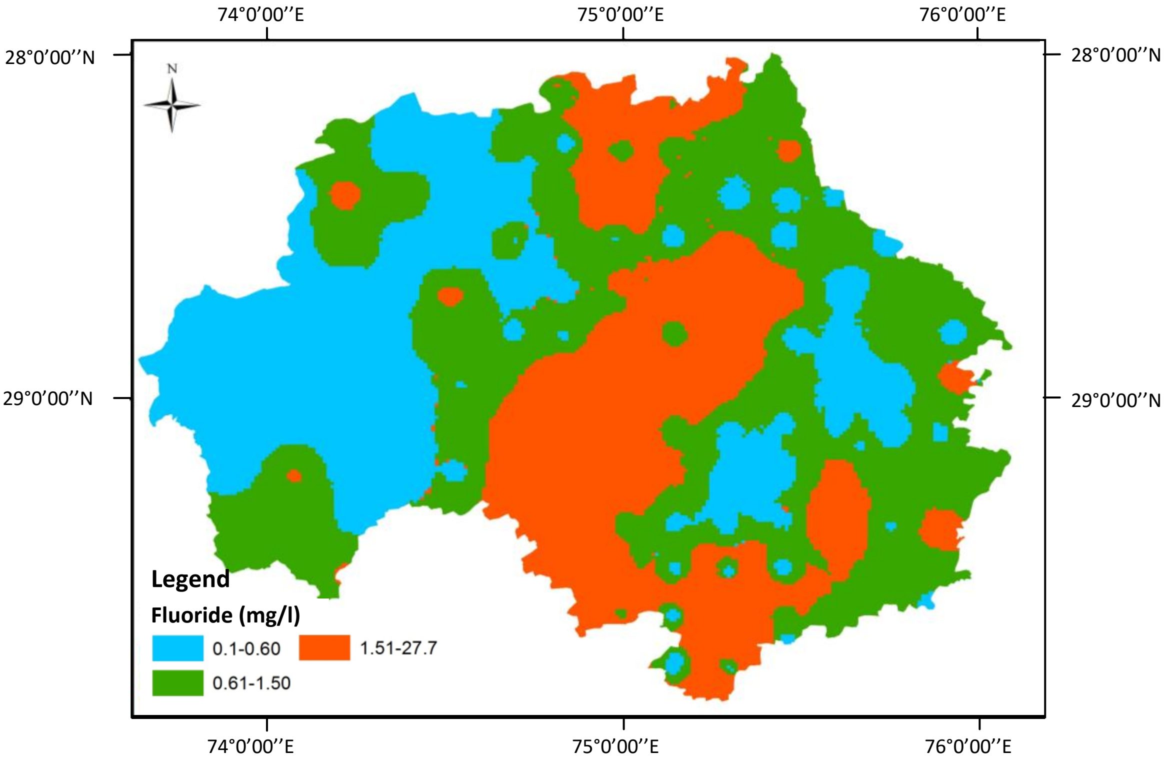

Figure 4.5: Spatial distribution of Fluoride in study area during pre monsoon

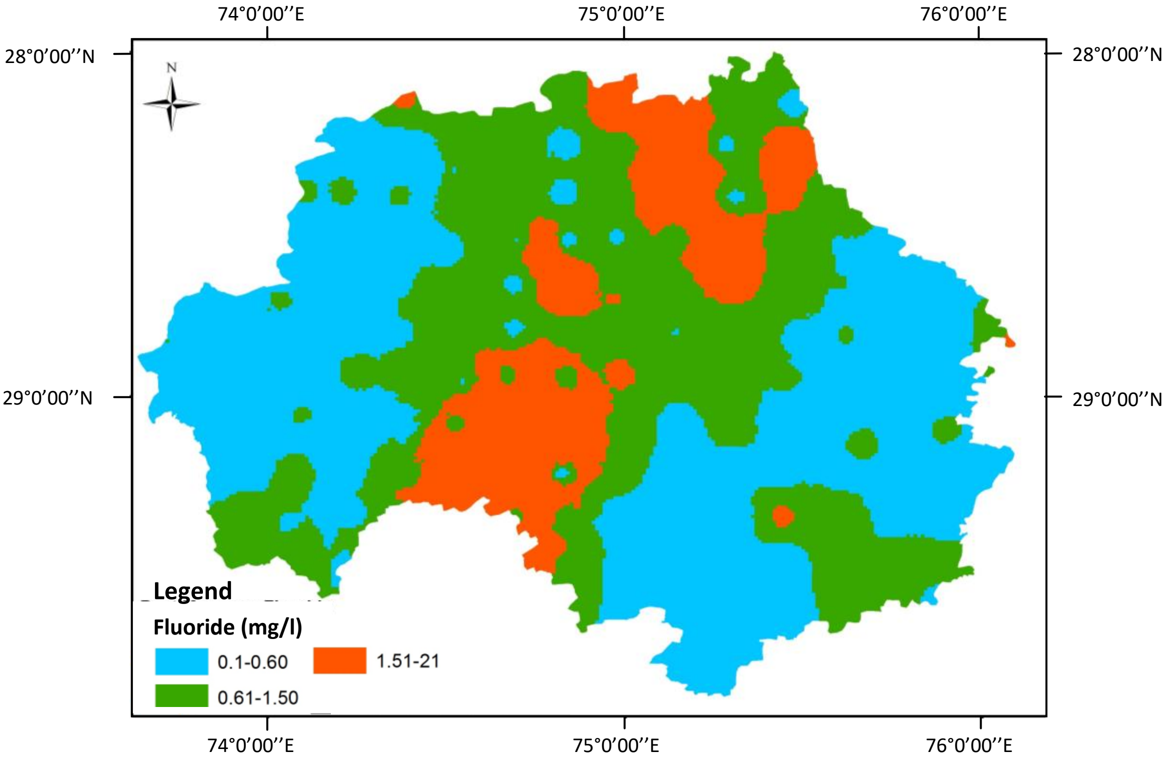

Figure 4.6: Spatial distribution of Fluoride in study area during post monsoon

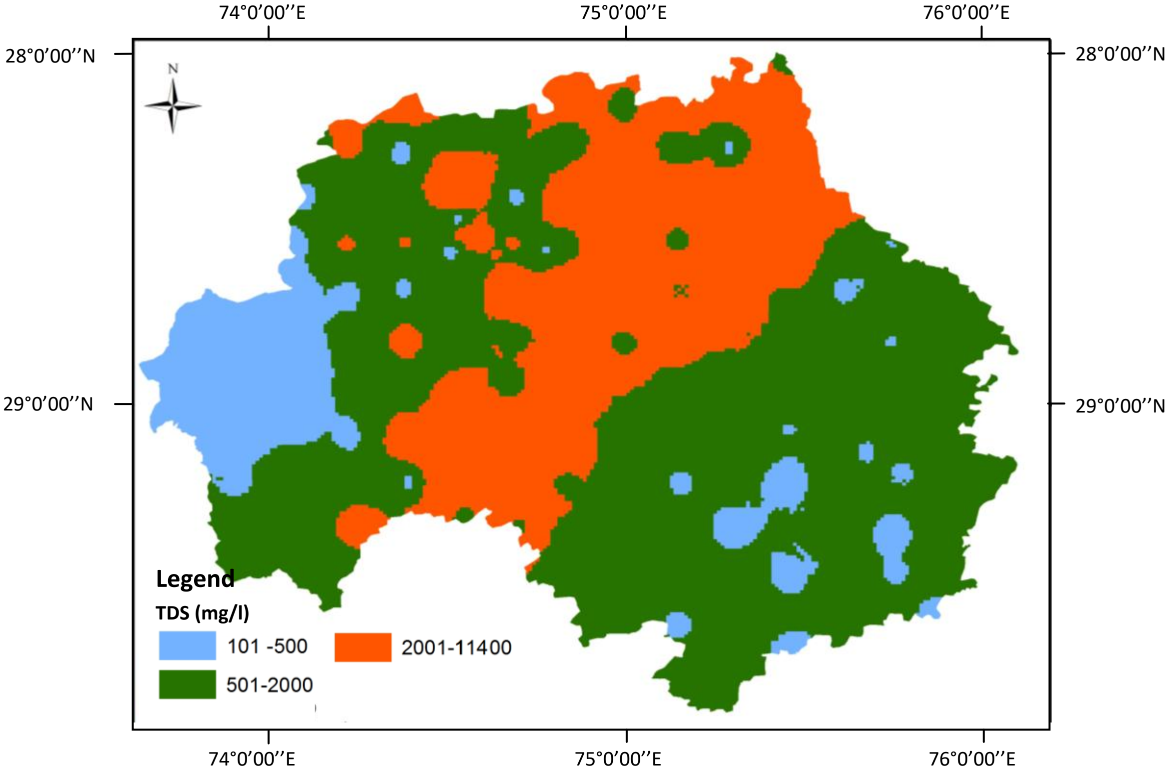

Figure 4.7: Spatial distribution of TDS in study area during pre monsoon

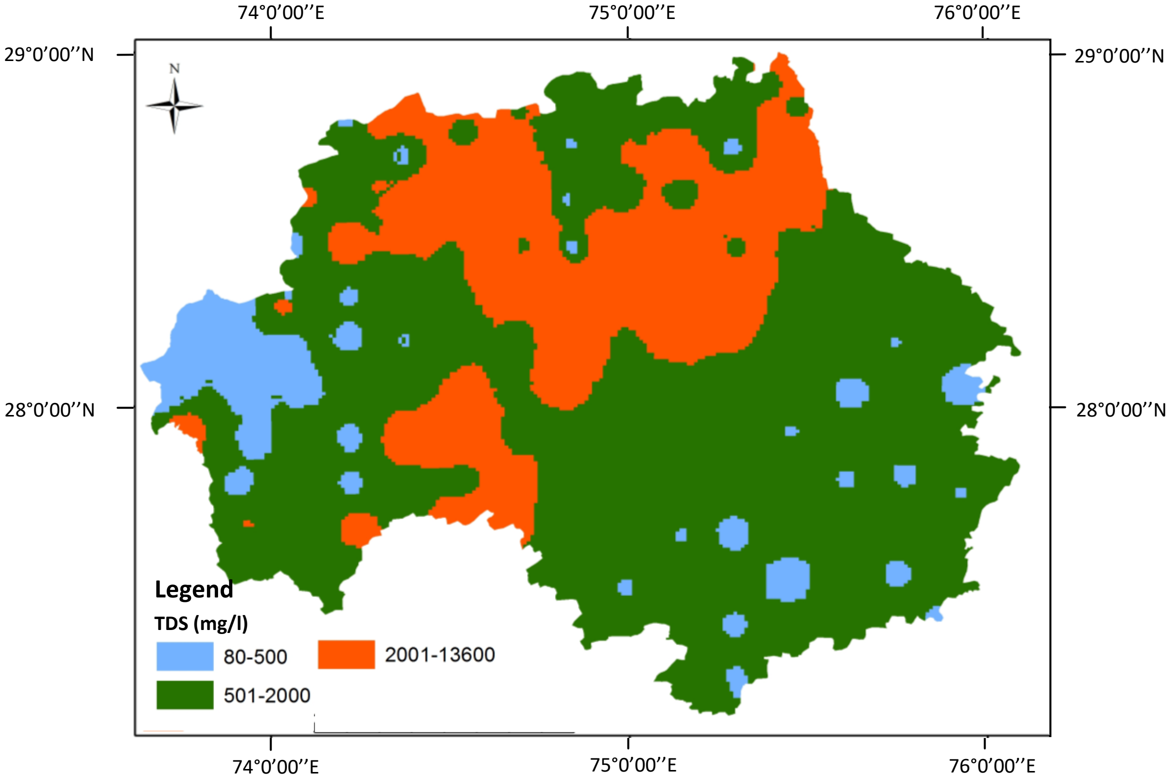

Figure 4.8: Spatial distribution of TDS in study area during post monsoon

Figure 4.7 & Figure 4.8 shows the spatial distribution of TDS in the study area for pre & post monsoon respectively. The three categories are used to show the spatial distribution of TDS values in the area. The first category has the range less than 500 *mg/l* of TDS, second category shows the range from 501-2000 *mg/l* of TDS and third category shows the range more than 2000 *mg/l* of TDS.

The changes in pre to post monsoon season are clearly visible under the extent of three categories for Fluoride & TDS and for Nitrate, the changes are under two categories. The Table 4.7 shows the area that lies under these categories and affected population respectively in the study area.

Table 4.7: Details of area coverage of vulnerability of different parameter and total population

		Pre Monsoon			**Post Monsoon**			
Sr	***Parameter***	***Below Limit***	***Safe Limit***	***Above Limit***	***Below Limit***	***Safe Limit***	***Above Limit***	**Total**
	Area (sq. km.)							
1	Fluoride	9580	11990	9053	14021	11324	5278	30623
2	Nitrate	-	9324	21299	-	5567	25056	30623
3	TDS	3749	17422	9452	2344	19843	8436	30623
	Population (numbers)							
1	Fluoride	1524376	2875954	2641382	3348999	2642771	1049942	70,41,712
2	Nitrate	-	2471901	4569811	-	676917	6364795	70,41,712
3	TDS	601637	4594628	1845447	387554	5117504	1536654	70,41,712

Figure 4.9 and Figure 4.10 shows the changes in areal and population coverage for Nitrate, Fluoride & TDS during pre & post monsoon season. It is clearly indicated that there is a huge change in area and population under the category of Below Limit from pre to post monsoon. Under the safe limit category, the changes between area and population are very low from pre to post monsoon seasons.

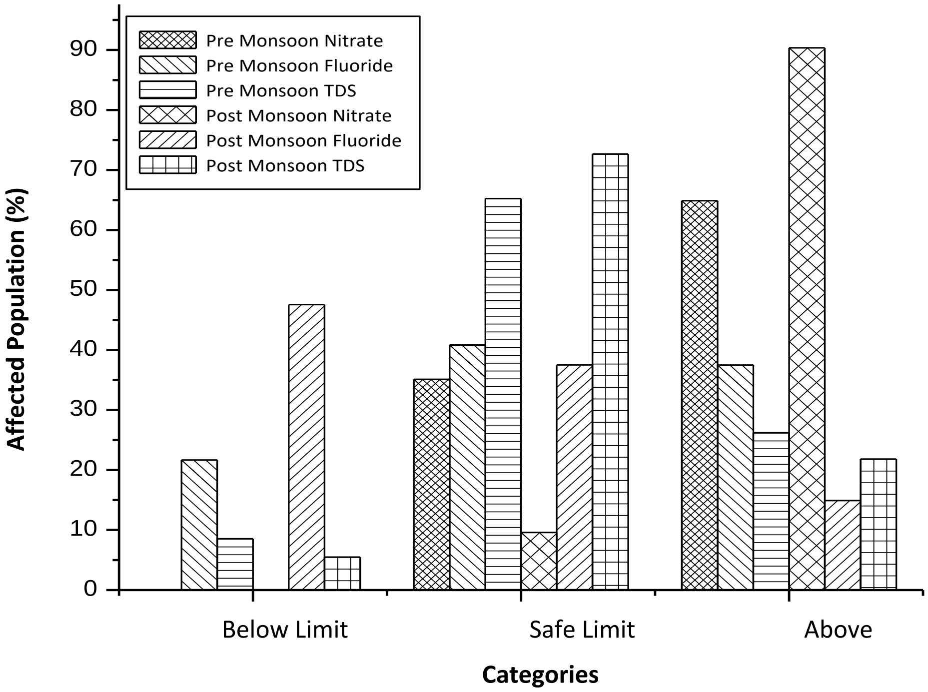

Figure 4.9: Plot showing affected population (%) under three categories for Nitrate, Fluoride and TDS for pre & post monsoon season

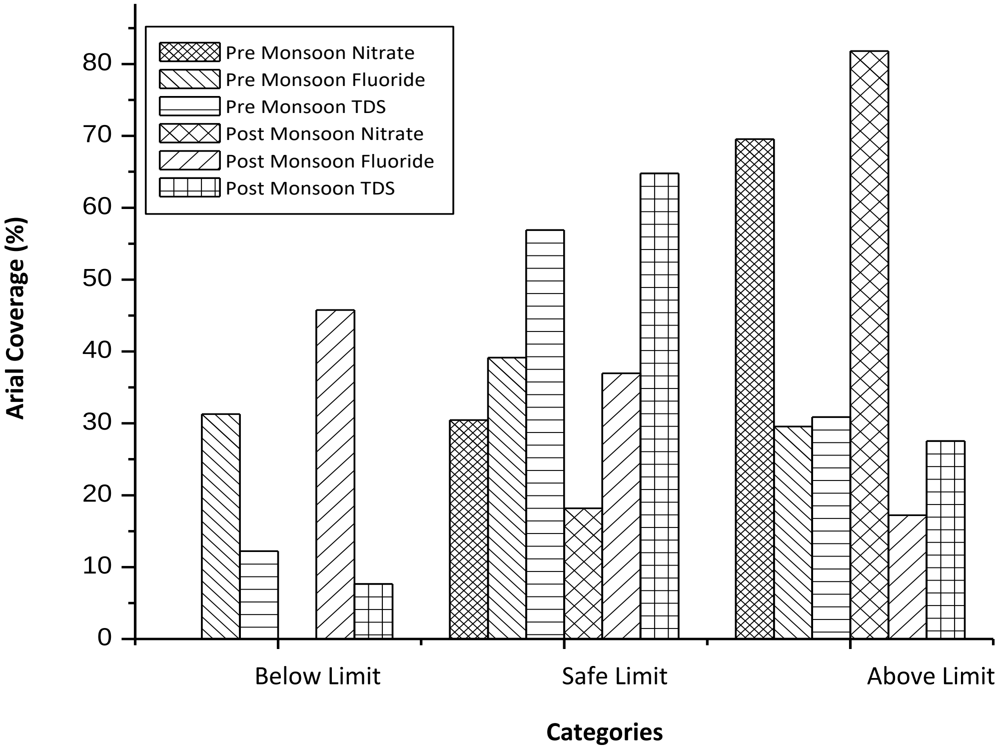

Figure 4.10: Plot showing areal coverage (%) under three categories for Nitrate, Fluoride and TDS for pre & post monsoon season

4.3 Water quality index

Water quality index (WQI) is required when there is more than one parameter associated with characterization of water. The different parameters have diverse range of safe limit that we have seen earlier. To overcome problem of diverse range associated with concerned parameters, WQI is developed. It helps in projecting the values for all considerable parameters in a single scale. We have used following equations (Tiwari and Ali, 1988) 4.1 to 4.3 to measure WQI.

Quality rating (Q_i), for the ith water quality parameter can be obtained by the following relation

$$Q_i = \frac{V_i}{S_i} \times 100 \qquad (4.1)$$

The overall water quality index was calculated by aggregating these quality ratings linearly as follows,

$$WQI = \sum_{i=1}^{n} Q_i \qquad (4.2)$$

The average water quality index (AWQI) for n parameters was calculated using equation

$$AWQI = \frac{\sum_{i=1}^{n} Q_i}{n} = \frac{WQI}{n} \qquad (4.3)$$

where, Q_i = Quality rating for the ith parameter at a given sampling site, V_i = Observed value of the ith parameter at a given sampling site,

S_i = Water quality standard and n = Number of parameters.

The range of WQI determined by using the equations 4.1 to 4.3 are shown in Table 4.8. The values shown in Table 4.8 are based on calculation shown in Annexure 2C. The WQI is calculated using the values of maximum permissible value ($S_{i,\max}$). The minimum and maximum values of S_i are indicated in Table 4.3.

Table 4.8: Summary of WQI for pre and post monsoon season (Annexure 2C)

	Pre Monsoon Range	**Post Monsoon Range**
Parameter	***Min -Max***	***Min-Max***
WQI	8.98 - 788.89	8.93 - 804.44

Figure 4.11 and Figure 4.12 displays the WQI of 163 wells during pre monsoon and post monsoon seasons respectively. The WQI range lies between 8.98-788.89 and 8.93-804.44 for pre and post

monsoon season respectively and it has been observed that WQI range doesn't varied much during post monsoon compared to pre monsoon.

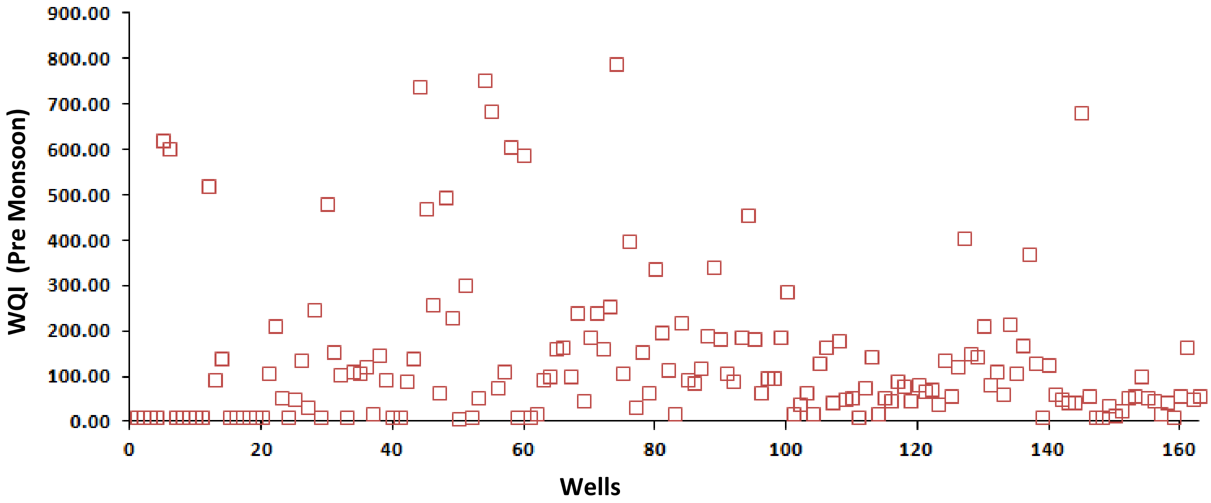

Figure 4.11: WQI distribution of wells during pre monsoon

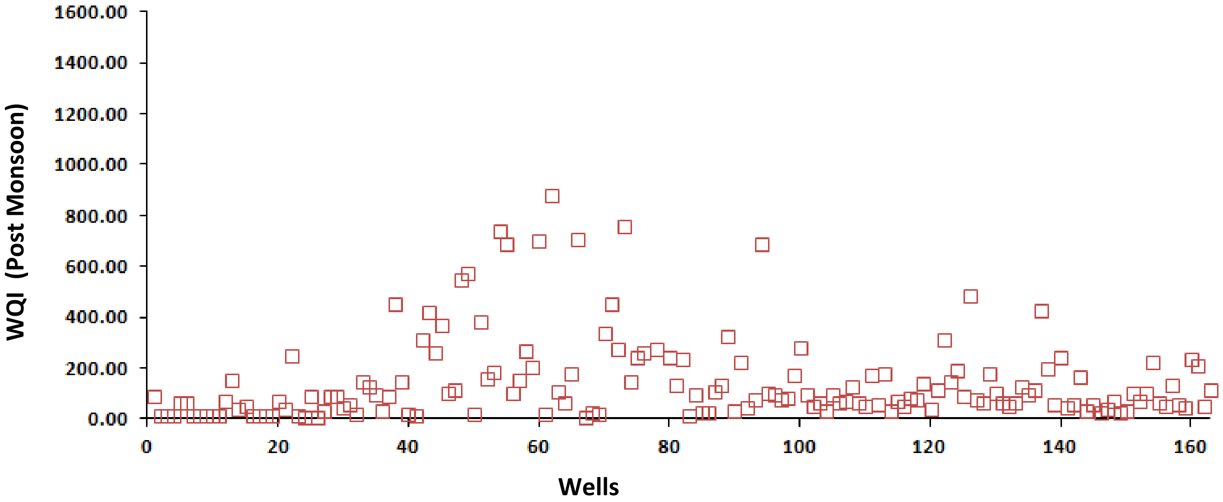

Figure 4.12: WQI distribution of wells during post monsoon

Figure 4.13 and Figure 4.14 shows the spatial distribution of WQI for pre & post monsoon respectively in study area. The safe area is verified by overlaying the wells having the values in safe range for three parameters used in the study for both season. Figure 4.15 shows the population density map (Census of India, 2011) of the region and helps in determining the number of habitants in region having access to safe or rejected quality of water. Table 4.9 shows the area and population covered under various categories of water quality index measured for pre and post monsoon.

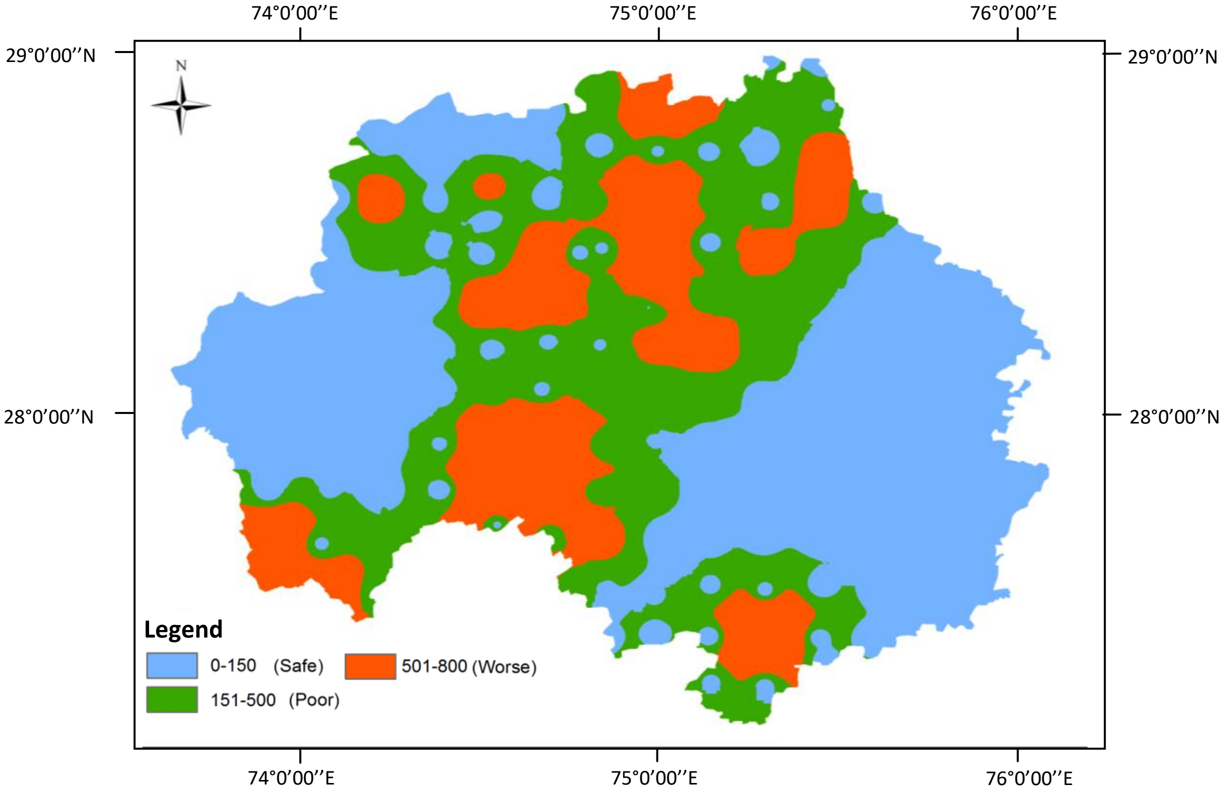

Figure 4.13: Spatial distribution of WQI in study area during pre monsoon

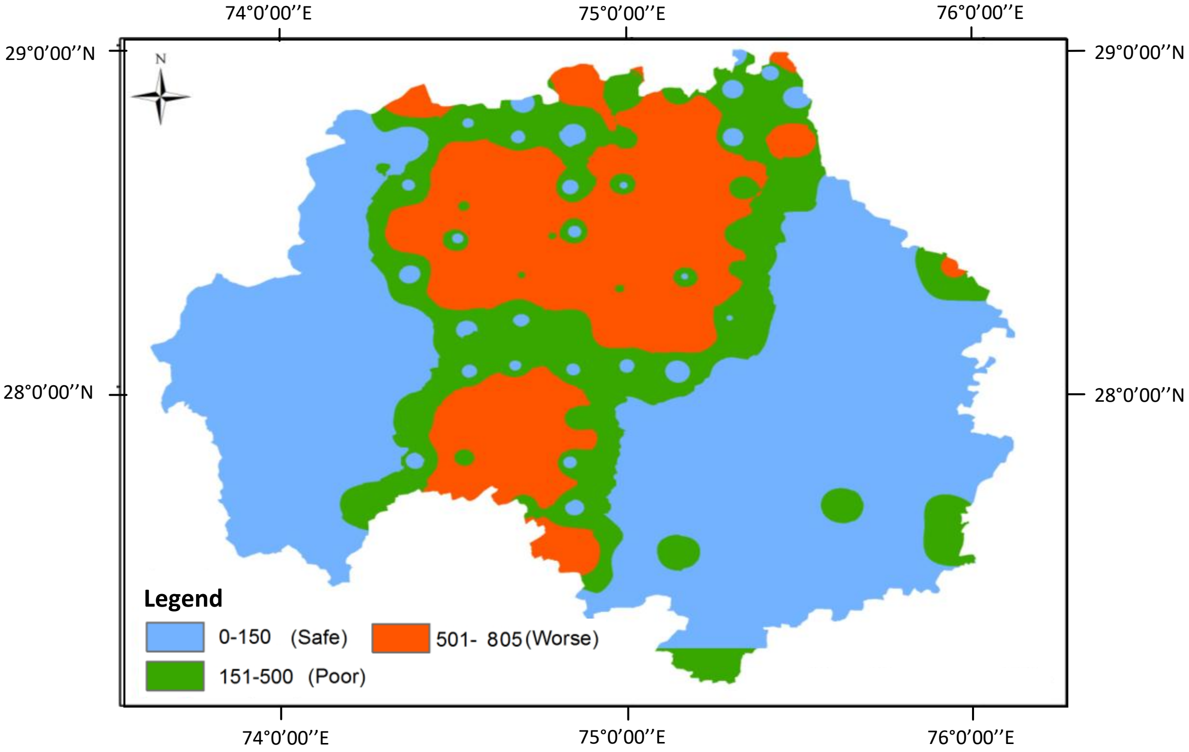

Figure 4.14: Spatial distribution of WQI in study area during post monsoon

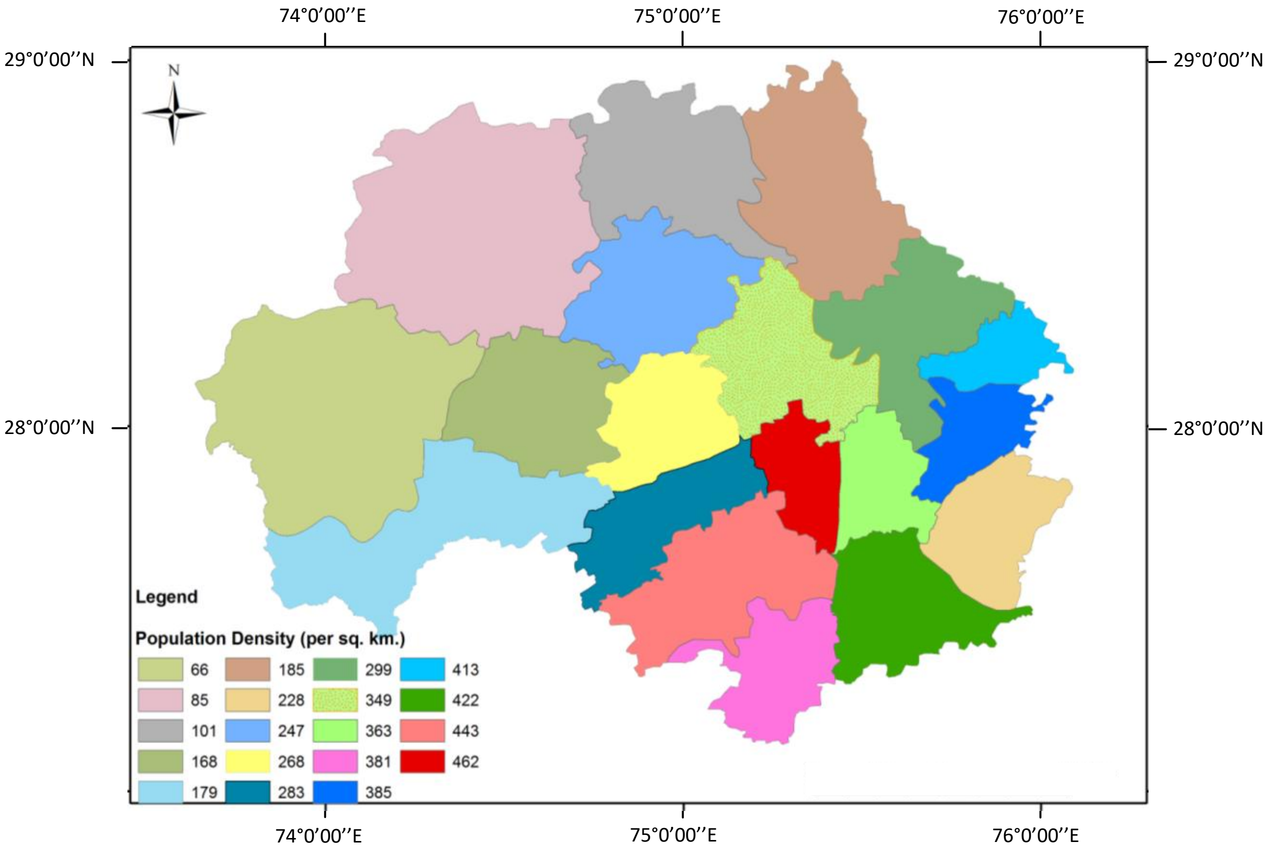

Figure 4.15: Population density map of the study area

Table 4.9: Spatial coverage of water quality

			Area (sq. km.)		*Population (number)*	
Category		**WQI range**	**Pre Monsoon**	**Post Monsoon**	**Pre Monsoon**	**Post Monsoon**
Safe	**Safe**	0-150	13304	15997	3351023	4159125
Rejected	**Poor**	151-500	10524	6752	2320328	1433009
	Worse	501-805	6795	7874	1370361	1449578
		Total	*30623*	*30623*	*7041712*	*7041712*

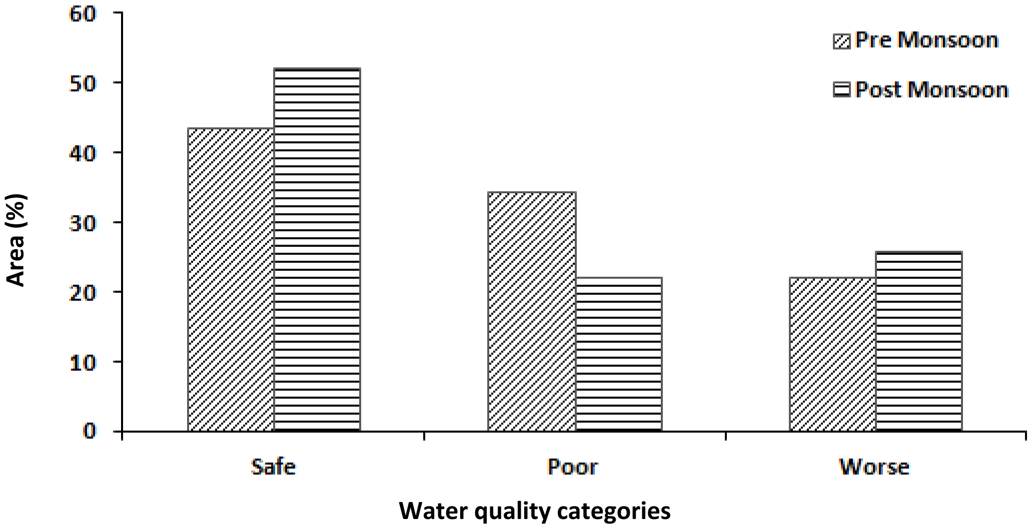

Figure 4.16: Arial coverage of WQI during pre & post monsoon

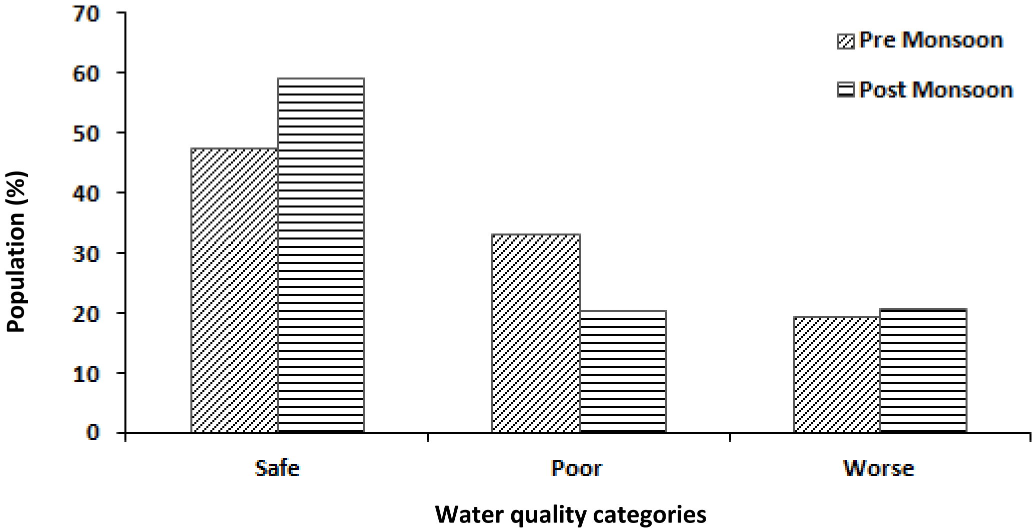

Figure 4.17: Population coverage of WQI during pre & post monsoon

Figure 4.16 and Figure 4.17 are graphical representations of data represented in Table 4.9. They show increment in area under safe category from pre monsoon to post monsoon and similarly increment is observed in population. In poor category of water quality index, the area declines and population also declines from pre monsoon to post monsoon. In worse category, the area increases and population also increases but it is very less from pre monsoon to post monsoon. It indicates the direct relation between the areal coverage and population.

4.4 3D Analysis

Groundwater is increasingly being sought as a source of drinking water due to the scarcity, non-availability and bacteriological pollution of surface water. To date, many modeling studies are done but very little is known about the variation of chemical parameters at vertical scale in any of the climatic zone and modeling are very objective specific. This work describes the important results of the chemical analysis of the groundwater samples of the tube wells of Shekhawati Region (Arid climate) of Rajasthan and has been modeled in 3 Dimensions using MATLAB (ver. 2012). The parameters viz. Nitrate, Fluoride and Total Dissolved Solids are used for generating 3D analysis for the area and their concentration attains more focus because of fluctuations in their values. These fluctuations have been shown in continuous surface (Figure 4.18) and there is no clear boundary exists between safe and rejected values of parameters.

Here we have developed 3 Dimensional model for the Shekhawati region, that represent the continuous changes in horizontal and vertical planes. Inverse Distance Weighting (IDW) method has been used to get different interpolated values at various depths. The data of pre monsoon and post monsoon have been used simultaneously to represent the variation of Nitrate, Fluoride and TDS.

The logical sequences have been evaluated to write a script in matrix form and series of the steps are followed. This systematic and logical steps followed to develop the 3 Dimensional model in Matlab is already shown in Figure 3.4. The data available for this work have been discussed in groundwater characterization section 3.3.2.

The 3D block model has been developed and represented for the three quality parameters. Further the points are categorized in three categories (below limit, safe limit and above limit) and 3D block model has been produced for the chosen parameters under study. The plots between the parameters concentration and depth have been generated to see the pattern of variation. The pattern of the generated graph shows and suggests that the points of same patterns may be combined. It is observed that few layers of substrata are uniform and few differ. Figure 4.18 shows the interpolated slice for Fluoride as an example to provide the easier understanding of variation.

The 3D block model developed is able to give synoptic view of the entire region and has the capability of rotating in any direction. Even it could be used to generate the slice or a complete filled block of study area. The model is capable of generating the graph between the chemical parameters and depth on demand. The various blocks have been marked based on the relation between parameter concentration and depth. The relation of concentration and depth shows that few blocks are identical due to same pattern followed in relation graph. Thus, it suggests that they may have similar geological matrix present beneath the surface in such area and their composition percentage may vary.

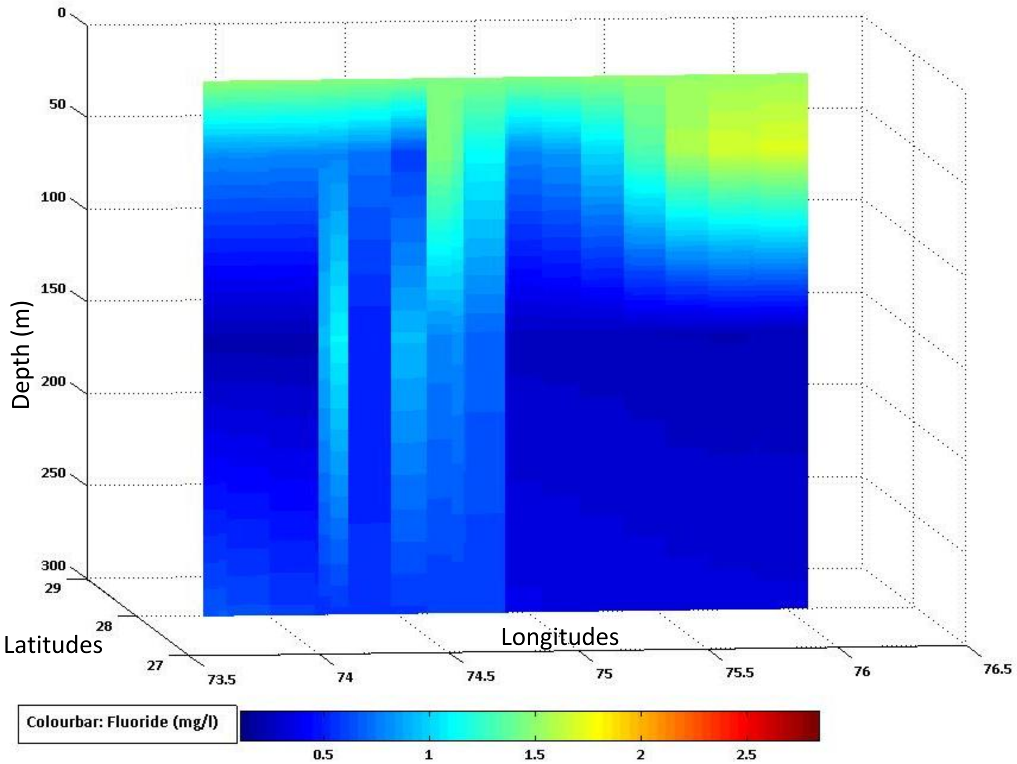

Figure 4.18: Slice of interpolated 3D block of study area

4.4.1 Nitrate

The Diagonal (Figure 4.19a) and Latitudinal view (Figure 4.19b) have been shown in Figure 4.19 for Nitrate during pre monsoon.

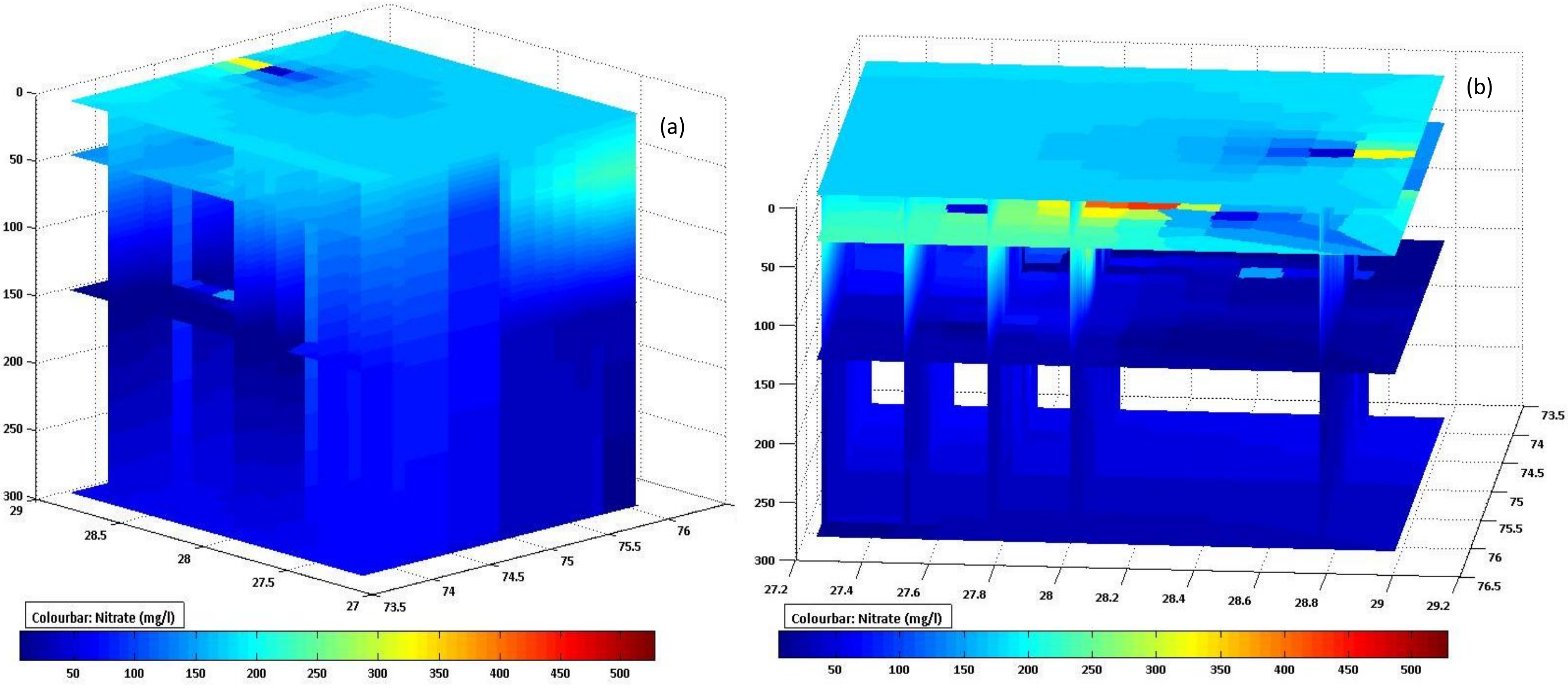

Figure 4.19: Nitrate variation in subsurface during pre monsoon (a) Diagonal view (b) Latitudinal view

The Diagonal (Figure 4.20a) and Latitudinal view (Figure 4.20b) have been shown in Figure 4.20 for Nitrate during post monsoon.

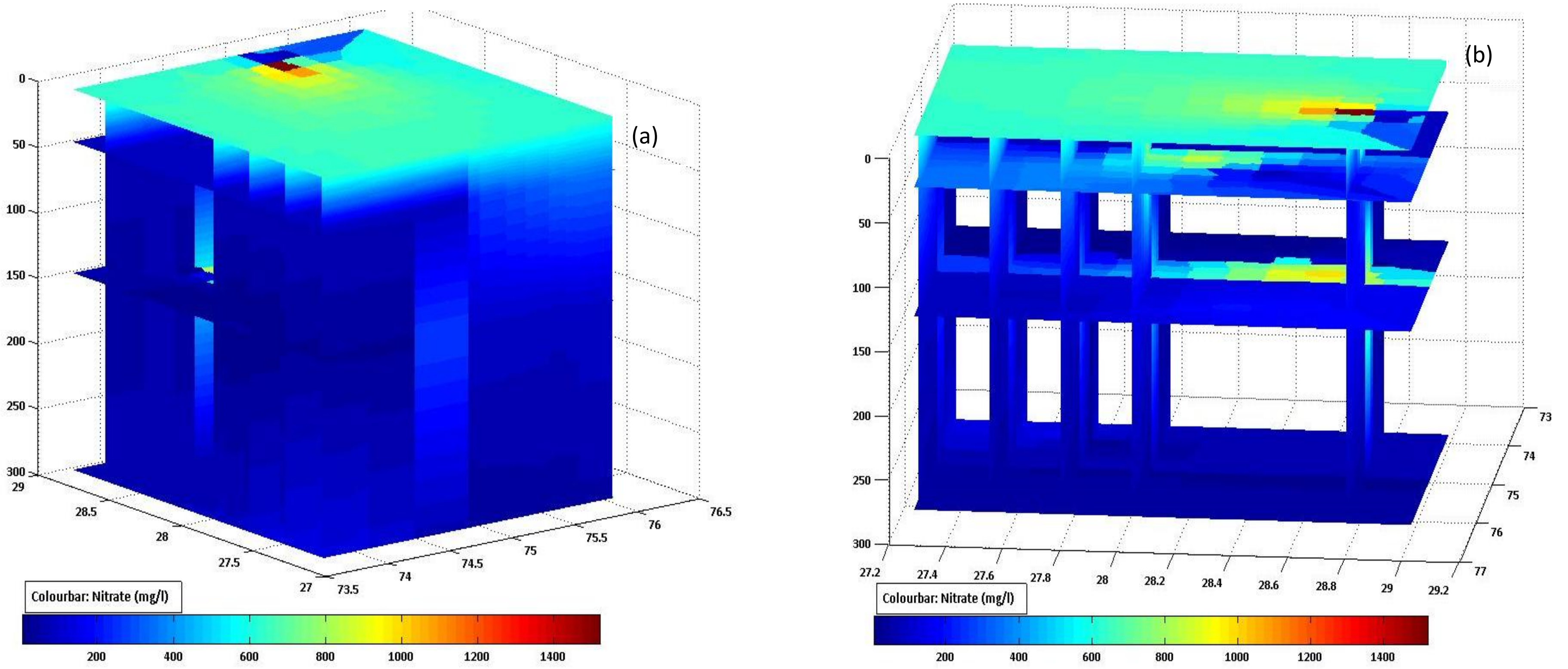

Figure 4.20: Nitrate variation in subsurface during post monsoon (a) Diagonal view (b) Latitudinal view

For easier understanding of these variations of the continuous surface shown in Figure 4.19 and Figure 4.20 is categorized in 3 classes and shown in Figure 4.21 for pre and post monsoon.

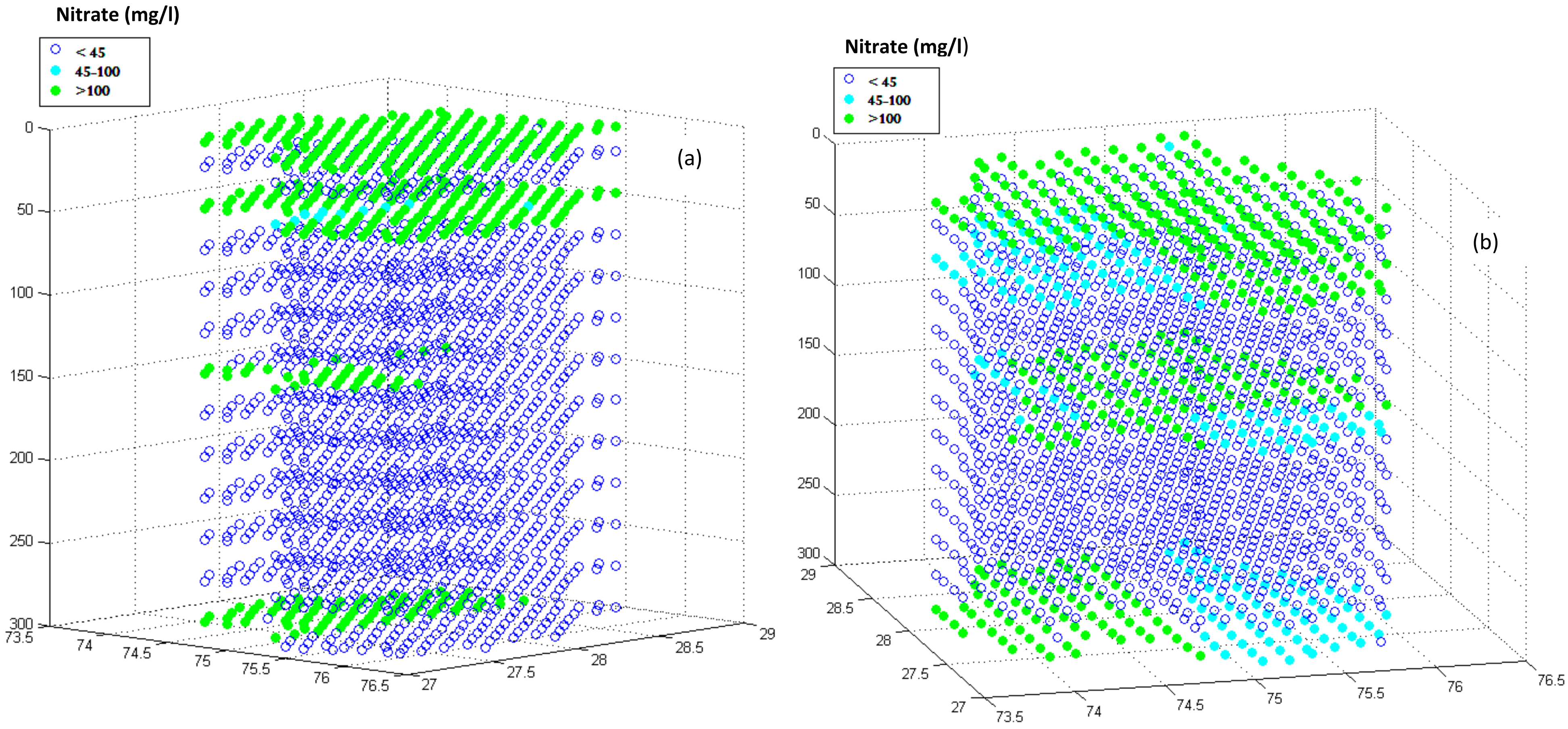

Figure 4.21: Nitrate variation in 3 category in subsurface during (a) Pre Monsoon (b) Post Monsoon

The map (Figure 4.22) showing the blocks categorized based on pattern identified from the plots between depth and concentration of Nitrate for pre monsoon. Seven blocks are identified where the Nitrates follows similar pattern of concentration variation in each block.

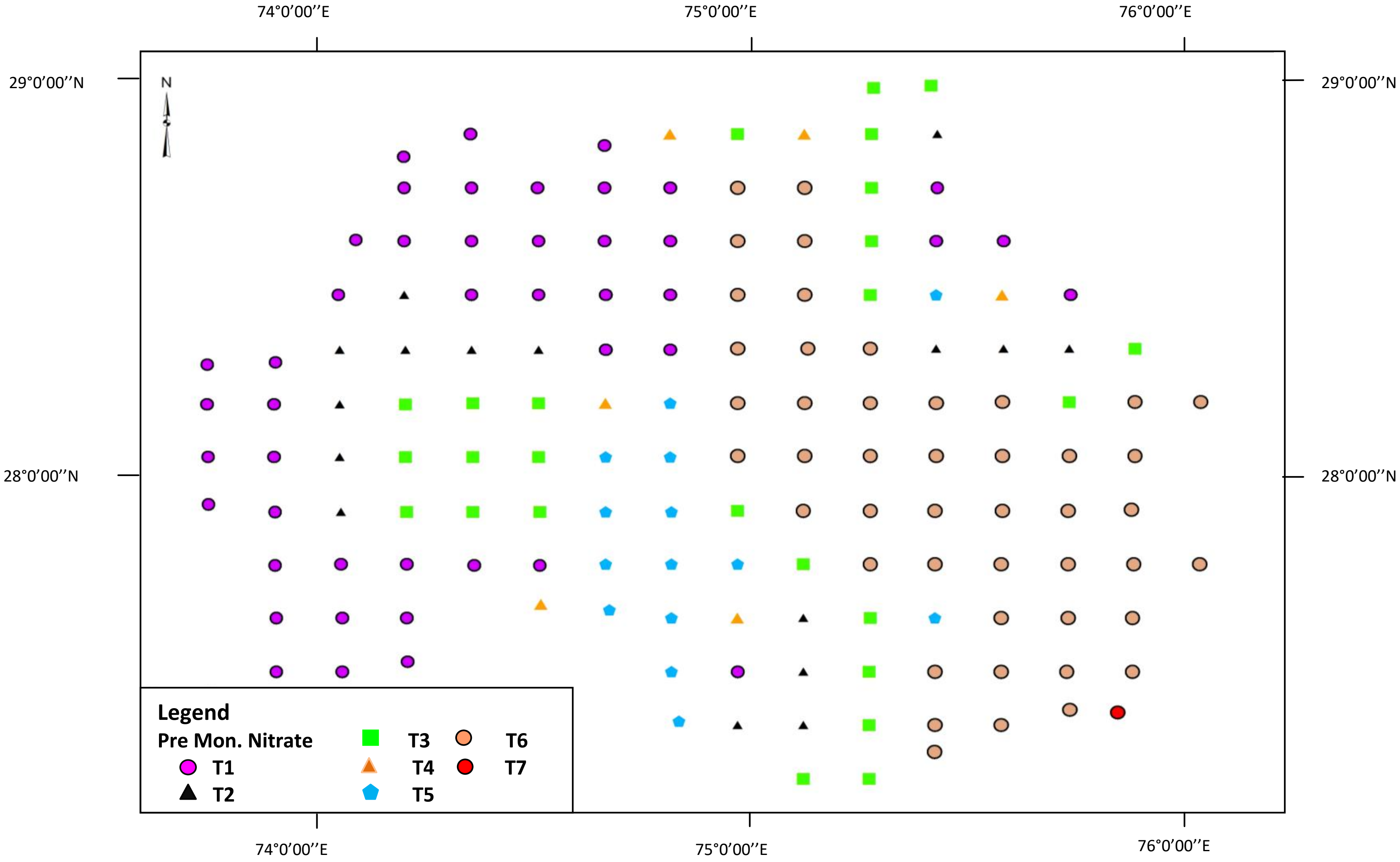

Figure 4.22: Map showing the blocks divided based on relation of Nitrate concentration and depth during pre monsoon

The map (Figure 4.23) showing the blocks categorized based on pattern identified from the plots between depth and concentration of Nitrate for post monsoon. Seven blocks are identified where the Nitrates follows similar pattern of concentration variation in each block.

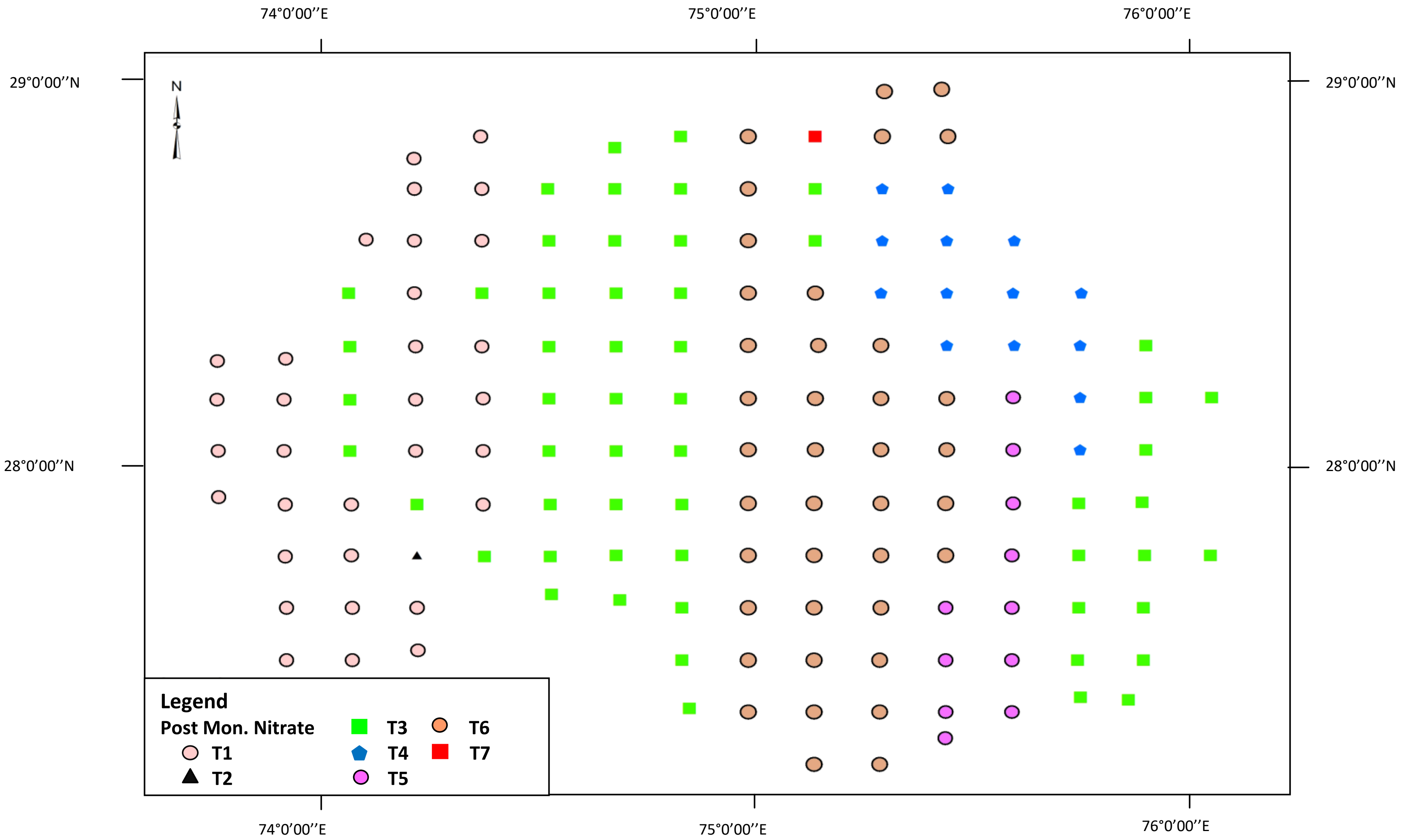

Figure 4.23: Map showing the blocks divided based on relation of Nitrate concentration and depth during post monsoon

The Figure 4.24 and Figure 4.25 show the trend of Nitrate concentration with depth for pre and post monsoon respectively for all blocks together.

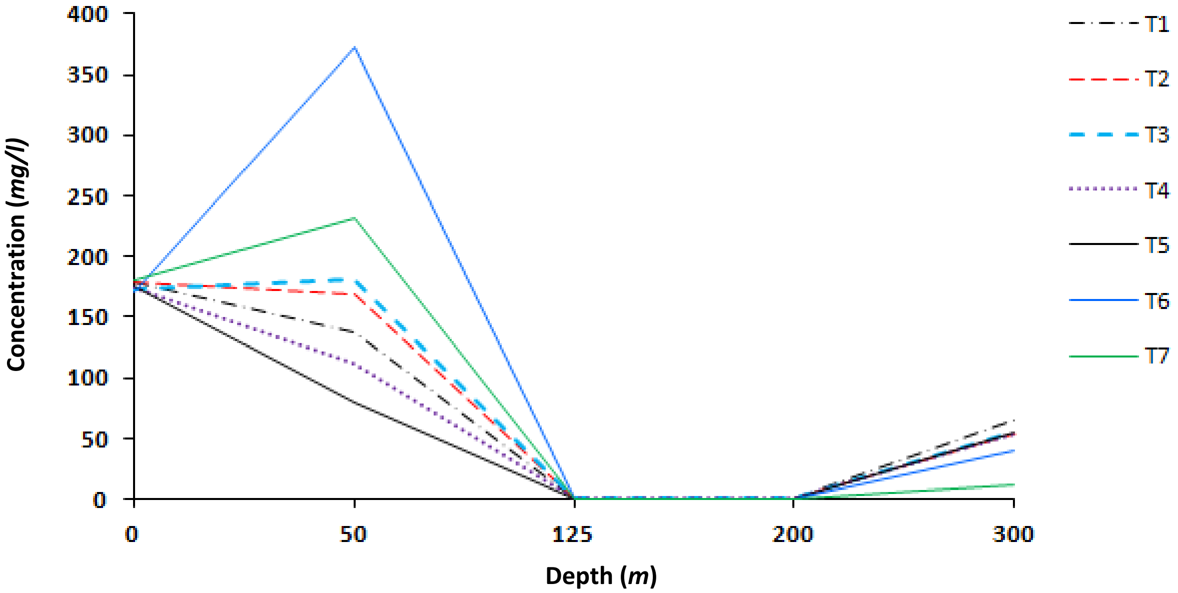

Figure 4.24: Nitrate concentration vs. depth plot for all blocks during pre monsoon

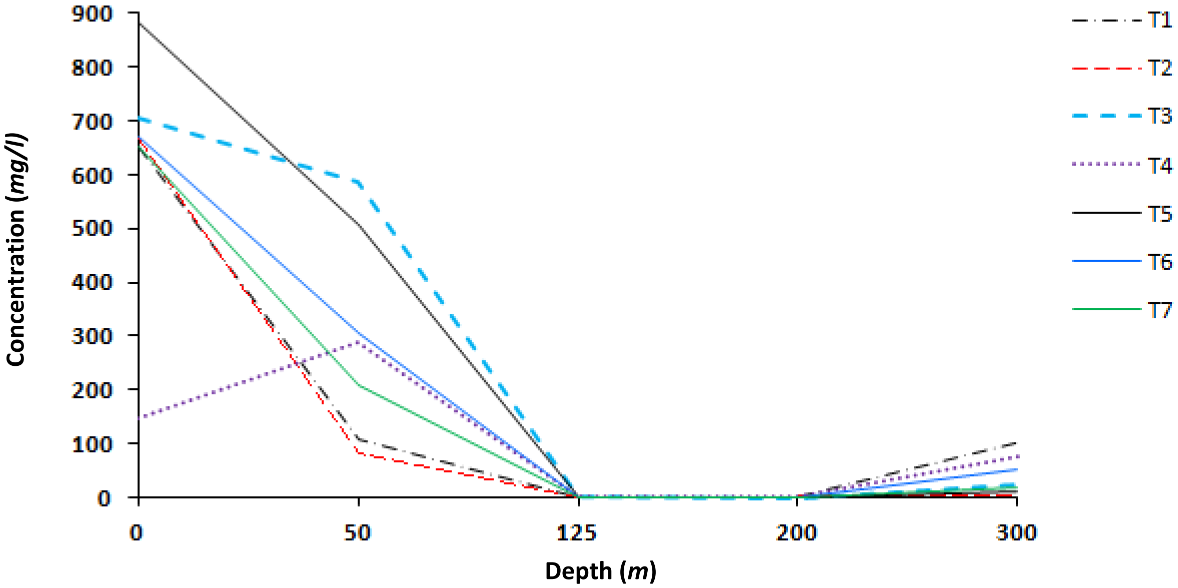

Figure 4.25: Nitrate concentration vs. depth plot for all blocks during post monsoon

The Figure 4.24 and Figure 4.25 show the trend of variation in Nitrate concentration with depth for pre monsoon and post monsoon season for the blocks shown in Figure 4.22 and Figure 4.23

respectively. It provides the easier way to interpret the information about pattern of all blocks. Table 4.10 discusses in details for each block mentioned in Figure 4.22 and Figure 4.23.

Table 4.10: Discussion of variation of Nitrate concentration in subsurface strata

Pre Monsoon	Post Monsoon
Block T1, Block T2, Block T4, Block T5 shows the reduction in Nitrate concentration upto 50 *m* depth and further reduction in concentration is increased upto 125 *m* depth. Between 125 *m* and 200 *m*, the variation in Nitrate is not observed and above 200 *m*, the concentration of Nitrate increased.	Block T1, Block T2, Block T3, Block T5, Block T6, Block T7 and Block T8 shows the reduction in Nitrate concentration upto 50 *m* depth and further reduction in concentration increased upto 125 *m* depth. Between 125 *m* and 200 *m*, the variation in Nitrate is not observed and above 200 *m*, the concentration of Nitrate increased.
Block T3, Block T6, Block T7 shows the increment in Nitrate concentration upto 50 *m* depth and further reduction in concentration is increased upto 125 *m* depth. Between 125 *m* and 200 *m*, the variation in Nitrate is not observed and above 200 *m*, the concentration of Nitrate increased. .	Block T4 shows the increment in Nitrate concentration upto 50 *m* depth and further reduction in concentration is increased upto 125 *m* depth. Between 125 *m* and 200 *m*, the variation in Nitrate is not observed and above 200 *m*, the concentration of Nitrate increased.

4.4.2 Fluoride

The Diagonal (Figure 4.26a) and Latitudinal view (Figure 4.26b) have been shown in Figure 4.26 for Fluoride during pre monsoon.

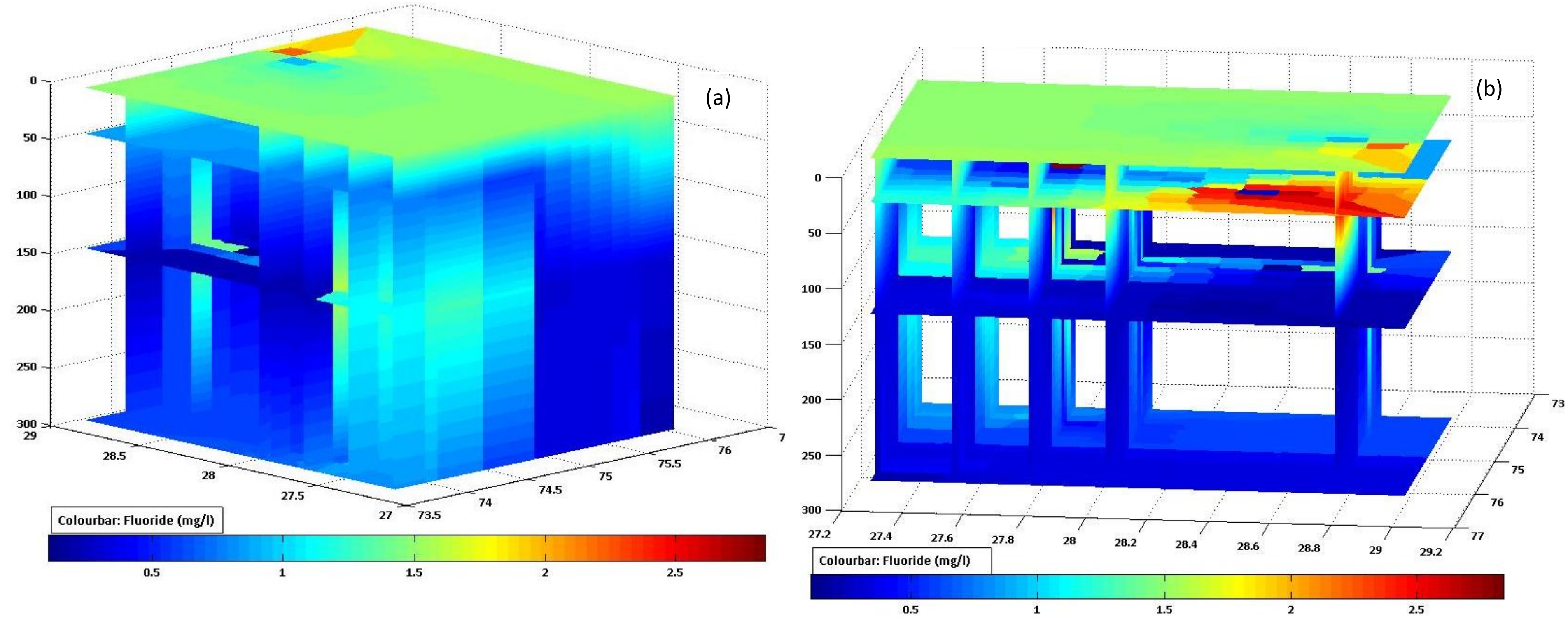

Figure 4.26: Fluoride variation in subsurface during pre monsoon (a) Diagonal view (b) Latitudinal view

The Diagonal (Figure 4.27a) and Latitudinal view (Figure 4.27b) have been shown in Figure 4.27 for Fluoride during post monsoon.

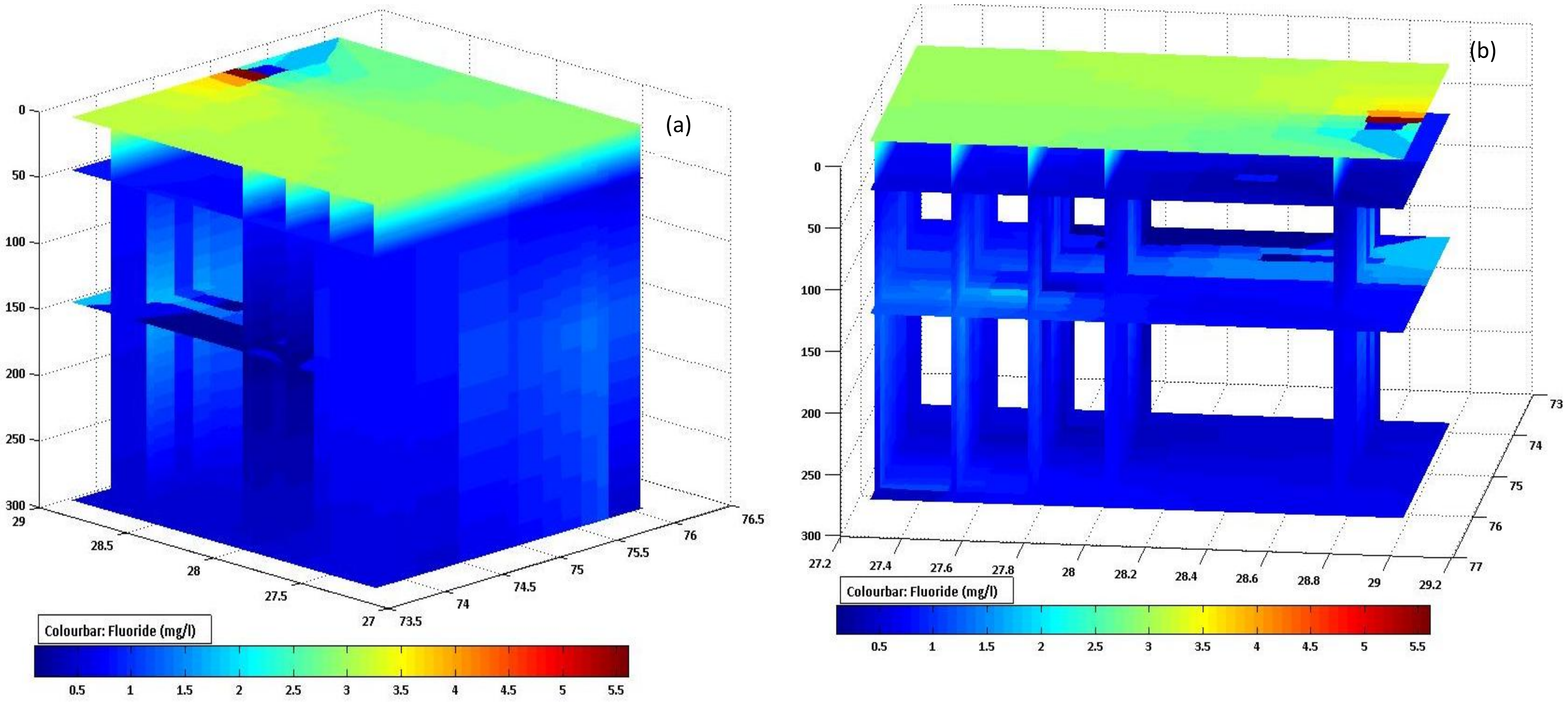

Figure 4.27: Fluoride variation in subsurface during post monsoon (a) Diagonal view (b) Latitudinal view

For easier understanding of these variations of the continuous surface shown in Figure 4.26 and Figure 4.27 is categorized in 3 classes and shown in Figure 4.28 for pre and post monsoon.

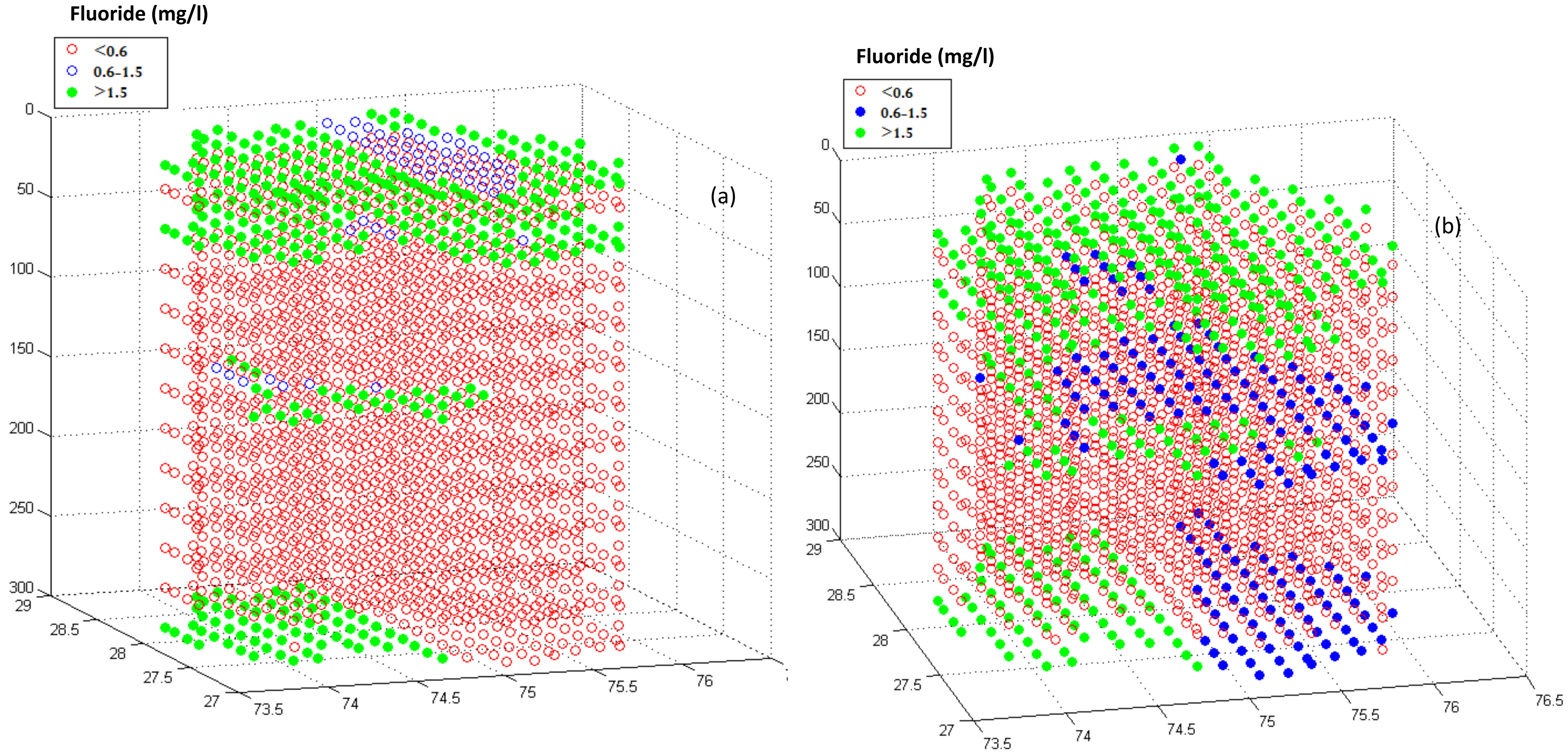

Figure 4.28: Fluoride variation in 3 category in subsurface during (a) Pre Monsoon (b) Post Monsoon

The map (Figure 4.29) showing the blocks categorized based on pattern identified from the plots between depth and concentration of Fluoride for pre monsoon. Six blocks are identified where the Fluoride follows similar pattern of concentration variation in each block.

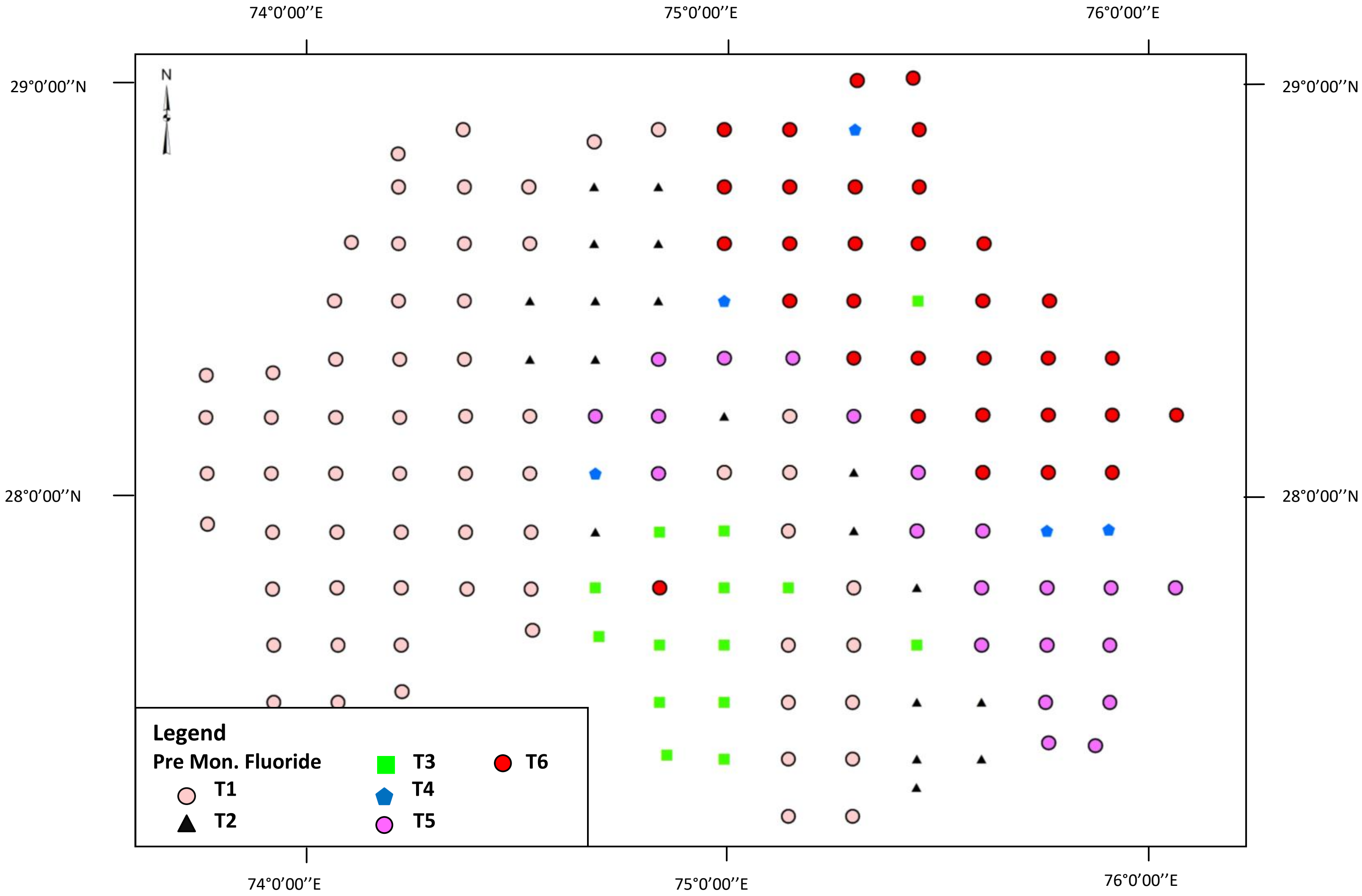

Figure 4.29: Map showing the block divided based on relation of Fluoride concentration and depth for pre monsoon

The map (Figure 4.30) showing the blocks categorized based on pattern identified from the plots between depth and concentration of Fluoride for post monsoon. Four blocks are identified where the Fluoride follows similar pattern of concentration variation in each block.

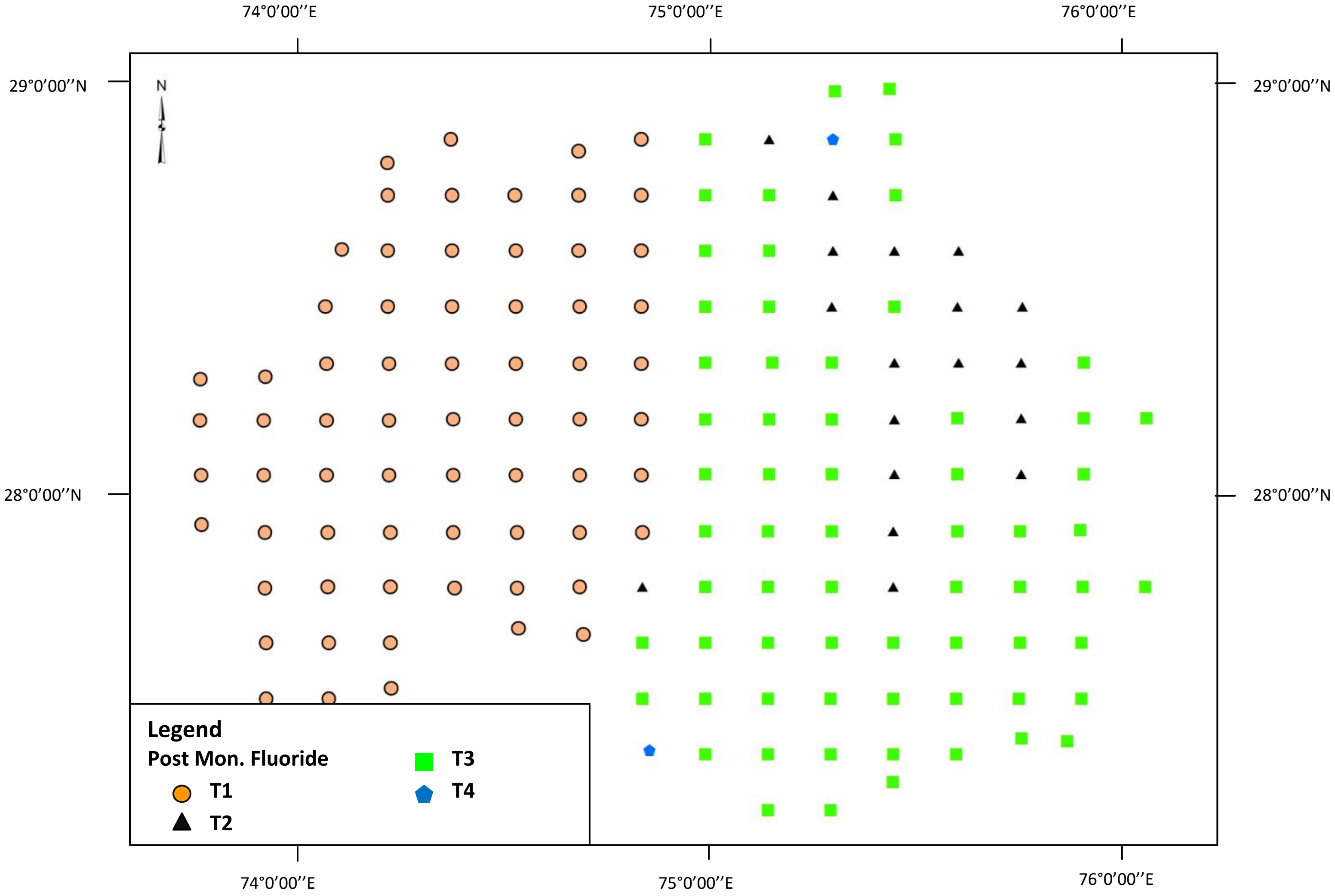

Figure 4.30: Map showing the block divided based on relation of Fluoride concentration and depth during post monsoon

The Figure 4.31 and Figure 4.32 show the trend of variation in fluoride concentration with depth for pre and post monsoon for all blocks shown in Figure 4.29 and Figure 4.30 respectively.

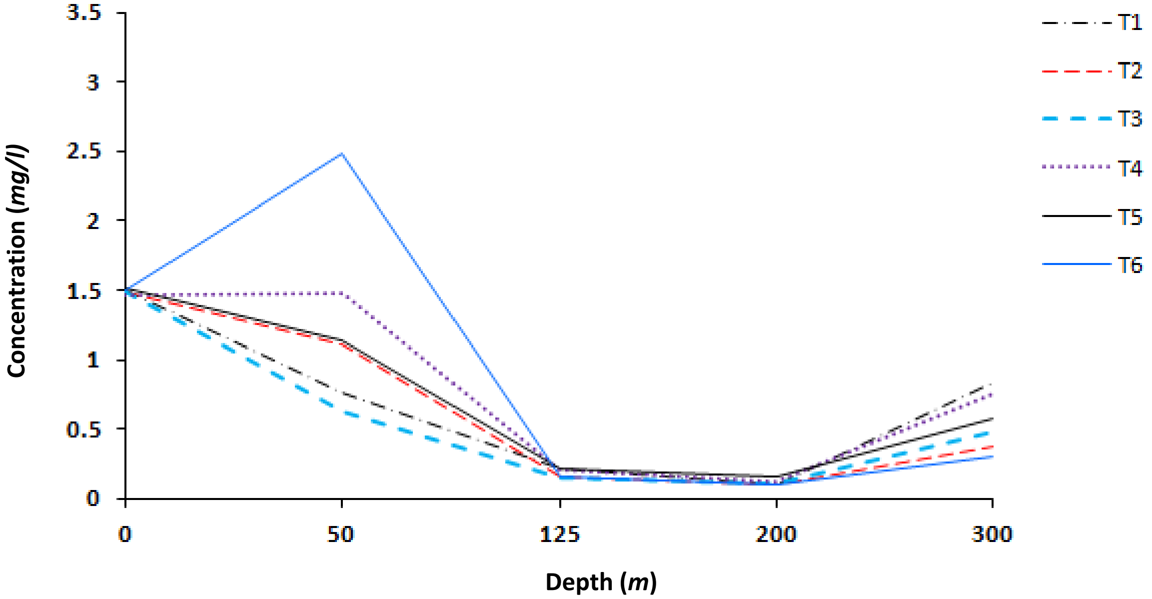

Figure 4.31: Fluoride concentration vs. depth plot for all blocks during pre monsoon

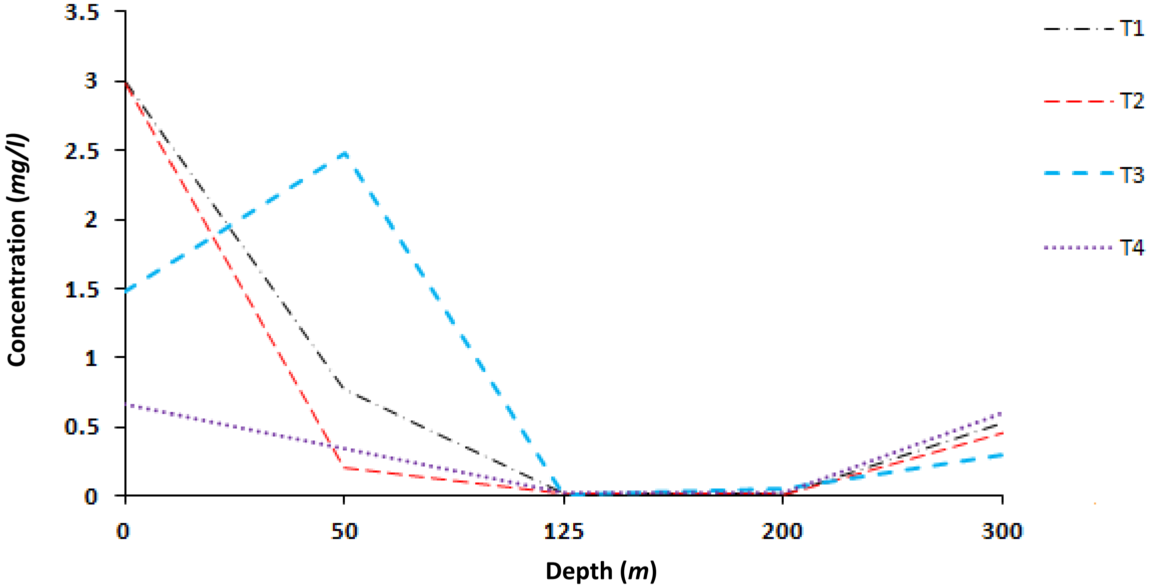

Figure 4.32: Fluoride concentration vs. depth plot for all blocks during post monsoon

The Figure 4.31 and Figure 4.32 show the trend of variation in Fluoride concentration with depth for pre monsoon and post monsoon season for the blocks shown in Figure 4.29 and Figure 4.30 respectively.

It provides the easier way to interpret the information about pattern of all blocks. The Table 4.11 discusses the relation of Fluoride concentration with subsurface depth for both seasons in details.

Table 4.11: Discussion of variation of Fluoride concentration in subsurface strata

Pre Monsoon	**Post Monsoon**
Block T1, Block T2, Block T3, Block T5 shows the reduction in Fluoride concentration upto 50 *m* depth and further reduction in concentration is increased upto 125 *m* depth. Between 125 *m* and 200 *m*, the variation in Fluoride is not observed and above 200 *m*, the concentration of Fluoride increased.	Block T1, Block T2, Block T4 shows the reduction in Fluoride concentration upto 50 *m* depth and further reduction in concentration is increased upto 125 *m* depth. Between 125 *m* and 200 *m*, the variation in Fluoride is not observed and above 200 *m*, the concentration of Fluoride increased.
Block T4, Block T6 shows the increment in Fluoride concentration upto 50 *m* depth and further reduction in concentration is increased upto 125 *m* depth. Between 125 *m* and 200 *m*, the variation in Fluoride is not observed and above 200 *m*, the concentration of Fluoride increased.	Block T3 shows the increment in Fluoride concentration upto 50 *m* depth and further reduction in concentration is increased upto 125 *m* depth. Between 125 *m* and 200 *m*, the variation in Fluoride is not observed and above 200 *m*, the concentration of Fluoride increased.

4.4.3 Total Dissolved Solids

The Diagonal (Figure 4.33a) and Latitudinal view (Figure 4.33b) have been shown in Figure 4.33 for TDS during pre monsoon.

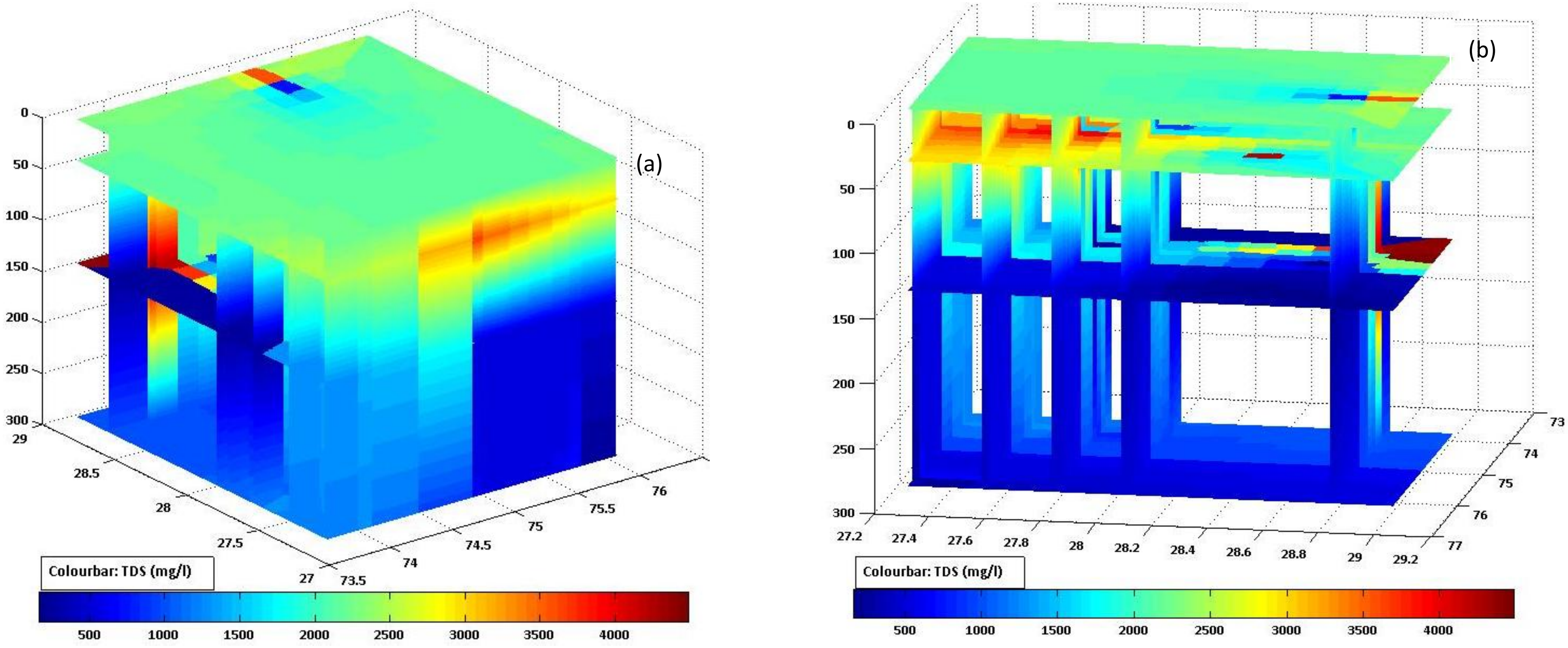

Figure 4.33: TDS variation in subsurface during pre monsoon (a) Diagonal view (b) Latitudinal view

The Diagonal (Figure 4.34a) and Latitudinal view (Figure 4.34b) have been shown in Figure 4.34 for TDS during pre monsoon.

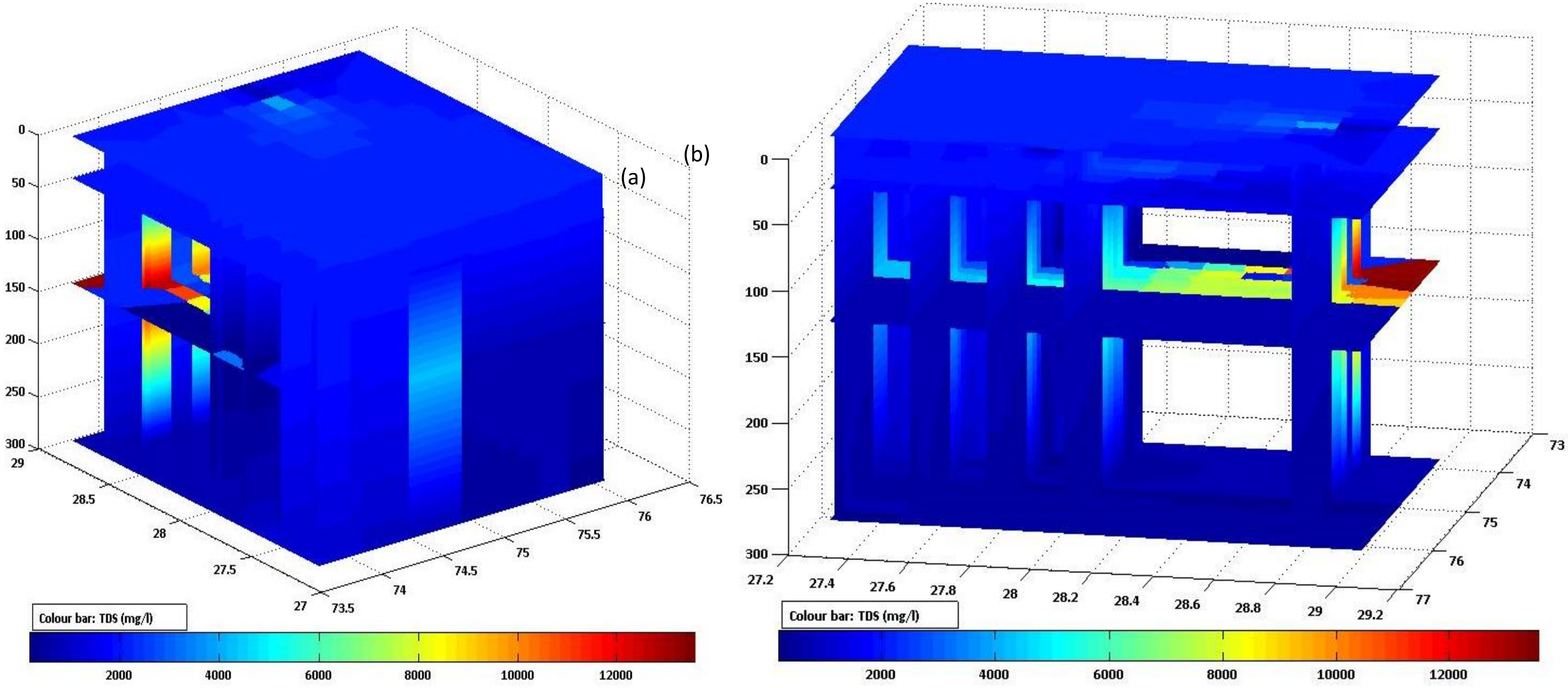

Figure 4.34: TDS variation in subsurface during post monsoon (a) Diagonal view (b) Latitudinal view

For easier understanding of these variations of the continuous surface shown in Figure 4.33 and Figure 4.34 is categorized in 3 classes and shown in Figure 4.35 for pre and post monsoon.

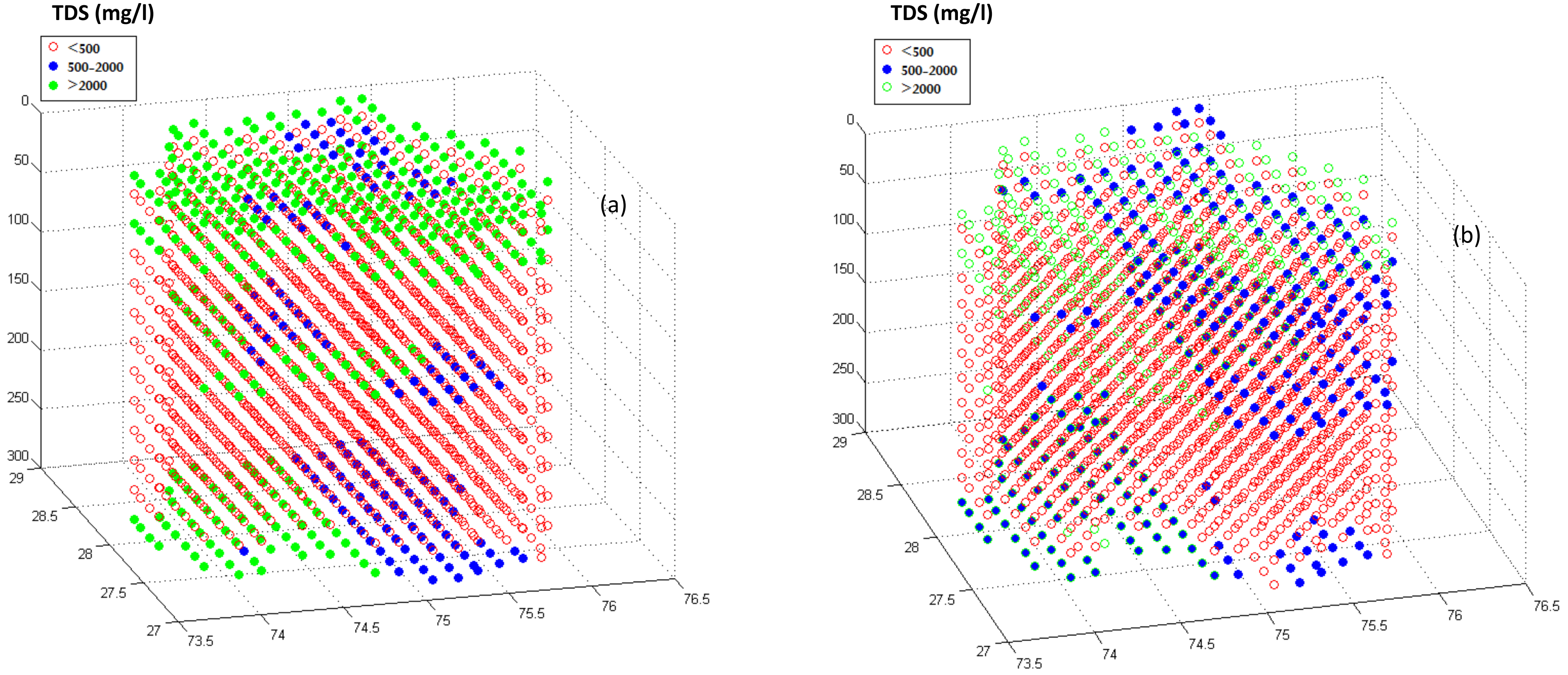

Figure 4.35: TDS variation in 3 category in subsurface during (a) Pre Monsoon (b) Post Monsoon

The map (Figure 4.36) showing the blocks categorized based on pattern identified from the plots between depth and concentration of TDS for pre monsoon. Six blocks are identified where the TDS follows similar pattern of concentration variation in each block.

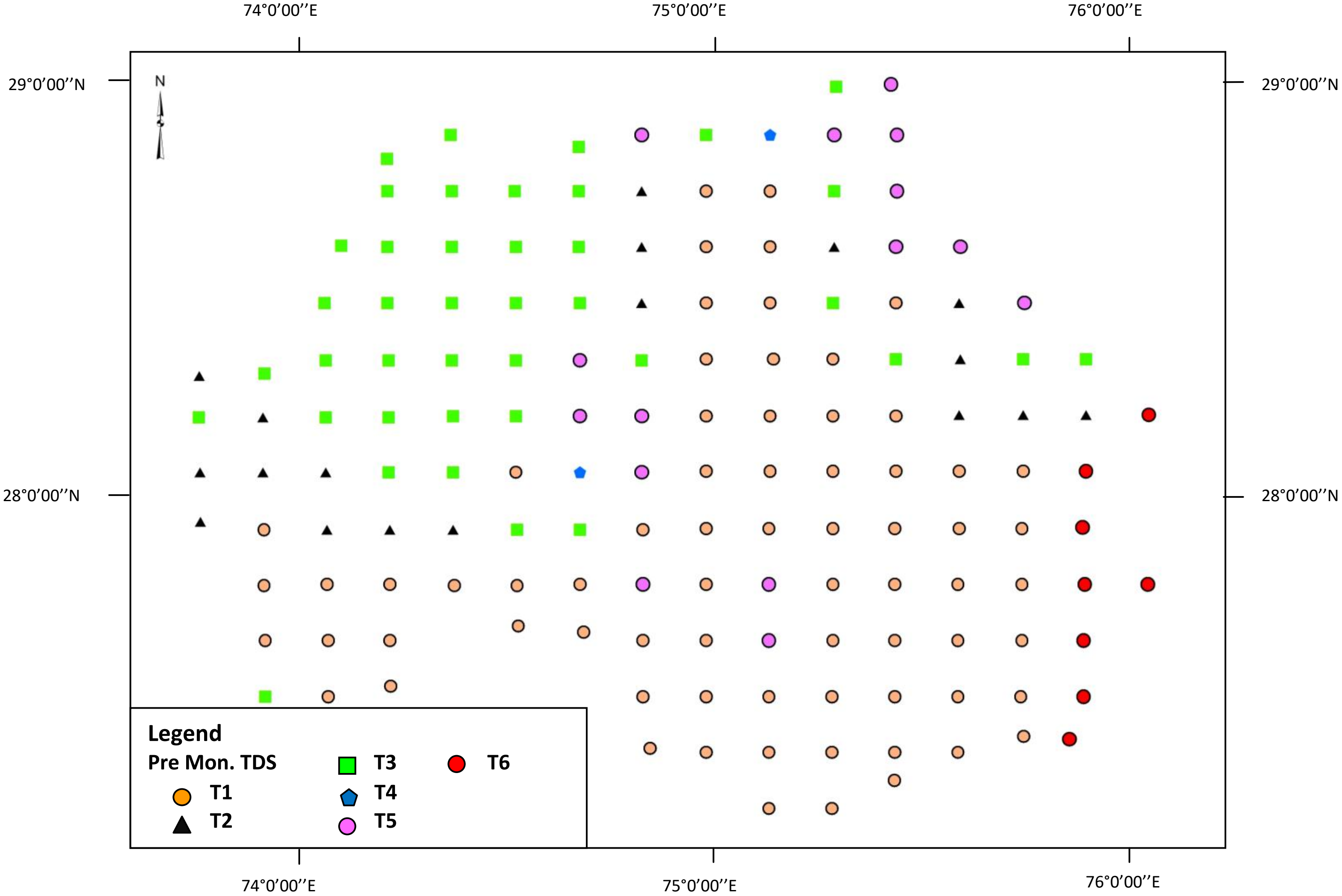

Figure 4.36: Map showing the block divided based on relation of TDS concentration and depth during pre monsoon

The map (Figure 4.37) showing the blocks categorized based on pattern identified from the plots between depth and concentration of TDS for post monsoon. Seven blocks are identified where the TDS follows similar pattern of concentration variation in each block.

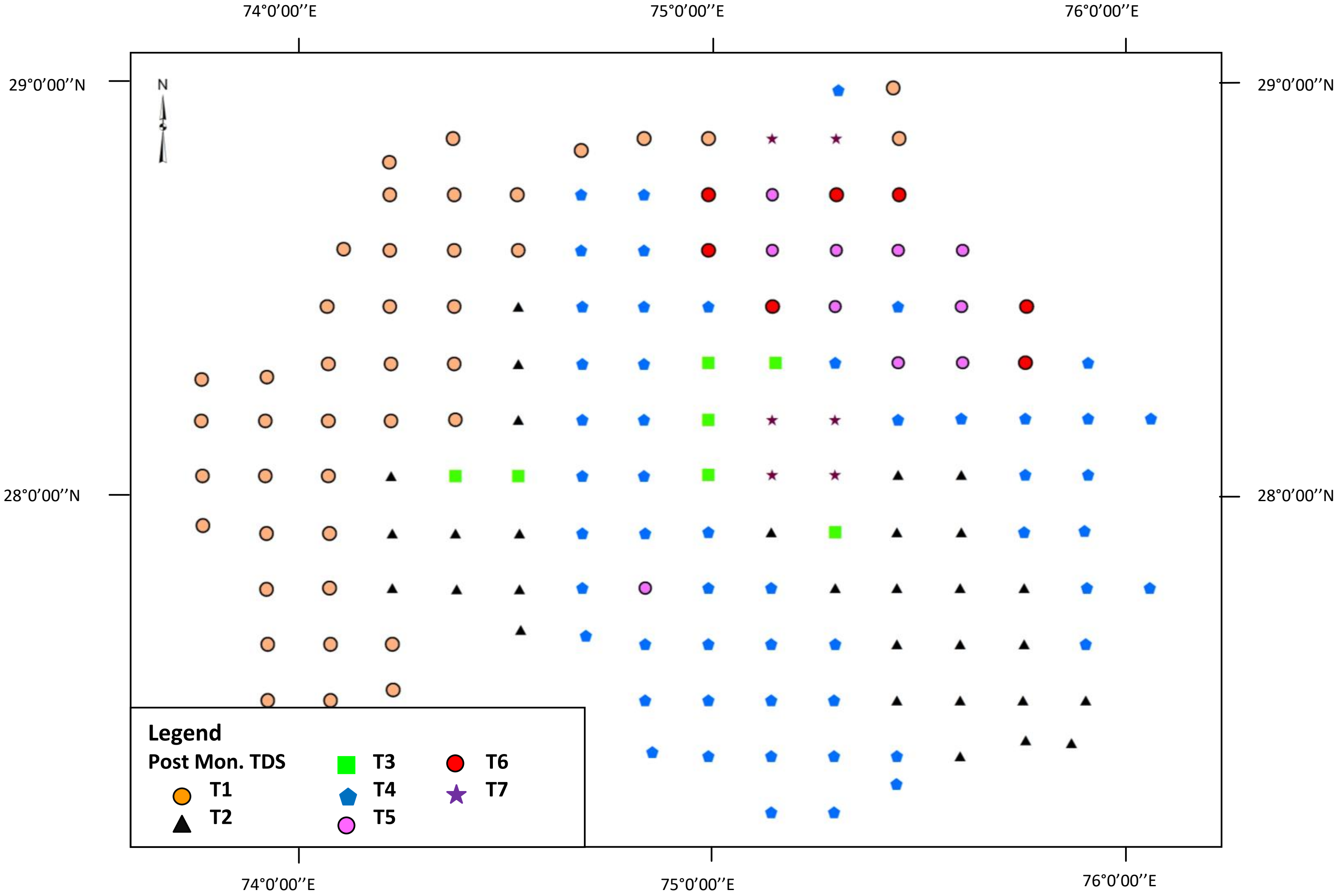

Figure 4.37: Map showing the block divided based on relation of TDS concentration and depth during post monsoon

The Figure 4.38 and Figure 4.39 shows the trend of variation in TDS concentration with depth for pre and post monsoon for the blocks shown in Figure 4.36 and Figure 4.37 respectively.

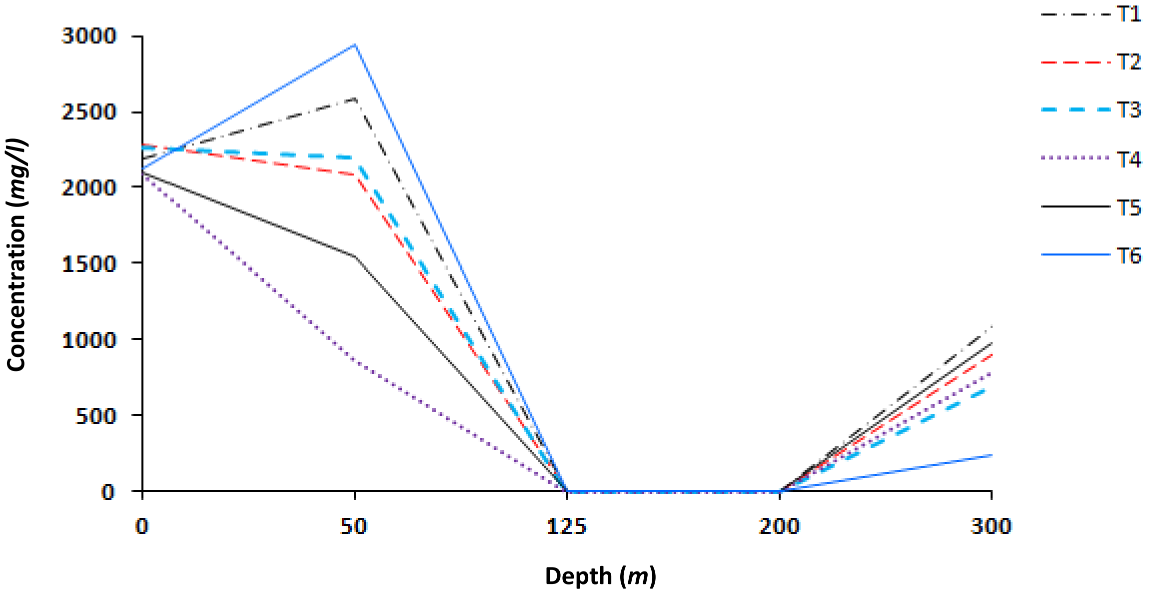

Figure 4.38: TDS concentration vs. depth plot for all blocks during pre monsoon

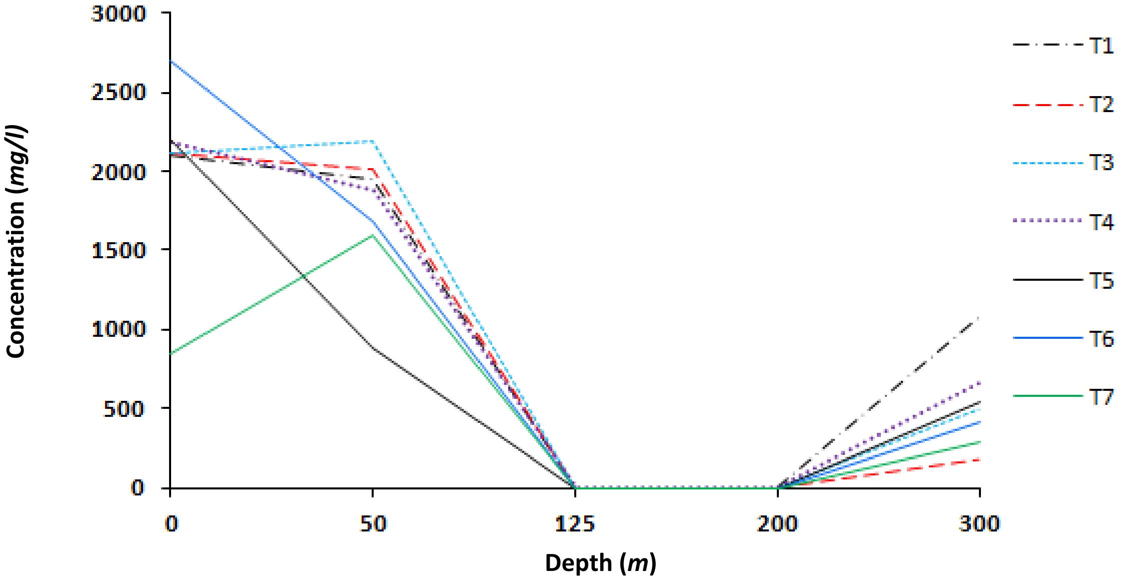

Figure 4.39: TDS concentration vs. depth plot for all blocks during post monsoon

The Figure 4.38 and Figure 4.39 show the trend of variation in TDS concentration with depth for pre monsoon and post monsoon seasons for the blocks shown in Figure 4.36 and Figure 4.37 respectively. It provides the easier way to interpret the information about pattern of all blocks. The Table 4.12 discusses the relation of TDS with subsurface depth for both seasons.

Table 4.12: Discussion of variation of TDS concentration in subsurface strata

Pre Monsoon	**Post Monsoon**
Block T1, Block T2, Block T6 shows the increment in TDS concentration upto 50 *m* depth and further reduction in concentration is increases upto 125 *m* depth. Between 125 *m* and 200 *m*, the variation in TDS is not observed and above 200 *m*, the concentration of TDS increased.	Block T1, Block T2, Block T4, Block T5, Block T6 shows the reduction in TDS concentration upto 50 *m* depth and further reduction in concentration is increased upto 125 *m* depth. Between 125 *m* and 200 *m*, the variation in TDS is not observed and above 200 *m*, the concentration of TDS increased.
Block T3, Block T4, Block T5 shows the reduction in TDS concentration upto 50 *m* depth and further reduction in concentration is increased upto 125 *m* depth. Between 125 *m* and 200 *m*, the variation in TDS is not observed and above 200 *m*, the concentration of TDS increased.	Block T3, Block T7 shows the increment in TDS concentration upto 50 *m* depth and further reduction in concentration is increased upto 125 *m* depth. Between 125 *m* and 200 *m*, the variation in TDS is not observed and above 200 *m*, the concentration of TDS increased.

4.5 Model Interpretation and verification

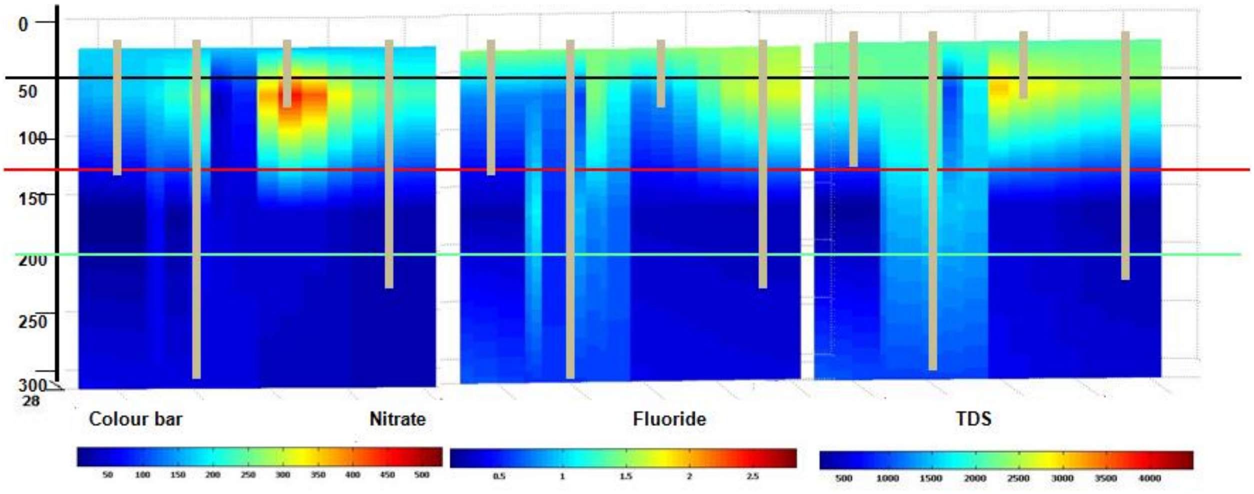

Figure 4.40: Interpretation of water quality parameters at 28° 0’ 00”N.

The latitudinal view at 28°N of three quality parameters (Nitrate, Fluoride and Total Dissolved Solids) are illustrated in Figure 4.40. This sliced view helps in interpreting the quality of water for each parameter at desired latitude and longitude. The depth of few wells has been marked so that the well will be clearly identifiable for vulnerability and its use. The water table depth varies between 40 *m* to 340 *m* at this latitude for a stretch of 230 *km*. The observations based on condition when, interpolated values profile is overlaid with wells are disucced here. Concedering the 300 *m* deep well at nitrate concentration slice, it is observed that if the well is depper than 200 *m* the nitrate concentration is lower (<50 *mg/l*) but at depth between ground surface and 200 *m* it tends to heigher end (> 100 *mg/l*). For the fluoride, if we consider the well 300 *m* deep, then it is observed that the concentration of fluoride varies between 0.6-1.5 *mg/l* for the depth range of 150 *m* to 300 *m*. The fluoride concentration is very high in depth zone between ground to 150 *m*. If we observe the well 300 *m* deep for TDS variation then it is found that between 125 – 300 *m* depth the TDS concentration varies between 800-2000 *mg/l*, while the TDS concentration is higher between ground and 125 *m* depth.

Further, Landuse map (Figure 4.41) is used to identify the co-relation between variation among quality parameters and shallow depth. Few wells have shown the increase in concentration of water parameters and could be linked to irrigation and agricultural activities. But few wells have shown the deviation from this and only support the existence of natural strata behind the subsurface for increase in Nitrate, Fluoride and Total Dissolved Solids concentration.

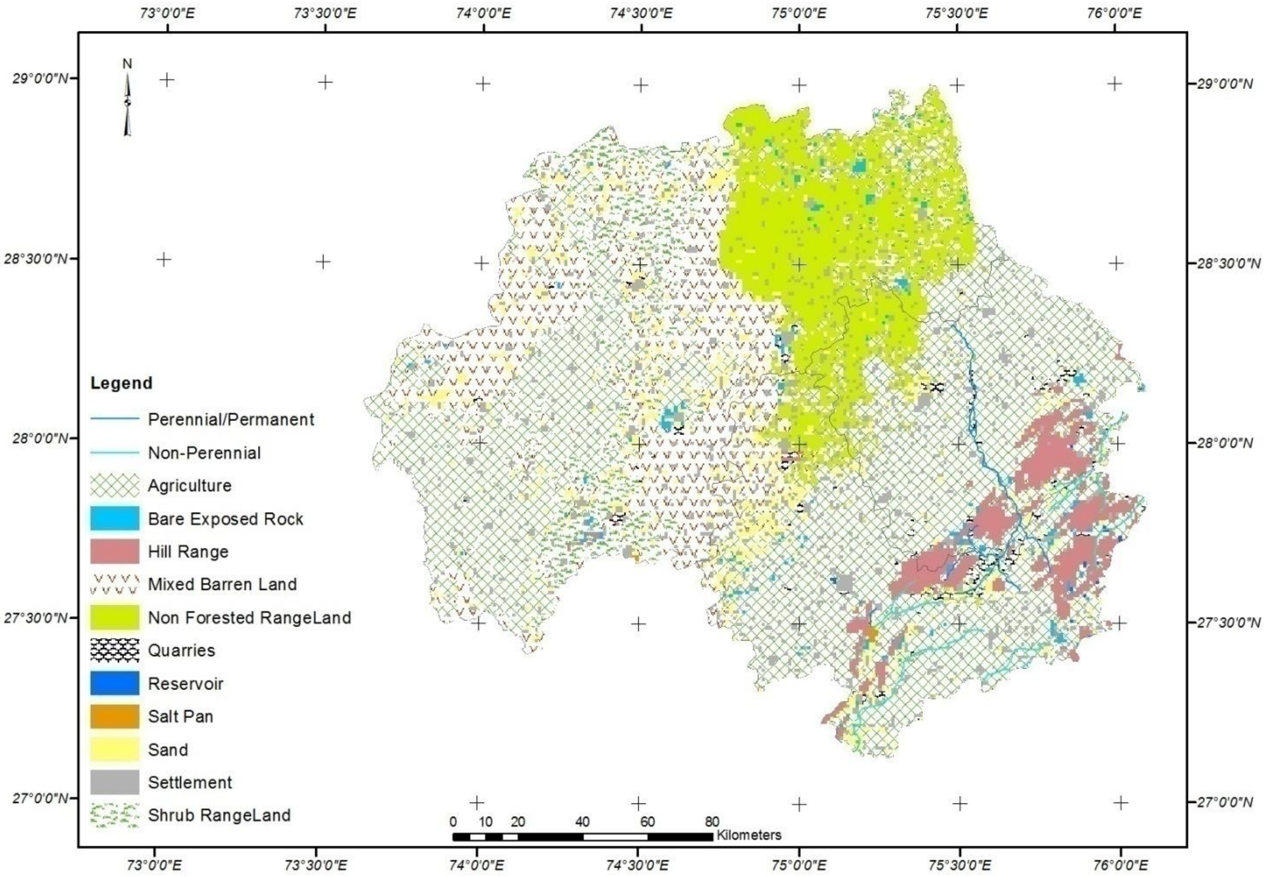

Figure 4.41: Landuse map of Shekhawati (interpreted from IRS-P6 data)

As per the concentration and depth plots (Figure 4.24, Figure 4.25, Figure 4.31, Figure 4.32, Figure 4.38 and Figure 4.39), it is indicated clearly that soil matrix changes at 50 *m* depth, at 125 *m* depth and at 200 *m* depth and this information is summarized in Table 4.13.

Table 4.13: Depth of layers proposed from 3D analysis

Depth (*m*)	**Layer Number**
0-50	Layer 1
50-125	Layer 2
125-200	Layer 3
200-300	Layer 4

The Figure 3.7 shown in chapter 3 indicates the presence of 42 monitoring wells. Out of these monitoring wells, only four State Ground Water Board (SGWB) wells lie in proximity of sampling wells (< 1*km*). Soil log is available for these four wells lying in proximity of sampling location. Thus, these well locations are used to verify the accuracy of the modeling carried out during the study. Figure

4.42 shows our sampling wells and state ground water board wells which have soil log upto 130 *m* (Table 4.14) depth.

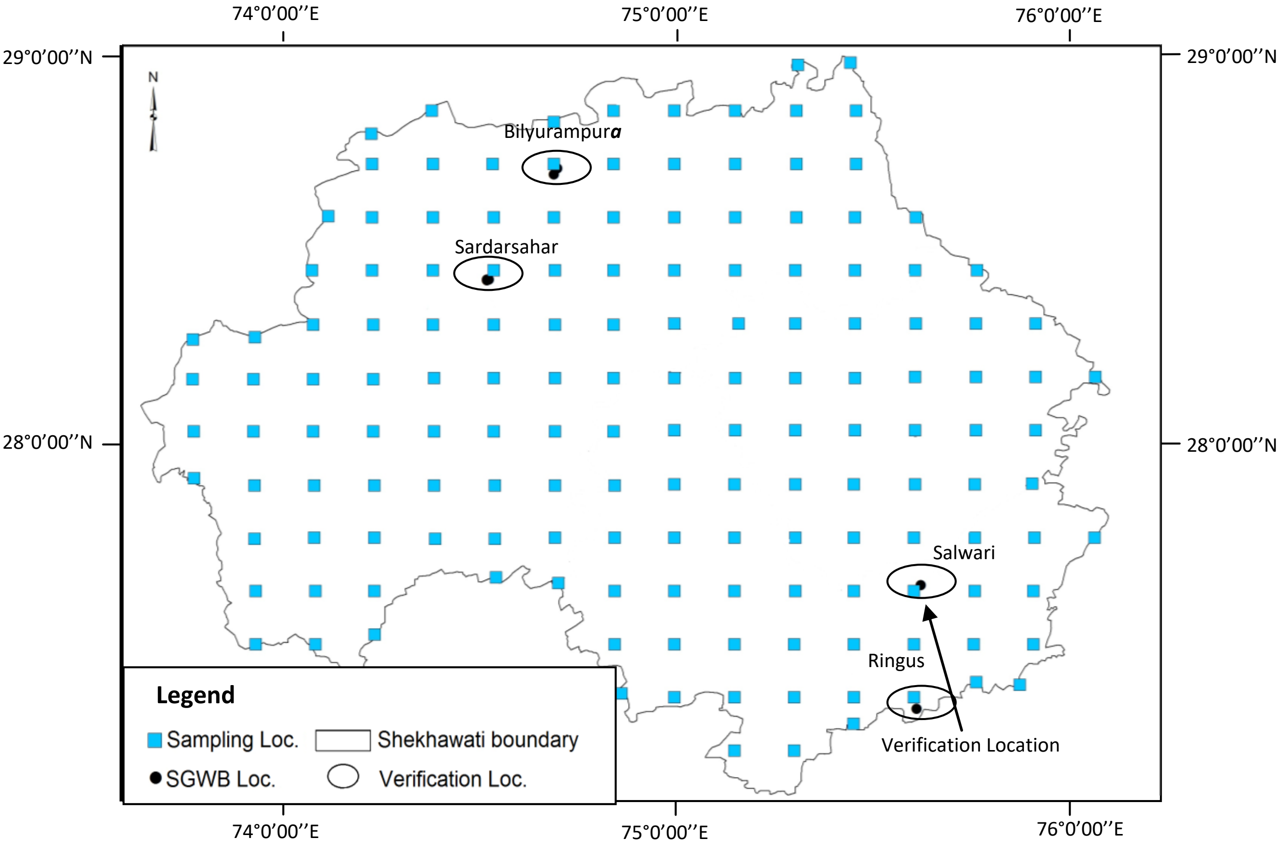

Figure 4.42: Map showing the location used to verify accuracy of the model

The log of subsurface only provides data upto depth of 130 *m*. Thus, comparison between depths has been carried out between 3D block model layers and SGWB data for accuracy estimation of depth upto 2 layers (i.e. 125 *m*).

Table 4.14: Litholog at monitoring well by SGWB (SGWB, 2014)

S. No.	***Lithological Unit (Formation)***	***Depth range in (meter)***		***Thickness in (meter)***
		From	***To***	
	Salwari			
1.	Sandy clay with kankars	0.00	9.00	9.00
2.	Sand very coarse grained with Gravels unconsolidated.	9.00	52.00	43.00
3.	Quartzitic Biotite Schist, compact, blackish in	52.00	57.00	5.00

	colour			
4.	Biotite Schist Saturated black in colour	57.00	119.00	62.00
5.	Quartz , Gnessis Hard & Compact	119.00	Break-down	NA
Ringus				
1.	Sand very fine and medium grained with clay & kankars unconsolidated.	0.00	48.00	48.00
2.	Quartzite rocks with little Biotite, Biotite Schist, compact, blackish in colour	48.00	110.00	62.00
3.	Quartz Biotite Schist Hard & Compact	110.00	128.00	18.00
4.	Very Fine grained Biotite Quartz Schist dry in nature with little Garnet mineral	128.00	Break-down	NA
Bilyurampura				
1.	Fine grained sand	0.00	53.00	53.00
2.	Unconsolidated to semi consolidated medium grained sandstone mixed with feldspar particles and clay	53.00	105.00	52.00
3.	Shale greenish in colour with Quartz fragment	105.00	130.00	25.00
		After 130 *m*, work stopped		
Sardarsahar				
1.	Sand, fine yellowish brown in colour	0.00	20.00	20.00
2.	Sand, with minor amount of clay, sand fine grayish brown in colour. Clays light brown in colour sticky in nature	20.00	49.00	29.00
3.	Sand + clay + kankar+phyllite. Sand: fine coarse. Caly: light brown in colour, sticky in nature. Kankar: fine rounded aggregates, earth white in colour. Phyllite with free quartz pieces. Phyllite: weathered light grey in colour.	49.00	124.00	75.00
4.	Sand with fragments of quartz, feldspar and ferromagncians with some clay & kankar. Probably for granitic source.	124.00	126.00 (break-down)	2.00

If we see the matrix change (of litholog) as a major controlling factor of change in concentration of various parameters (Nitrate, Fluoride and TDS) by using lithologs data it is clear that the changes occurs at depth of 48-53 *m* and 119-130 *m*. Layer 1 indicates changes at 50 *m* depth and layer 2 indicates changes at 125 *m* depth which are close enough to the lithologs depth. The deviation in depth prediction by the model at four locations is provided in Table 4.15. The deviation of predicted layer depth to lithologs data varies from 0.8% to 16% for common locations and should be accepted for the layer change prediction. Thus, groundwater characterization and modeling has been done with proper validation. Few SGWB wells don't have litholog details and 21 wells have lithologs (SGWB, 2014) and their detail is provided in Annexure 2D. The location of these wells are more than 3 km from sampling well thus not included in error calculation between real and modeled depth.

Table 4.15: Error between real and modelled depth

	Common location of sampling and monitoring well			
Layer Depth	***Salwari***	***Ringus***	***Bilyurampura***	***Sardarsahar***
0-50 (Layer 1)	3.85%	4.16%	5.6%	2%
50-125 (Layer 2)	4.8%	2.34%	16%	0.8%
125-200 (Layer 3)	NA	No data available after 128 m	No data available after 130 m	NA
200-300 (Layer 4)				

The mineralogical and chemical composition of mineral rocks (Gulbrandsen, 1974; William, 1984; Wilson, 2010; Edward and Ford, 1932; Nesse, 2011) are illustrated in Table 4.16 that helps out in understanding the lithologs provided by SGWB (SGWB, 2014). Mostly, the mineralogical composition may be responsible for increment of Nitrate, Fluoride and TDS in groundwater.

Table 4.16: Mineralogical constituents of litholog matrix present in layers

	Common location of sampling and monitoring well			
Layer Depth	***Salwari***	***Ringus***	***Bilyurampura***	***Sardarsahar***
0-50 (Layer 1)	Sandy clay + kankars	Sand + clay + kankars	Sand	Sand + clay
50-125 (Layer 2)	Quartzite + Biotite Schist	Quartzite + Biotite Schist	Sandstone + feldspar + clay	Sand + clay + kankar+phyllite + feldspar
125-200 (Layer 3)	NA	Biotite Quartz Schist (up to 128 *m*)	Shale + Quartz (upto 130 *m*)	Clay + kankar + ferromagnesians (upto 126 *m*)
200-300 (Layer 4)				

Mineralogical/Chemical composition
Sandyclay (Sand+clay): $SiO_2 + Al_2Si_2O_5(OH)_{4,}$ Kankars: contains CaO, MgO, Mn, Al_2, Fe, Na in matrix
Quartzite: SiO_2, Fe_2O_3, Al_2O_3, Na_2O, KrO, CaO, MgO; Quartz: SiO_2
Biotite:$K(Mg,Fe)_3$-Al_2-$Si_3O_{10}(OH,F)_2$
Schist:Biotite,Chlorite, Muscovite,quartz, Plagioclase, Garnet Chlorite:$(Fe,Mg,Al)_6\ (Si,Al)_4O_{10}(OH)_8$; Garnet:$(Fe^{2+},Ca,Mg,Mn)_3\ (Fe^{3+},Al,Cr)_2Si_3O_{12}$ Muscovite:$KAl_3Si_3O_{10}(OH)_2$; Plagioclase: $(Ca, Na)Al_2Si_2O_8$,$NaAlSi_3O_8$
Sandstone: Quartz and Orthoclase, Plagioclase and varying minor amounts of other minerals. Orthoclase: $(K,Na)AlSi_3O_8$
Shale: Quartz, clay mineral, Calcite, Feldspar, Mica, Pyrite, Phosphate, Organic matter Calcite: $CaCO_3$ with traces of N & K; Pyrite: FeS_2 ; Mica ($X_2Y_{4–6}Z_8O_{20}(OH, F)_4$): $K(Al,\underline{Cr},\underline{Mn})_3Si_3O_{10}(OH,F)_2$, *[where K, Na, Ca at position X with traces of Ba, Rb Cs, & Al, Mg, Fe at position of Y with traces of Mn, Cr, Ti, Li and Si or Al at position of Z with traces of* Fe^{3+} *or Ti];* Phosphate: $X_5Y(PO_4)_3$ *[*Ca^{2+} *or* Pb^{3+} *are in position of X and is* F^-, Cl^-, *or* OH^- *in position of Y].*
Feldspar (AT_4O_8): $KAlSi_3O_8$-$NaAlSi_3O_8$-$CaAl_2Si_2O_8$, *[Ammonium (*NH_4*) & REE in A position and Heavy minerals (Ti, Ge, Ga, B, P) in T position are also associated].*
Phyllite: includes Muscovite, Biotite, Quartz, Plagioclase
Ferromagnesians : $(Fe_{2,}\ Mg_2)\ SiO_{3-4}$

Mostly clay have the ability to soak up ions (electrically charged atoms and molecules) from a solution and release the ions later when conditions change and even clay act as a carrier of ions (Nora, 1999). Other property of clay is to exchange ions which are related to the charged surface of clay minerals. Ions can be attracted to the surface of a clay particle or taken up within the structure of these reacting minerals surface. Clays can act as a medium for transporting and widely dispersing contaminants from one area to another due to its ion releasing and carrying properties (Nora, 1999). Thus, Clay as part of matrix of soil, works as carrier of various ion in groundwater of Shekhawati region. Table 4.16 suggest (Gulbrandsen, 1974; William, 1984; Wilson, 2010; Edward and Ford, 1932; Nesse, 2011; White, 2013) that the presence of Fluorine ion (F^-) in biotite and mica, ammonium (NH_4) in feldspar and nitrogen in calcite must be contributing to Fluoride and Nitrate in water, while TDS may exist due to presence of various cations and anions in matrix of soil and rock as a part of aquifer.

4.6 Conclusion

The result of 163 wells for pre and post monsoon season illustrated that average Nitrate concentration in groundwater is above the prescribed limit while average Fluoride and TDS concentration lies in the prescribed limit. It has been observed that 48.47%, 26.38% and 46.01% wells for Nitrate, Fluoride and TDS respectively exist in safe category during pre monsoon. It has been observed that 36.19%, 38.04% and 51.53% wells for Nitrate, Fluoride and TDS respectively exist in safe category during post monsoon. The WQI determined for pre and post monsoon indicates that range of WQI for post monsoon is higher than range of WQI for pre monsoon. The 3D analysis has carried out to visualize the quality of three quality parameters in 3D space. Based on this 3D block model, the plots between these quality parameters concentration and depth have been developed for all sample locations. The presence of different pattern between concentration of parameters and depth lead to group the groundwater wells in different blocks. The subsurface information in term of layers has been extracted from these plots. Further these layers accuracy have been evaluated with help of Rajasthan state groundwater board generated soil log information. Over verification of lithologs, it is found that minerals are main contributors of Nitrate, Fluoride and TDS concentration in groundwater of Shekhawati region.

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5. Removal of Nitrate, Fluoride and Total Dissolved Solids

*This chapter deals with the bio-sorption process adopted for reduction of Nitrate, Fluoride and Total Dissolved Solids (TDS) in potable water. The results of batch study, column study and parameters optimization have been illustrated. Finally, the column run for 144 hour has been performed to check the reduction of Nitrate, Fluoride and Total Dissolved Solids***.**

The batch and continuous study have been carried out to reduce the concentration of nitrate, fluoride and total dissolved solids in drinking water. In this study, we have used nine low cost materials available locally. The materials used are namely (1) Wheat Husk (Triticum) (WH), (2) Rice Husk (Oryza sativa) (RH), (3) Banana peel Husk (Musa) (BH), (4) Bagasse (Saccharum officinarum) (SH), (5) Coconut Coir (Cocos nucifera) (CC), (6) Amla Seed (Phylanthus emblica) (AS), (7) Aloevera Gel (Aloe barbadensis miller) (AG), (8) Amla Bark (Phyllanthus emblica) (AB) and (9) Potato Flakes (Solanum tuberosum) (PF). These materials have been prepared for the experimentation by following steps.

a) Washing of material at room temperature for removal of dust particles.
b) Materials are oven dried at Temp. 103 ± 3 °C to remove moisture content (Reeb and Milota, 1999).
c) Oven dried samples are grinded to the size of 10 µm.
d) Coconut coir and Aloevera gel have not been grinded and used as such.

We have applied the trial and error method to find out the material by which Nitrate, Fluoride and TDS can be reduced. A number of materials have been selected due to the reason of availability of the materials locally.

Biosorption is a physiochemical process that occurs naturally in certain biomass which allows it to bind contaminants on its cellular structure (Velasquez and Dussan, 2009). This process doesn't require energy and amount of contaminants removal by sorbent is dependent on kinetic equilibrium and composition of sorbent's cellular surface. Biosorption is largely influenced by pH, the concentration of biomass, the time of reaction and the interaction between different metallic ions (Ahalya et al., 2003; Velasquez and Dussan, 2009).

5.1 Batch Study

5.1.1 Time optimization

Time optimization has been done for the removal of Nitrate, Fluoride and Total Dissolved Solids by taking nine different materials and details are given in Table 5.1, Table 5.2, Table 5.3 and Table 5.4 respectively.

Table 5.1: Time optimization for Nitrate reduction with nine materials

Sample code	**Contact Time (*min*)**	**Adsorbent weight (*g*)**	**Nitrate in influent (*mg/l*)**	**Nitrate in effluent (*mg/l*)**	**Increase (%)**	**Reduction (%)**
WH1	10	2	50	94.17	88.34	-
WH2	20	2	50	88.42	76.84	-
WH3	40	2	50	88.36	76.73	-
WH4	60	2	50	87.84	75.67	-
WH5	80	2	50	84.08	68.16	-
RH1	10	2	50	78.71	57.41	-
RH2	20	2	50	100.91	101.81	-
RH3	40	2	50	121.39	142.78	-
RH4	60	2	50	121.58	143.16	-
RH5	80	2	50	121.61	143.21	-
BH1	10	2	50	122.76	145.52	-
BH2	20	2	50	125.67	151.35	-
BH3	40	2	50	131.08	162.16	-
BH4	60	2	50	131.39	162.79	-
BH5	80	2	50	146.47	192.95	-
SH1	10	2	50	123.91	147.83	-
SH2	20	2	50	123.74	147.48	-
SH3	40	2	50	126.71	153.41	-
SH4	60	2	50	129.58	159.15	-
SH5	80	2	50	135.43	170.87	-
CC1	10	2	50	69.55	39.10	-
CC2	20	2	50	81.28	62.56	-
CC3	40	2	50	111.55	123.09	-
CC4	60	2	50	114.76	129.51	-
CC5	80	2	50	115.48	130.95	-
AS1	10	2	50	50.91	1.83	-
AS2	20	2	50	66.39	32.79	-
AS3	40	2	50	69.67	39.34	-
AS4	60	2	50	70.87	41.74	-
AS5	80	2	50	78.37	56.73	-
AG1	10	2	50	77.63	55.26	-
AG2	20	2	50	75.57	51.14	-
AG3	40	2	50	61.12	22.24	-

AG4	60	2	50	39.84	-	20.32
AG5	80	2	50	39.82	-	20.36
AB1	10	2	50	102.23	104.46	-
AB2	20	2	50	106.62	113.24	-
AB3	40	2	50	107.63	115.26	-
AB4	60	2	50	108.69	117.38	-
AB5	80	2	50	108.65	117.30	-
PF1	10	2	50	47.59	-	4.82
PF2	20	2	50	39.23	-	21.55
PF3	40	2	50	25.16	-	49.69
PF4	60	2	50	25.99	-	48.02
PF5	80	2	50	38.95	-	22.10

WH- samples of Wheat Husk, RH- samples of Rice Husk, BH- samples of Banana peel Husk, SH- samples of Bagasse, CC- samples of Coconut Coir, AS- samples of Amla seed, AV- samples of Aloevara Gel, AB- samples of Amla Bark, PF- samples of potato flakes,

Table 5.2: Time optimization for Nitrate reduction by potato gel

Sample code	**Contact Time (*min*)**	**Adsorbent weight (*g*)**	**Nitrate in influent (*mg/l*)**	**Nitrate in effluent (*mg/l*)**	**Reduction (*%*)**
PG1	10	2 g	50	46.17	7.66
PG2	20	2 g	50	38.44	23.12
PG3	40	2 g	50	24.29	51.42
PG4	60	2 g	50	24.47	51.06
PG5	80	2 g	50	26.47	47.06

PG- samples of potato gel

Table 5.3: Time optimization for Fluoride reduction with nine materials

Sample code	**Contact Time (*min*)**	**Adsorbent weight (*g*)**	**Fluoride in influent (*mg/l*)**	**Fluoride in effluent (*mg/l*)**	**Increase (*%*)**	**Reduction (*%*)**
WH6	10	2	1.5	1.62	7.67	-
WH7	20	2	1.5	1.77	18.00	-
WH8	40	2	1.5	1.76	17.33	-
WH9	60	2	1.5	1.74	16.00	-
WH10	80	2	1.5	1.75	16.67	-
RH6	10	2	1.5	1.51	0.67	-
RH7	20	2	1.5	1.58	5.57	-
RH8	40	2	1.5	1.64	9.33	-
RH9	60	2	1.5	1.77	18.00	-
RH10	80	2	1.5	1.95	30.00	-
BH6	10	2	1.5	1.80	20.00	-
BH7	20	2	1.5	1.80	20.00	-
BH8	40	2	1.5	1.69	12.67	-
BH9	60	2	1.5	1.56	4.00	-

BH10	80	2	1.5	1.55	3.33	-
SH6	10	2	1.5	1.25	-	16.67
SH7	20	2	1.5	1.16	-	22.67
SH8	40	2	1.5	1.20	-	20.00
SH9	60	2	1.5	1.36	-	9.33
SH10	80	2	1.5	1.45	-	3.33
CC6	10	2	1.5	1.68	12.00	-
CC7	20	2	1.5	1.69	12.93	-
CC8	40	2	1.5	1.70	13.33	-
CC9	60	2	1.5	1.73	15.33	-
CC10	80	2	1.5	1.74	15.87	-
AS6	10	2	1.5	1.55	3.47	-
AS7	20	2	1.5	1.54	2.60	-
AS8	40	2	1.5	1.63	8.60	-
AS9	60	2	1.5	1.66	10.33	-
AS10	80	2	1.5	1.69	12.67	-
AG6	10	2	1.5	1.43	-	4.43
AG7	20	2	1.5	1.42	-	5.33
AG8	40	2	1.5	1.34	-	10.67
AG9	60	2	1.5	1.32	-	12.00
AG10	80	2	1.5	1.38	-	8.00
AB6	10	2	1.5	1.51	0.67	-
AB7	20	2	1.5	1.65	10.00	-
AB8	40	2	1.5	1.67	11.20	-
AB9	60	2	1.5	1.72	14.67	-
AB10	80	2	1.5	1.88	25.33	-
PG6	10	2	1.5	1.18	-	21.33
PG7	20	2	1.5	1.20	-	20.00
PG8	40	2	1.5	0.91	-	39.33
PG9	60	2	1.5	1.08	-	28.00
PG10	80	2	1.5	1.36	-	9.33

WH- samples of Wheat Husk, RH- samples of Rice Husk, BH- samples of Banana peel husk, SH- samples of Bagasse, CC- samples of Coconut Coir, AS- samples of Amla seed, AG- samples of Aloevara Gel, AB- samples of Amla Bark, PG- samples of potato gel

Table 5.4: Time optimization for TDS reduction with nine materials

Sample code	**Contact Time (*min*)**	**Adsorbent weight (*g*)**	**TDS in influent (*mg/l*)**	**TDS in effluent (*mg/l*)**	**Increase (*%*)**	**Reduction (*%*)**
WH11	10	2	2200	1834.33	-	16.62
WH12	20	2	2200	1814.33	-	17.53
WH13	40	2	2200	1814.00	-	17.55

WH14	60	2	2200	1800.00	-	18.18
WH15	80	2	2200	1800.00	-	18.18
RH11	10	2	2200	2053.00	-	6.68
RH12	20	2	2200	2063.13	-	6.22
RH13	40	2	2200	2078.70	-	5.51
RH14	60	2	2200	2075.03	-	5.68
RH15	80	2	2200	2074.72	-	5.69
BH11	10	2	2200	2052.05	-	6.73
BH12	20	2	2200	2047.05	-	6.95
BH13	40	2	2200	2052.05	-	6.73
BH14	60	2	2200	2002.00	-	9.00
BH15	80	2	2200	2002.00	-	9.00
SH11	10	2	2200	2089.92	-	5.00
SH12	20	2	2200	2089.92	-	5.00
SH13	40	2	2200	2089.92	-	5.00
SH14	60	2	2200	2039.92	-	7.28
SH15	80	2	2200	2039.92	-	7.28
CC11	10	2	2200	2035.51	-	7.48
CC12	20	2	2200	2035.51	-	7.48
CC13	40	2	2200	1968.84	-	10.51
CC14	60	2	2200	1985.51	-	9.75
CC15	80	2	2200	2035.51	-	7.48
AS11	10	2	2200	2044.60	-	7.06
AS12	20	2	2200	2044.60	-	7.06
AS13	40	2	2200	2044.60	-	7.06
AS14	60	2	2200	2044.60	-	7.06
AS15	80	2	2200	2044.60	-	7.06
AG11	10	2	2200	2053.00	-	6.68
AG12	20	2	2200	2053.00	-	6.68
AG13	40	2	2200	1853.00	-	15.77
AG14	60	2	2200	1886.33	-	14.26
AG15	80	2	2200	1886.33	-	14.26
AB11	10	2	2200	2182.38	-	0.80
AB12	20	2	2200	2182.38	-	0.80
AB13	40	2	2200	2149.05	-	2.32
AB14	60	2	2200	2149.05	-	2.32
AB15	80	2	2200	2182.38	-	0.80
PG11	10	2	2200	2000.00	-	9.09
PG12	20	2	2200	1866.67	-	15.15
PG13	40	2	2200	1516.67	-	31.06
PG14	60	2	2200	2000.00	-	9.09
PG15	80	2	2200	1966.67	-	10.61

WH- samples of Wheat Husk, RH- samples of Rice Husk, BH- samples of Banana husk, SH- samples of Bagasse, CC- samples of Coconut Coir, AS- samples of Amla seed, AG- samples of Aloevara Gel, AB- samples of Amla Bark, PG- samples of potato gel

5.1.1.1 Nitrate

The adsorbtion studies for the nine materials have been carried out. It is noted that Nitrate is removed only by the potato flakes for all the contact time and by aloevera gel at specific time. Nitrate removal was 20.32% and 20.36% at reaction time of 60 *min* and 80 *min* respectively for aloevera gel. Nitrate removal was 49.69% and 48.02% at contact time of 40 *min* and 60 *min* respectively for potato flakes. The problem of odour was noticed during the preparation of samples from potato flakes. The problem of color was also observed with other materials.

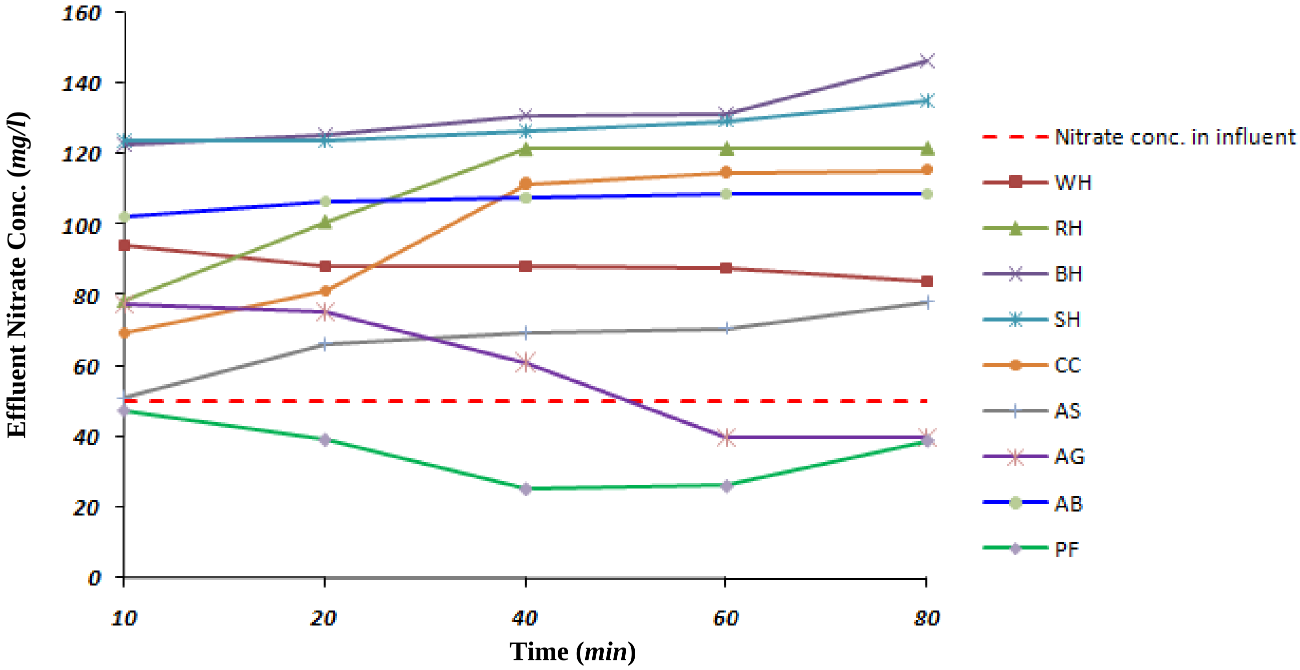

Figure 5.1: Changes in Nitrate concentration for different adsorbent material

Figure 5.1 reveals that out of nine materials studied, wheat husk, rice husk, banana peel husk, bagasse, coconut coir, amla seeds and amla bark demonstrated the rise in Nitrate. While, aloevera gel and potato flakes have shown the reduction in nitrate. Potato flakes have demonstrated the reduction in Nitrate concentration in effluent between 4.82% and 49.69% at all duration of contact. The maximum reduction of 49.69% is observed at 40 minute of reaction time.

It has been observed that wheat husk, rice husk, banana peel husk, bagasse, coconut coir, amla seeds and amla bark shown increase in Nitrate concentration in the effluent. The probable reason for the same is the presence of Nitrogen compound in plants (Turner, 1960; Brady and Weil, 1999).

Again, the experiment was repeated for potato gel and results are shown in Table 5.2. Following measures were taken to eliminate the odour from potato flakes.

1. Changing the phase of potato by adding 250 *ml* distilled water in potato slurry and heating it at 55-60 °C for 24 *h* (Hans et al., 2004). Thus it is converted into gel and odour is removed.
2. From the jelly substance of potato, gel balls (dia. 1*cm*) are prepared for column study, while direct gel is used for batch study.

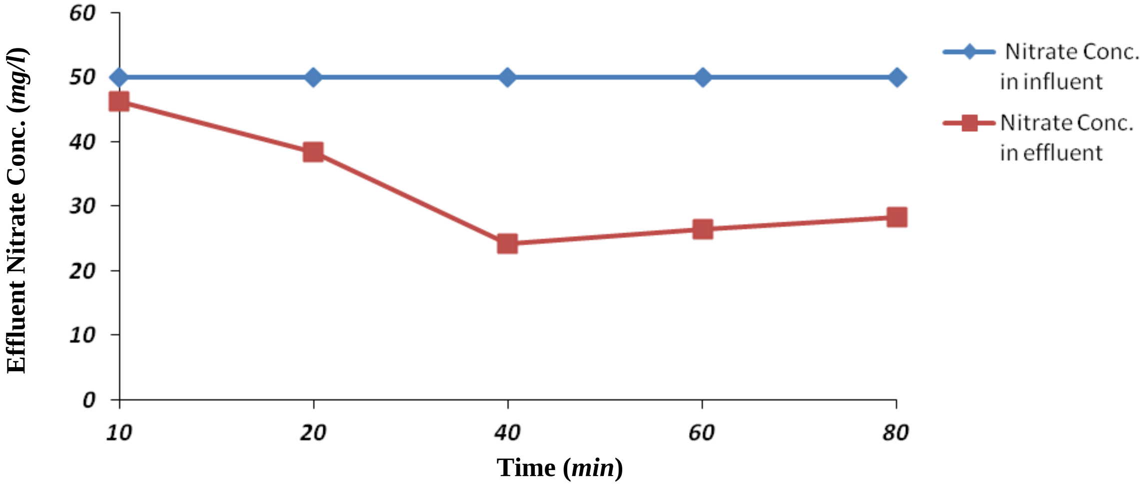

Figure 5.2: Change in nitrate concentration for potato gel as an adsorbent

Figure 5.2 shows potato gel is better adsorbent in comparison to potato flakes. Nitrate reduction varies between 7.66% and 51.42% for potato gel during all contact time. The maximum reduction (51.42%) has been observed at 40 *min* contact time so opted as optimal reaction time for the study.

5.1.1.2 Fluoride

The details of material response for time optimization for reducing the Fluoride with nine materials are given in Table 5.3. Potato gel is taken in place of potato flakes for time optimization study to reduce Fluoride to avoid the odour problem associated with potato flakes.

The adsorbtion studies for the nine materials have been carried out. It is noted that Fluoride is removed by the potato gel, bagasse and aloevera gel for all the contact times. Fluoride removal was 39.33% and 28.00% at contact time of 40 *min* and 60 *min* respectively by using potato gel. Fluoride removal was 22.67% and 20.00% at contact time of 20 *min* and 40 *min* respectively by using bagasse. Fluoride removal was 10.67% and 12.00% at reaction time of 40 *min* and 60 *min* respectively by using aloevera gel. In this paragraph, maximum removal of fluoride has been reported for all three materials.

Figure 5.3 reveals that; out of nine materials studied; wheat husk, rice husk, banana peel husk, coconut coir, amla seeds and amla bark demonstrated the rise in Fluoride. While, aloevera gel, bagasse and potato gel have shown the reduction in Fluoride. Potato gel has demonstrated the reduction in Fluoride concentration in effluent ranging from 9.33% to 39.33% at all duration of contact times. The maximum reduction in Fluoride concentration of 39.33% is observed at 40 *min* of contact time.

It has been observed that wheat husk, rice husk, banana peel husk, coconut coir, amla seeds and amla bark shown increase in Fluoride concentration in the effluent. The reason for the same is the presence of Fluoride compound in plants through pesticides and form C-F bonds. (Gribble, 2002; Hagan et al., 2002).

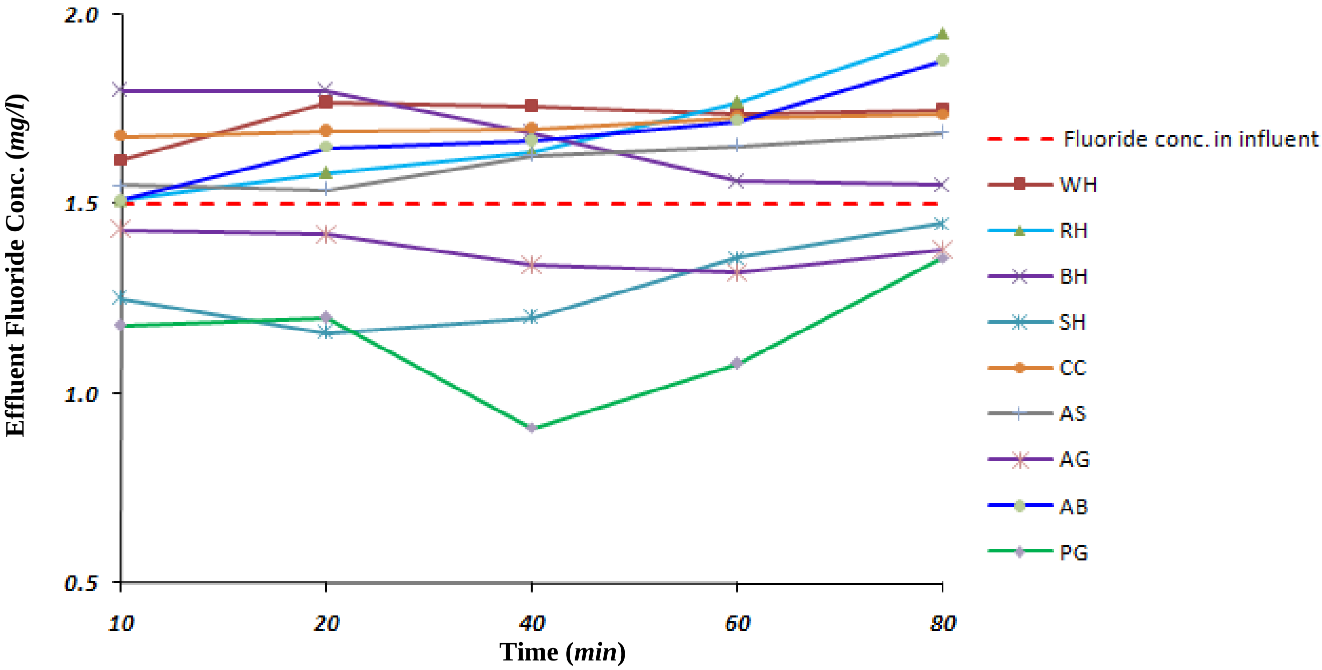

Figure 5.3: Changes in Fluoride concentration for different adsorbent material.

Figure 5.3 shows potato gel is better adsorbent in comparison to bagasse and aloevera gel. The maximum Fluoride reduction (39.33%) has been observed at 40 *min* contact time in potato gel, so it is opted as optimal reaction time for this study.

5.1.1.3 Total Dissolved Solids

The details of material response for time optimization for reducing the total dissolved solids with nine materials are given in Table 5.4. Due to the odour associated with potato flakes, potato gel is used during the optimization of time for TDS reduction. It is noted that TDS has been removed by all the materials (wheat husk, rice husk, banana peel husk, bagasse, coconut coir, amla seed, aloevera gel, amla bark and potato gel) tested at all contact times. Wheat husk, coconut coir, aloevera gel and potato gel have shown very good reduction in Total Dissolved Solids concentration. The TDS reduction achieved by different materials varied between 1% and 31% and has been shown for nine experimental materials in Figure 5.4. Even all of the materials have depicted the reduction potential for TDS from effluent but maximum reduction is achieved only by potato gel.

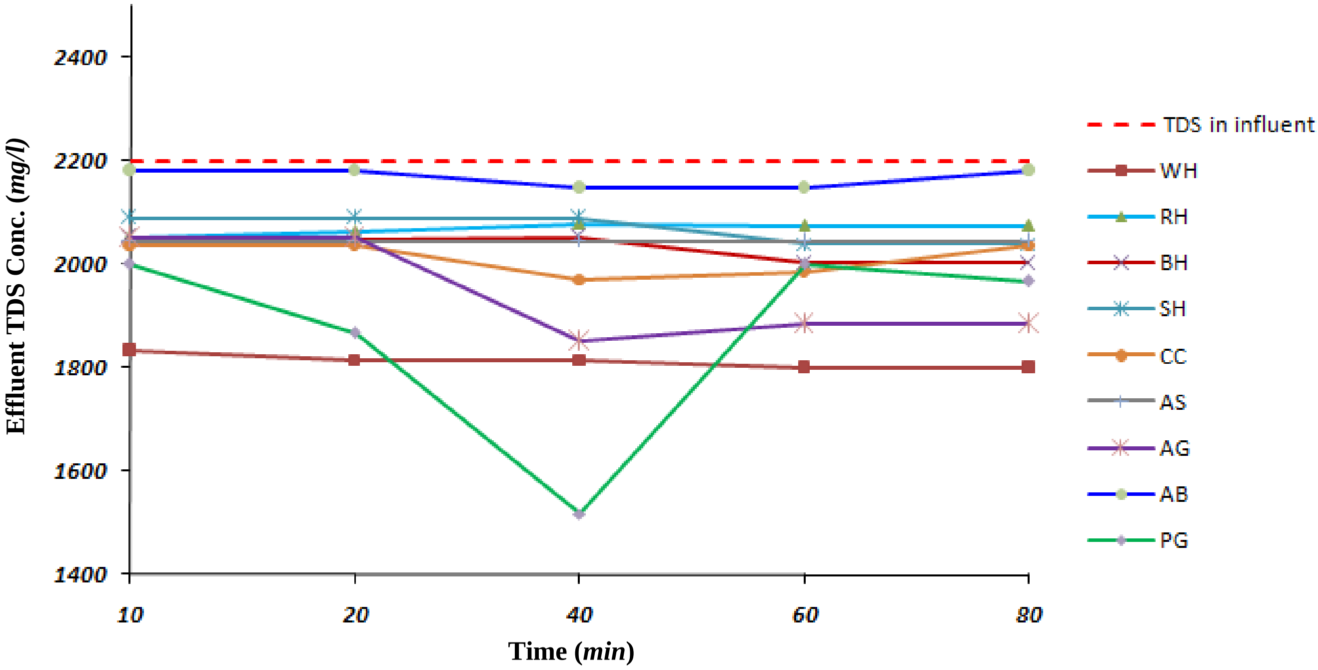

Figure 5.4: Changes in TDS concentration for different adsorbent material

Figure 5.4 shows potato gel is better adsorbent in comparison to other eight materials (wheat husk, rice husk, banana peel husk, bagasse, coconut coir, amla seed, aloevera gel, amla bark). The maximum TDS reduction (31.06%) has been observed at 40 *min* contact time in potato gel, so it is opted as optimal contact time for this study.

The time optimization study with nine materials showed that poato gel provides better result in reduction of Nitrate, Fluoride and TDS collectively. Aloevera gel has shown 20.36%, 12% & 15.7% reduction in Nitrate, Fluoride & TDS respectively. Bagasse have shown 22.67% & 7.28% reduction in Fluoride & TDS respectively. Potato gel have shown 51.4%, 39% & 31% reduction in Nitrate, Fluoride & TDS respectively. The percentage reduction of Nitrate, Fluoride and TDS with potato gel is higher then other possible potential materials, thus potato gel as the adsorbent material is used alone further, for optimization of other parameters in this study.

5.1.2 Adsorbent optimization

Adsorbent optimization (weight of adsorbent) has been done after taking the reading of time optimization. Potato gel has shown the maximum reduction in Nitrate, Fluoride and TDS. The details are given in Table 5.5, Table 5.6 and Table 5.7 respectively.

Table 5.5: Weight optimization of potato gel for Nitrate reduction

Sample code	**Contact Time (*min*)**	**Adsorbent weight (*g*)**	**Nitrate in influent (*mg/l*)**	**Nitrate in effluent (*mg/l*)**	**Reduction (*%*)**
PG16	40	0.1	50.00	17.11	65.78
PG17	40	0.5	50.00	17.22	65.56
PG18	40	1.0	50.00	19.53	60.94
PG19	40	1.5	50.00	21.74	56.52
PG20	40	2.0	50.00	24.67	50.66
PG21	40	2.5	50.00	29.04	41.92
PG22	40	3.0	50.00	36.87	26.26

PG- samples of potato gel

Table 5.6: Weight optimization result by potato gel for Fluoride reduction

Sample code	**Contact Time (*min*)**	**Adsorbent weight (*g*)**	**Fluoride in influent (*mg/l*)**	**Fluoride in effluent (*mg/l*)**	**Reduction (*%*)**
PG23	40	0.1	1.50	0.42	72.00
PG24	40	0.5	1.50	0.43	71.33
PG25	40	1.0	1.50	0.65	56.67
PG26	40	1.5	1.50	0.81	46.00
PG27	40	2.0	1.50	1.12	25.33
PG28	40	2.5	1.50	1.31	12.67
PG29	40	3.0	1.50	1.33	11.33

PG- samples of potato gel

Table 5.7: Weight optimization result by potato gel for TDS reduction

Sample code	**Contact Time (*min*)**	**Adsorbent weight (*g*)**	**TDS in influent (*mg/l*)**	**TDS in effluent (*mg/l*)**	**Reduction (%)**
PG30	40	0.1	2200.00	1756.00	20.18
PG31	40	0.5	2200.00	1599.20	27.31
PG32	40	1.0	2200.00	1614.50	26.61
PG33	40	1.5	2200.00	1608.00	26.91
PG34	40	2.0	2200.00	1618.68	26.42
PG35	40	2.5	2200.00	1776.60	19.25
PG36	40	3.0	2200.00	1805.82	17.92

PG- samples of potato gel

5.1.2.1 Nitrate

The details of adsorbent optimization for Nitrate reduction is given in Table 5.5. Seven samples were prepared for different weight of potato gel and kept for 40 *min* contact time. Figure 5.5 dipicts that as the weight of adsorbent (potato gel) was increased, the decline in Nitrate reduction have been occured. Nitrate reduction in effluent varies between 26.3% and 65.78% for all contact weight and maximum reduction(65.8%) has been observed at 0.1 *g* weight of adsorbent.

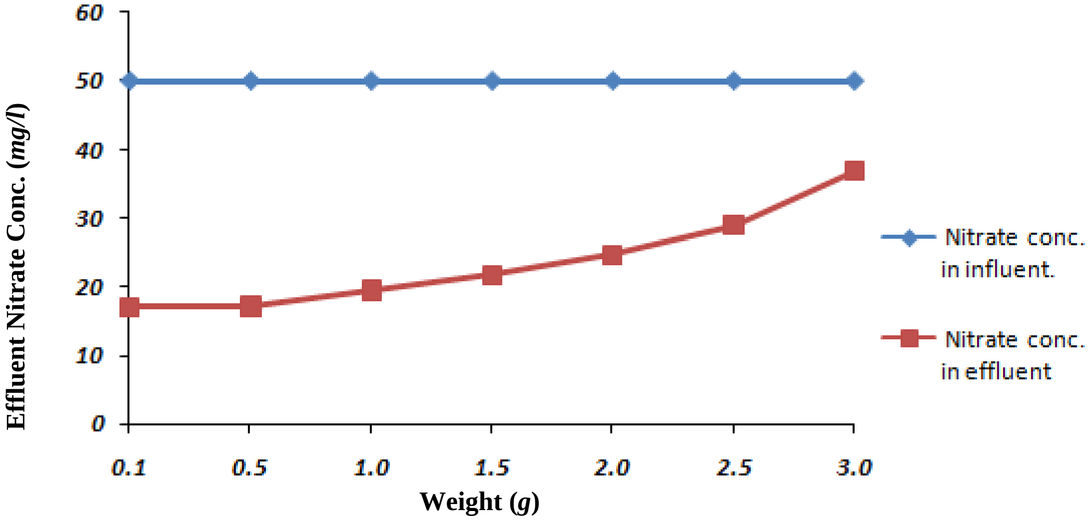

Figure 5.5: Plot between potato gel weight and Nitrate concentration

The maximum reduction of 65.78% and 65.56% in Nitrate was shown by the samples having weight of 0.1 *g* and 0.5 *g* of potato gel. The difference between reduction achieved by 0.1 *g* and 0.5 *g* is very negligible so either of the weight could be used as optimized amount of adsorbent.

5.1.2.2 Fluoride

The details of adsorbent optimization for Fluoride reduction are given in Table 5.6. Seven samples were prepared for different weight of adsorbent (potato gel) and kept for 40 *min* contact time. Figure 5.6 reveals that as the weight of adsorbent (potato gel) was increased, the decline in Fluoride reduction have been occurred. Fluoride reduction in effluent varies between 11.33% and 72% for all contact weight and maximum reduction (72%) has been observed at 0.1 *g* weight of adsorbent.

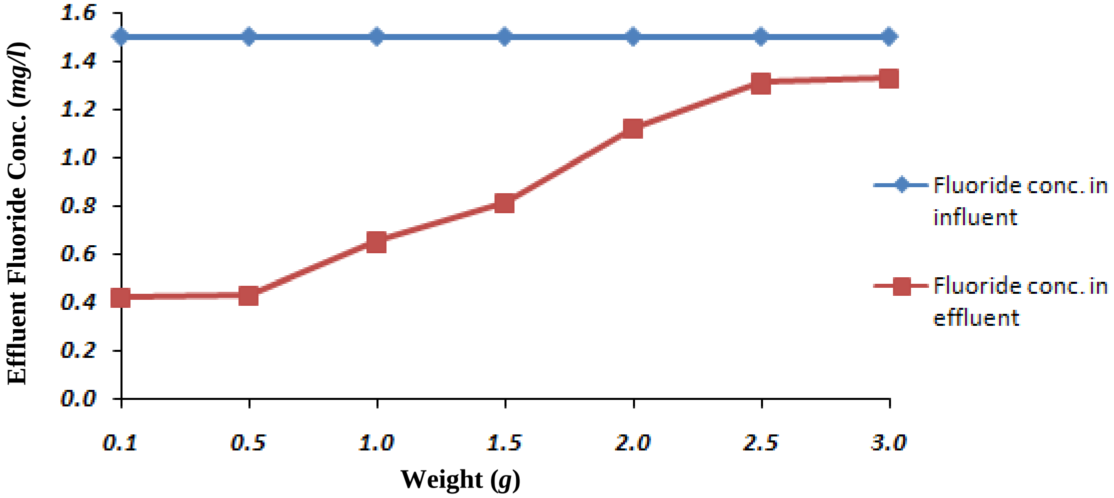

Figure 5.6: Plot between potato gel weight and Fluoride concentration

The maximum reduction of 72% and 71.33% in Fluoride is shown by the samples having weight of 0.1 *g* and 0.5 *g* of potato gel. The difference between reduction achieved by 0.1 g and 0.5 g is very negligible so either of the weight could be used as optimised amount of adsorbent.

5.1.2.3 Total Dissolved Solids

The details of adsorbent optimization for Total Dissolved Solids reduction are given in Table 5.7. Seven samples were prepared for different weight of potato gel and kept for 40 *min* contact time. Figure 5.7 reveals that as the weight of adsorbent (potato gel) was increased, the decline in TDS reduction have been occurred. TDS reduction in effluent varies between 17.9% and 27.3% for all contact weight and maximum reduction (27.31%) has been observed at 0.5 *g* weight of adsorbent. Thus, the maximum TDS (27.31%) removal was undertaken by 0.5 *g* weight of potato gel.

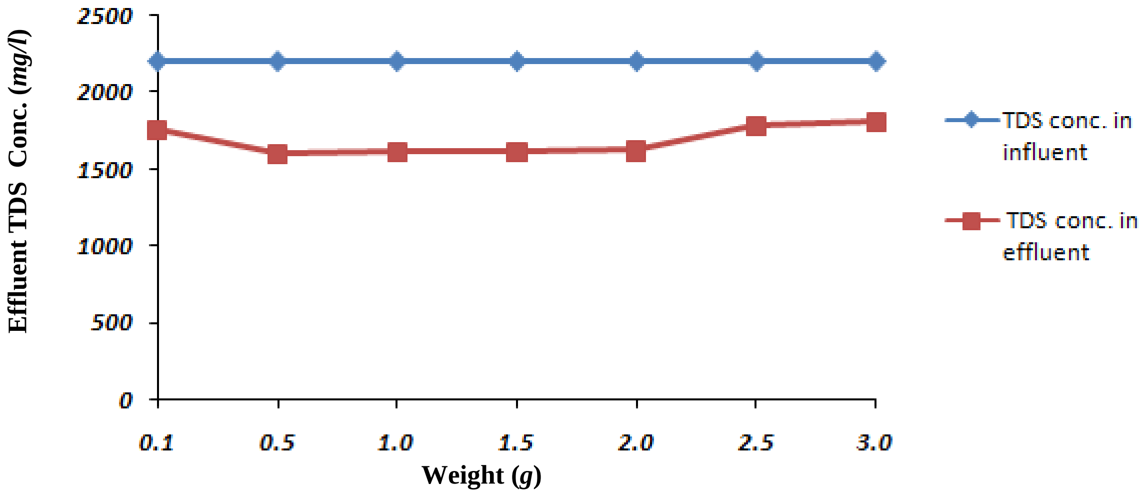

Figure 5.7: Plot between potato gel weight and TDS concentration

It is found that the difference in reduction of Nitrate and Fluoride at 0.1 *g* and 0.5 *g* is negligible and maximum reduction in TDS is achieved at 0.5 *g*. Hence, 0.5 *g* of absorbent weight is chosen as optimised weight for next parameter optimization. The adsorbent optimization study with potato gel showed that the better results were obtained at lesser weight of adsorbent. It has been found that 65.6%, 71.3% and 27.3% reduction is achieved for Nitrate, Fluoride and TDS at 0.5 *g* weight of adsorbent.

5.1.3 Adsorbate optimization

A number of samples have been tested for optimization of influent concentration (adsorbate) after the optimization of time and adsorbent weight. The details are given in Table 5.8, Table 5.9 and Table 5.10 for adsorbate optimization for Nitrate, Fluoride and TDS respectively.

Table 5.8: Nitrate concentration optimization in influent for potato gel

Sample code	**Contact Time (*min*)**	**Adsorbent weight (*g*)**	**Nitrate in influent (*mg/l*)**	**Nitrate in effluent (*mg/l*)**	**Reduction (%)**
PG37	40	0.5	50.00	21.05	57.90
PG38	40	0.5	90.00	33.68	62.57
PG39	40	0.5	145.00	45.47	68.64
PG40	40	0.5	200.00	56.55	71.72
PG41	40	0.5	260.00	61.22	76.45
PG42	40	0.5	301.00	85.37	71.63

PG- samples of potato gel

Table 5.9: Fluoride concentration optimization in influent for potato gel

Sample code	**Contact Time (*min*)**	**Adsorbent weight (*g*)**	**Fluoride in influent (*mg/l*)**	**Fluoride in effluent (*mg/l*)**	**Reduction (*%*)**
PG43	40	0.5	1.50	0.73	51.33
PG44	40	0.5	2.65	1.07	59.62
PG45	40	0.5	3.52	1.16	67.04
PG46	40	0.5	5.30	1.68	68.30
PG47	40	0.5	7.13	2.50	64.93
PG48	40	0.5	8.37	3.22	61.52

PG- samples of potato gel

Table 5.10: TDS concentration optimization in influent for potato gel

Sample code	**Contact Time (*min*)**	**Adsorbent weight (*g*)**	**TDS in influents (*mg/l*)**	**TDS in effluent (*mg/l*)**	**Reduction (*%*)**
PG49	40	0.5	400.00	205.00	48.75
PG50	40	0.5	600.00	280.00	53.33
PG51	40	0.5	860.00	420.00	51.16
PG52	40	0.5	1000.00	520.00	48.00
PG53	40	0.5	1250.00	650.00	48.00
PG54	40	0.5	1500.00	800.00	46.66
PG55	40	0.5	2200.00	1280.00	41.81

PG- samples of potato gel

5.1.3.1 Nitrate

The details for optimization of adsorbate for Nitrate reduction are given in Table 5.8. The Figure 5.8 shows that Nitrate reduction is more at higher influent concentration of adsorbate. To optimize the adsorbate concentration, six samples of Nitrate concentration viz. 50 *mg/l*, 90 *mg/l*, 145 *mg/l*, 200 *mg/l*, 260 *mg/l* and 301 *mg/l* have been prepared. Optimized weight of potato gel i.e. 0.5 *g* is mixed thoroughly and kept for contact time of 40 *min*. Figure 5.8 depicts that the Nitrate reduction varies between 57.9% and 76.5% for all influent concentration.

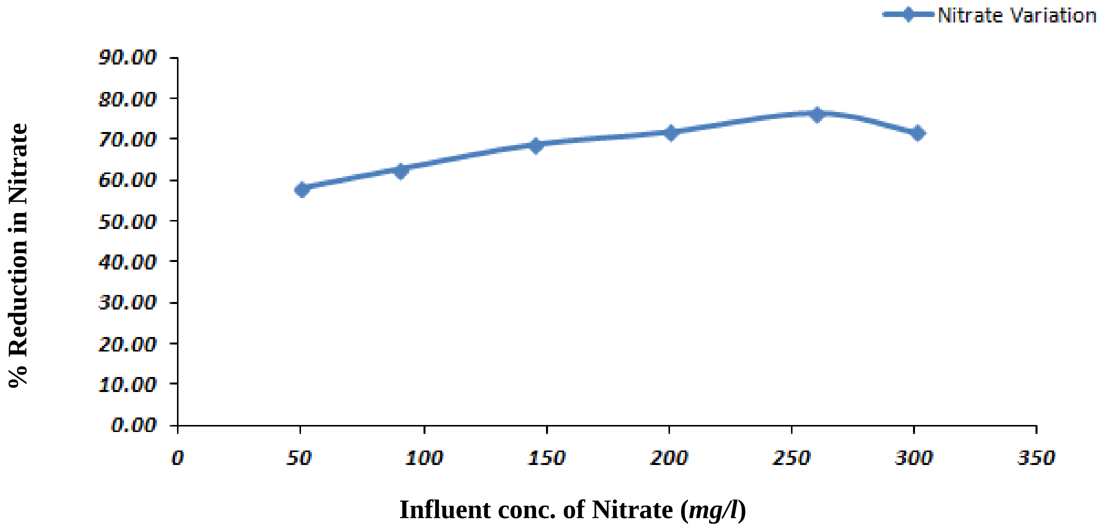

Figure 5.8: Plot between adsorbate concentration and Nitrate reduction

Maximum reduction (76.45%) in Nitrate was shown at adsorbate concentration of 260 *mg/l* so, it is preferred as optimized adsorbate for this study.

5.1.3.2 Fluoride

The details for optimization of adsorbate for Fluoride reduction are given in Table 5.9. The Figure 5.9 shows that Fluoride reduction is more at higher influent concentration of adsorbate. To optimize the adsorbate concentration, six samples of Fluoride concentration viz. 1.50 *mg/l*, 2.65 *mg/l*, 3.52 *mg/l*, 5.30 *mg/l*, 7.13 *mg/l* and 8.37 *mg/l* were prepared. Optimized weight of potato gel i.e. 0.5 *g* was mixed thoroughly and kept for contact time of 40 *min*. Fluoride reduction varies between 51.3% and 68.3% for all influent concentration.

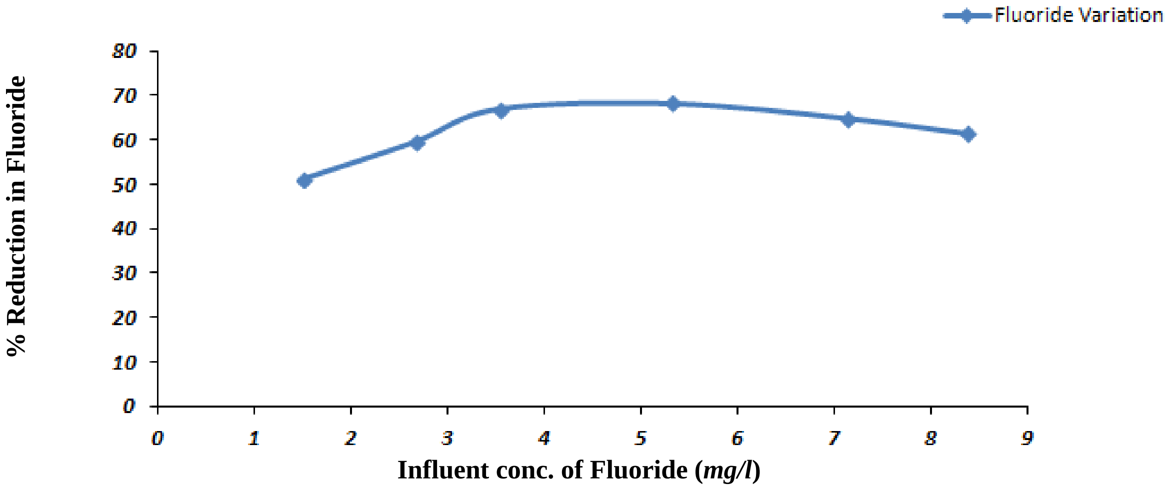

Figure 5.9: Plot between adsorbate concentration and Fluoride reduction

Maximum reduction (68.30%) in Fluoride was shown at an adsorbate concentration of 5.30 *mg/l* so, preferred as optimised adsorbate for this study.

5.1.3.3 Total Dissolved Solids

The details for optimization of adsorbate for total dissolved solids reduction are given in Table 5.10. The Figure 5.10 shows that TDS reduction is more at lower influent concentration of adsorbate. To optimize the adsorbate concentration, seven samples having concentration viz. 400 *mg/l*, 600 *mg/l*, 860 *mg/l*, 1000 *mg/l*, 1250 *mg/l*, 1500 *mg/l* and 2200 *mg/l* were prepared. Optimized weight of potato gel i.e. 0.5 *g* was mixed thoroughly and kept for contact time of 40 *min*. TDS reduction varies between 46.7% and 53.3% for all influent concentration.

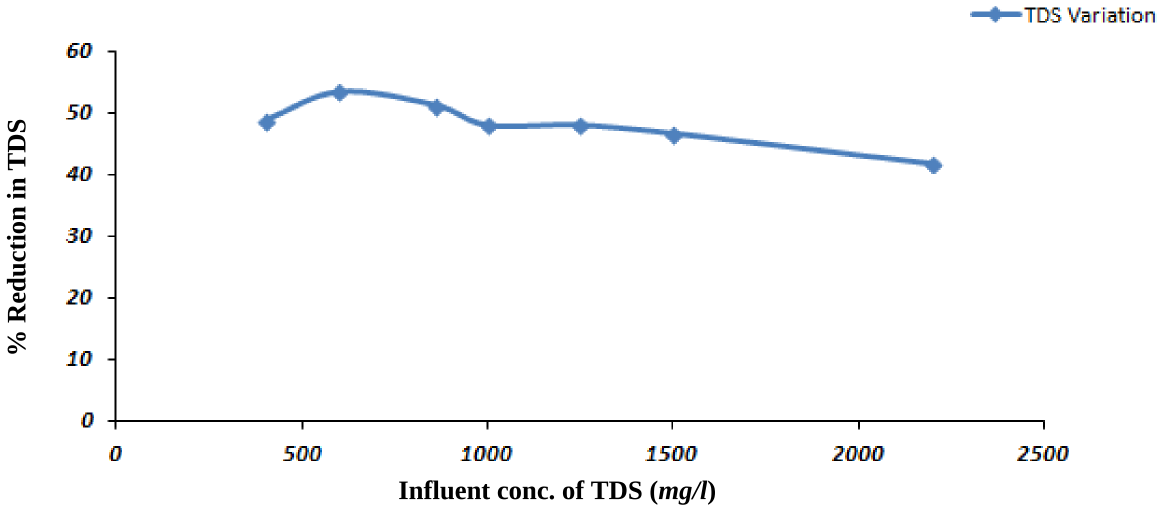

Figure 5.10: Plot between adsorbate concentration and TDS reduction

Maximum reduction (53.33%) in TDS was shown at an adsorbate concentration of 600 *mg/l* so, preferred as optimised adsorbate for this study.

It is found that 260 *mg/l*, 5.30 *mg/l* and 600 *mg/l* are optimised adsorbate concentrations and reduction is 76.5%, 68.3% and 53.3% for Nitrate, Fluoride and TDS respectively. After process parameters optimization, Isotherm and Kinetic study are carried out to understand the mechanism of adsorption occurring in potato gel.

5.1.4 Isotherms

The mechanism of biosorption is usually described through isotherms, that is, the amount of adsorbate on the adsorbent as a function of its concentration (liquid) at constant temperature. The quantity adsorbed is nearly always normalized by the mass of the adsorbent to allow comparison of different materials. Langmuir and Freundlich isotherm are universally accepted isotherms (Foo et. al., 2010) to describe such mechanism.

5.1.4.1 Nitrate

The Freundlich and Langmuir isotherm have been developed for the Nitrate reduction on the basis of batch study data shown in Table 5.8. It has been observed in the experiments that Nitrate concentration has been reduced from 57.9% to 76.45% for the different concentrations of adsorbate while the contact time was same in the readings. Freundlich (Figure 5.11) and Langmuir (Figure 5.12) isotherms have been plotted. Both the isotherm graphs follow the straight line but Langmuir has been more promising because the regression coefficient is higher (Table 5.11). The adsorption of Nitrate is taking place on the single layer of adsorbate surface.

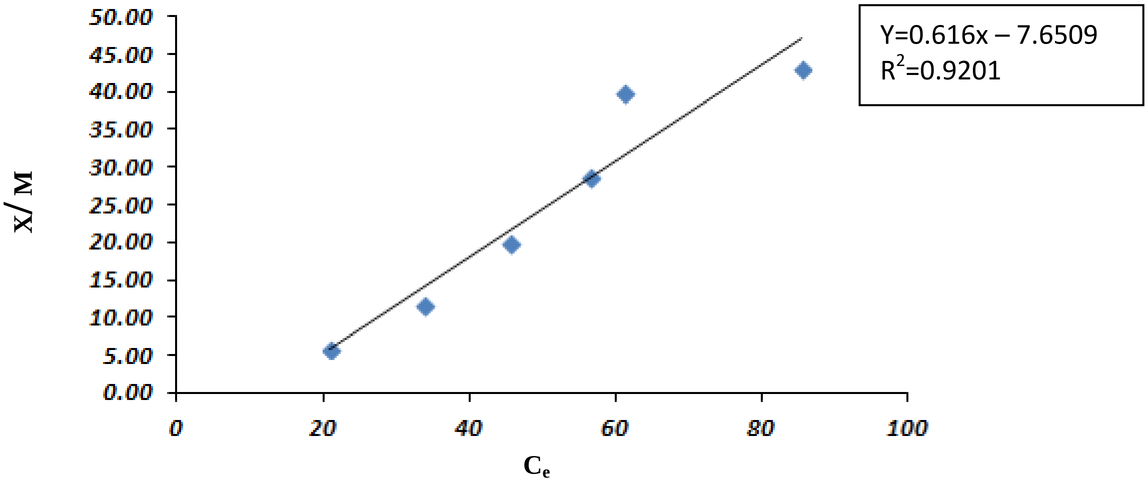

Figure 5.11: Freundlich isotherm for potato gel for Nitrate removal

The Freundlich and Langmuir isotherm constants are derived for reduction taking place in Nitrate and shown in Table 5.11.

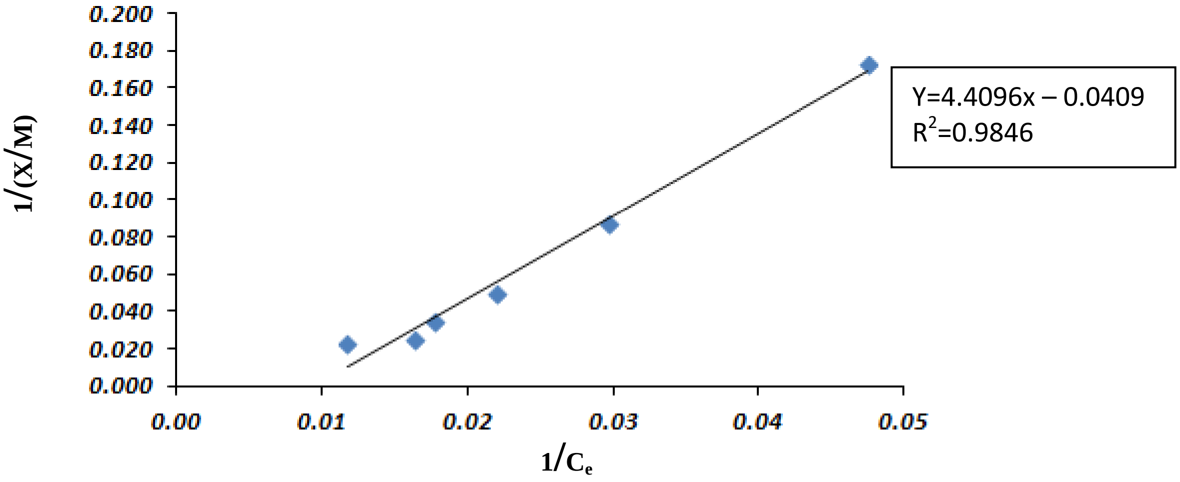

Figure 5.12: Langmuir isotherm for potato gel for Nitrate removal

Table 5.11: Freundlich and Langmuir isotherms constants for Nitrate reduction

Parameter	**Freundlich**	**Langmuir**
Slope (m)	0.6416	4.4096
Intercept (c)	-7.6509	-0.0409
n	1.558603	-
K	0.000476	-
Q_{max}	-	-24.4499
K	-	-0.00928
R^2	0.9201	0.9846
Standard Equation	$\frac{x}{m} = X = KC_e^{1/n}$	$Q = \frac{Q_{\max} KC_e}{1 + KC_e}$
Linear form of standard Equation	$\log\left(\frac{x}{m}\right) = \log X = \log K + \frac{1}{n}\log C_e$	$\frac{1}{Q} = \frac{1}{KQ_{\max}C_e} + \frac{1}{Q_{\max}}$
Trend line equation	Y= 0.6416x-7.6509	Y= 4.4096x-0.0409
Equation derived from experiment result	$X = 0.000476C_e^{(1/1.558603)}$	$\frac{1}{Q} = \frac{1}{0.2268C_e} + \frac{1}{24.4499}$

5.1.4.2 Fluoride

The Freundlich and Langmuir isotherm have been developed for the Fluoride reduction on the basis of batch study data shown in Table 5.9. It has been observed in the studies that Fluoride concentration has been reduced from 51.33% to 68.3% for the different concentration of adsorbate while the contact time was same in the readings. Freundlich (Figure 5.13) and Langmuir (Figure 5.14) isotherms have been plotted. The Freundlich isotherm graph followed the straight line and Langmuir isotherm deviated from the linear trend. Freundlich isotherm has been more promising because the regression coefficient is higher (Table 5.12). The adsorption of Fluoride is taking place in multilayers on the surface of adsorbate. It also indicates that quantity adsorbed rises more slowly and higher concentrations are required to saturate the surface.

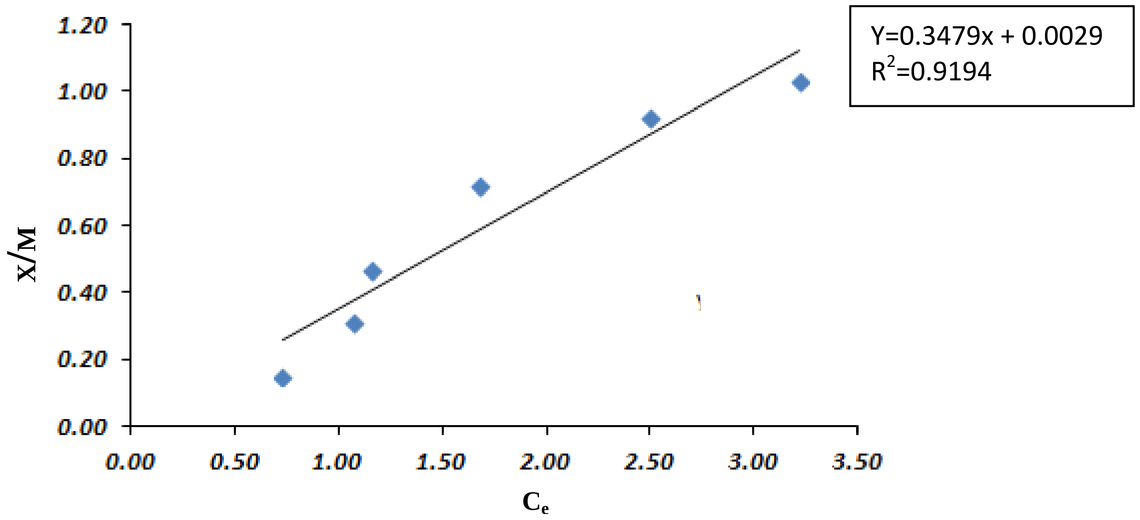

Figure 5.13: Freundlich isotherm for potato gel for Fluoride removal

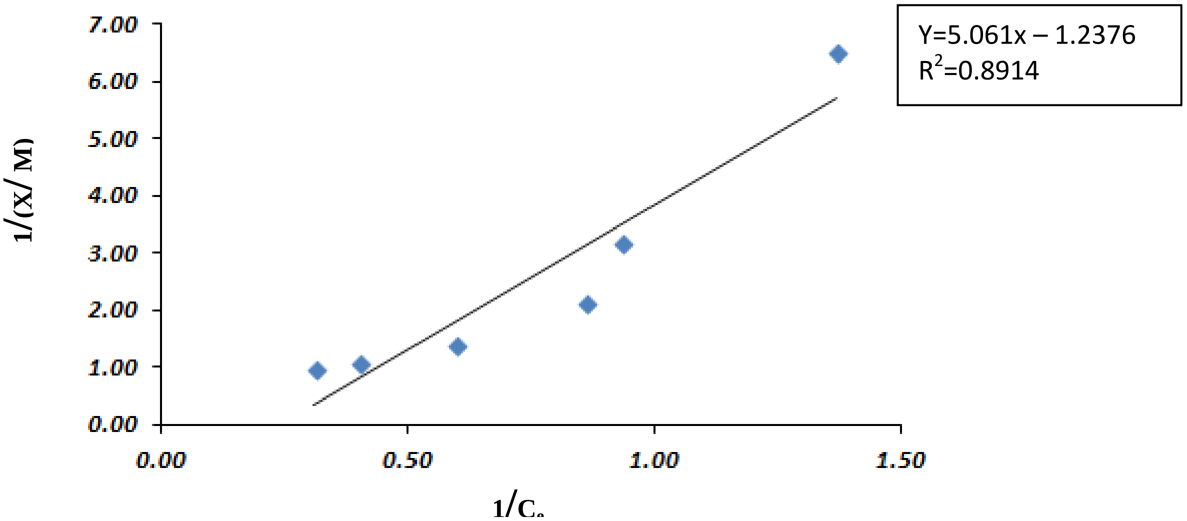

Figure 5.14: Langmuir isotherm for potato gel for Fluoride removal

The Freundlich and Langmuir isotherm constants are derived for reduction taking place in Fluoride and shown in Table 5.12.

Table 5.12: Freundlich and Langmuir isotherms constants for Fluoride reduction

Parameter	**Freundlich**	**Langmuir**
Slope (m)	0.3479	5.061
Intercept (c)	0.0029	-1.2376
n	2.8744	-
K	1.0029	-
Q_{max}	-	-0.8080
K	-	-0.2445
R^2	0.9194	0.8914
Standard Equation	$\frac{x}{m} = X = KC_e^{1/n}$	$Q = \frac{Q_{\max}KC_e}{1+KC_e}$
Linear form of standard Equation	$\log\left(\frac{x}{m}\right) = \log X = \log K + \frac{1}{n}\log C_e$	$\frac{1}{Q} = \frac{1}{KQ_{\max}C_e} + \frac{1}{Q_{\max}}$
Trend line equation	Y= 0.3479x+0.0029	Y= 5.061x-1.2376
Equation derived from experiment result	X= $1.0029C_e^{(1/2.8744)}$	$\frac{1}{Q} = \frac{1}{0.1975\,C_e} - \frac{1}{0.8080}$

5.1.4.3 Total Dissolved Solids

The Freundlich and Langmuir isotherm have been developed for the TDS reduction on the basis of batch study data shown in Table 5.10.

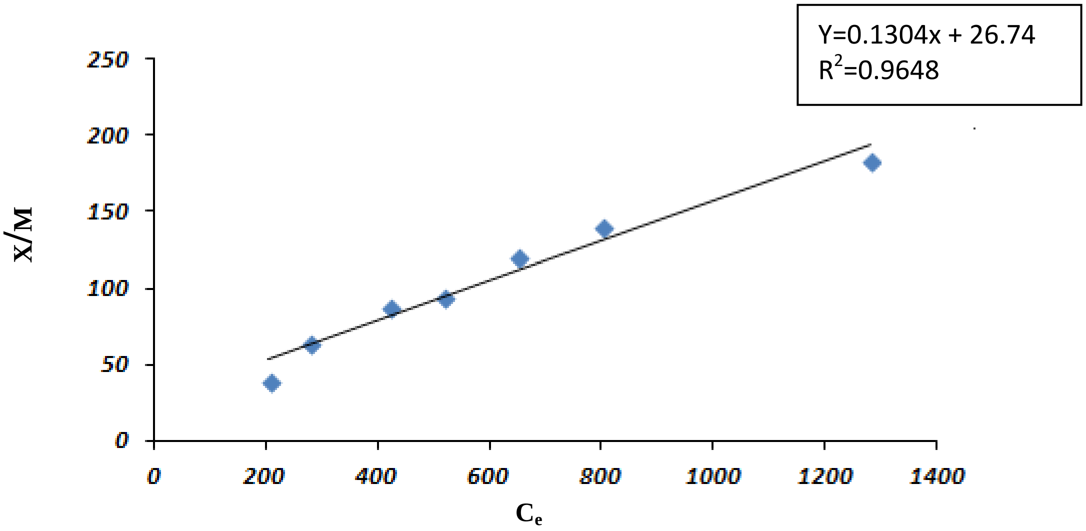

Figure 5.15: Freundlich isotherm for potato gel for TDS removal

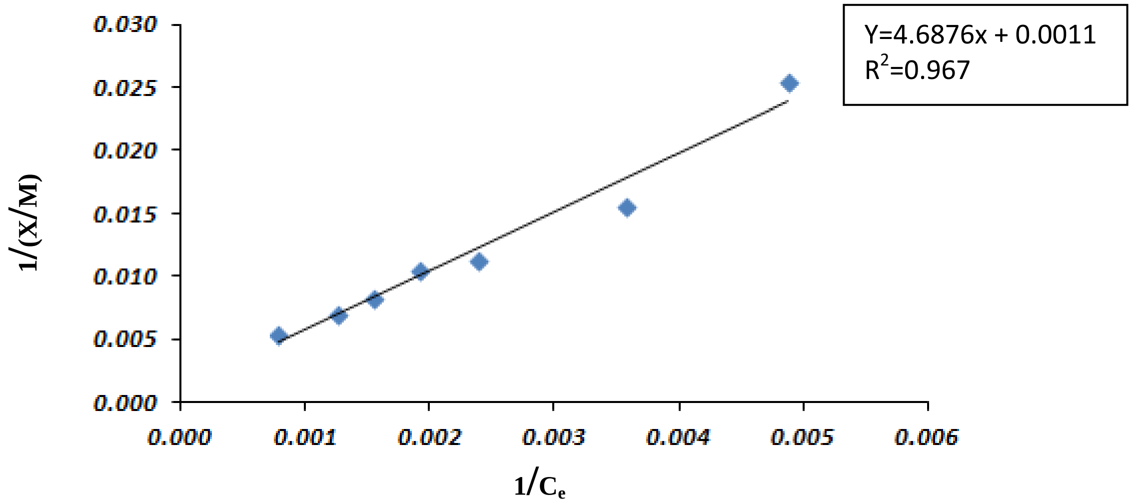

Figure 5.16: Langmuir isotherm for potato gel for TDS removal

It has been observed in the studies that TDS concentration has been reduced from 42% to 53.3% for the different concentration of adsorbate while the contact time was kept same. Freundlich (Figure 5.15) and Langmuir (Figure 5.16) isotherms have been plotted. Both the isotherm graphs follow the straight line but Langmuir isotherm is more promising because the regression coefficient is higher (Table 5.13). The adsorption of TDS has been taking place on the single layer over the surface of adsorbate. The Freundlich and Langmuir isotherm constants are derived for reduction taking place in TDS and shown in Table 5.13.

Table 5.13: Freundlich and Langmuir isotherms constants for TDS reduction

Parameter	**Freundlich**	**Langmuir**
Slope (m)	0.1304	4.6876
Intercept (c)	26.74	0.0011
n	7.6687	-
K	4.1×10^{11}	-
Q_{max}	-	909.091
K	-	0.00023
R^2	0.9648	0.967
Standard Equation	$\frac{x}{m} = X = KC_e^{1/n}$	$Q = \frac{Q_{\max} KC_e}{1+KC_e}$
Linear form of standard Equation	$\log\left(\frac{x}{m}\right) = \log X = \log K + \frac{1}{n}\log C_e$	$\frac{1}{Q} = \frac{1}{KQ_{\max}C_e} + \frac{1}{Q_{\max}}$

Trend line equation	Y=0.1304x+26.74	Y=4.6876x+0.0011
Equation derived from experiment result	$X= 4.1x10^{11}C_e^{(1/7.6687)}$	$\frac{1}{Q} = \frac{1}{0.2091C_e} + \frac{1}{909.091}$

5.2 Kinetic study

Kinetic study is the study of reaction rates (order of reaction), the changes in the concentrations of reactants and products with time. Here kinetic study have been undertaken to know the order of reaction taking place on surface of potato gel (Averill and Patricia, 2006). To know the order of reaction, 3 plots viz., (1) Time vs. Concentration difference (T vs. ΔC)), (2) Time vs. log of concentration difference (T vs. log ΔC) and (3) Time vs Inverse of concentration difference (T vs. 1/ ΔC) are plotted. The order of reaction would be determined as,

(a) If T vs. ΔC is straight line then, it is of Zero order reaction.
(b) If T vs. log ΔC is straight line, then it is of First order reaction.
(c) If T vs. 1/ ΔC is straight line, then it is of Second order reaction.

The optimized conditions (adsorbent weight and adsorbate concentration) are used to experiment for time and concentration relation. This experimental data has been used to determine the kinetics of reaction in batch study is given in Table 5.14, Table 5.15 and Table 5.16 for Nitrate, Fluoride and TDS respectively.

Table 5.14: Nitrate reduction with time with optimized parameters

Sample code	**Contact Time (*min*)**	**Adsorbent weight (*g*)**	**Nitrate in influent (*mg/l*)**	**Nitrate in effluent (*mg/l*)**
PG56	10	0.5	260.00	193.33
PG57	20	0.5	260.00	182.67
PG58	40	0.5	260.00	162.29
PG59	60	0.5	260.00	153.66
PG60	80	0.5	260.00	145.23

PG- samples of potato gel,

Table 5.15: Fluoride reduction with time with optimized parameters

Sample code	**Contact Time (*min*)**	**Adsorbate weight (*g*)**	**Fluoride in influent (*mg/l*)**	**Fluoride in effluent (*mg/l*)**
PG61	10	0.5	5.30	3.93
PG62	20	0.5	5.30	3.71
PG63	40	0.5	5.30	3.48
PG64	60	0.5	5.30	3.35
PG65	80	0.5	5.30	2.98

PG- samples of potato gel,

Table 5.16: TDS reduction with time with optimized parameters

Sample code	**Contact Time (*min*)**	**Adsorbate weight (*g*)**	**TDS in influent (*mg/l*)**	**TDS in effluent (*mg/l*)**
PG66	10	0.5	600.00	459.10
PG67	20	0.5	600.00	471.81
PG68	40	0.5	600.00	498.20
PG69	60	0.5	600.00	531.80
PG70	80	0.5	600.00	574.54

PG- samples of potato gel,

5.2.1 Nitrate

The data recorded from batch study for Nitrate (Table 5.14) is used to calculate the order for potato gel for Nitrate reduction and 3 plots are plotted for (1) T vs. ΔC, (2) T vs. log ΔC and (3) T vs. 1/ ΔC plotted respectively.

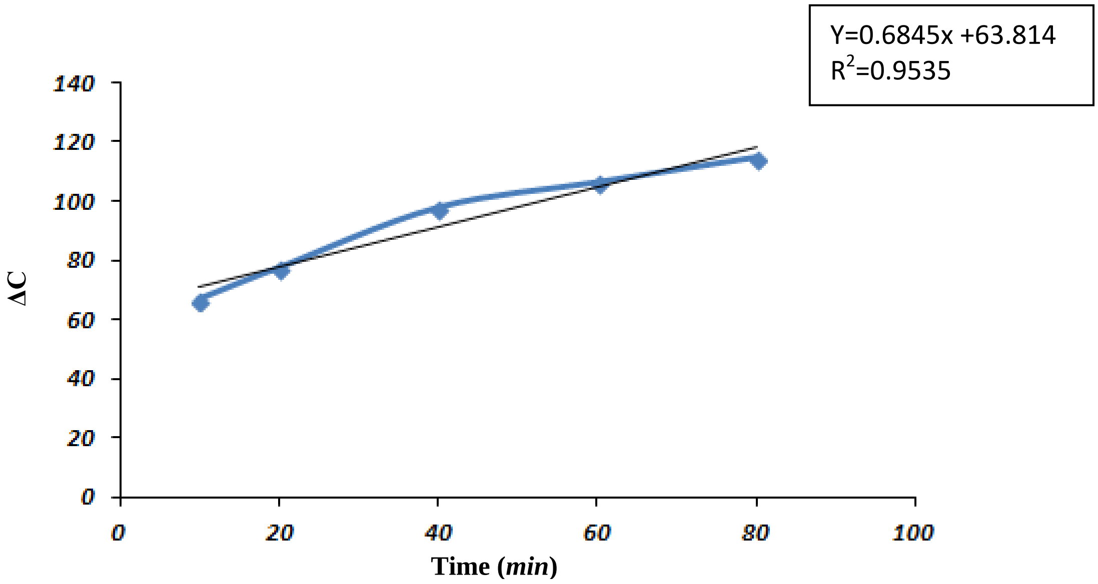

Figure 5.17: Plot between Time and ΔC for Nitrate

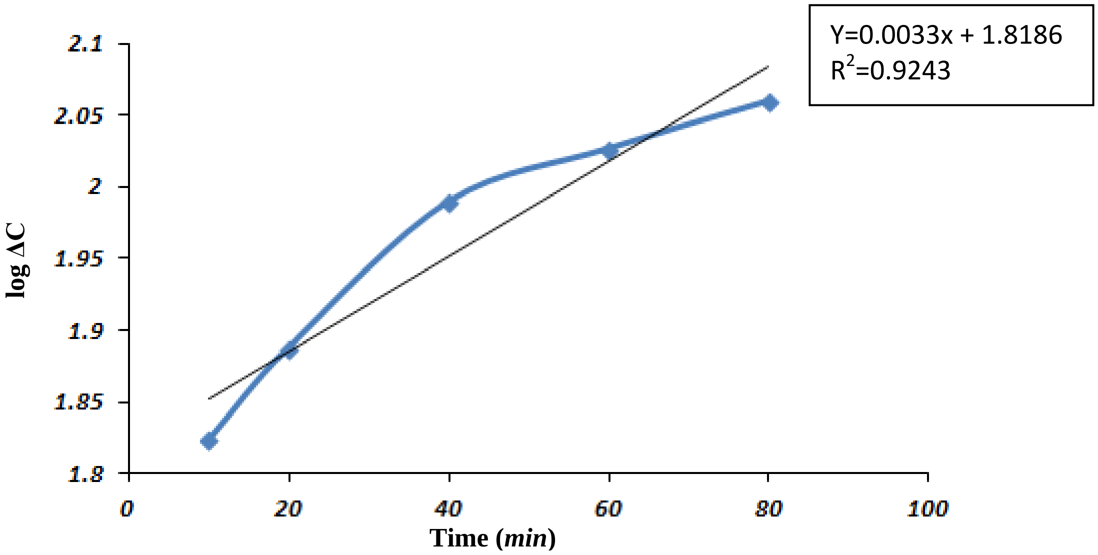

Figure 5.18: Plot between Time and log ΔC for Nitrate

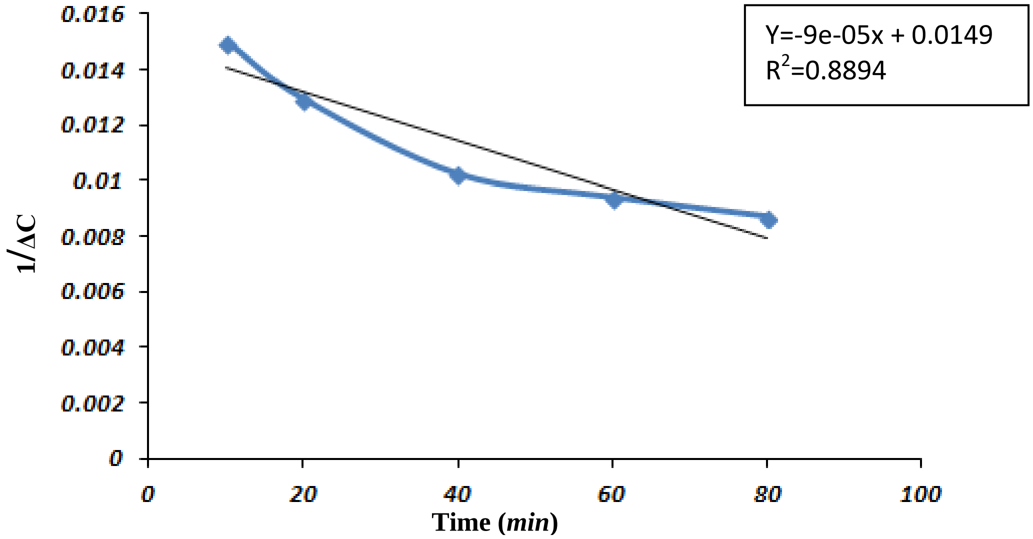

Figure 5.19: Plot between Time and 1/ ΔC for Nitrate

By analyzing the Figure 5.17, Figure 5.18 and Figure 5.19, we find that the straight line pattern is followed in plot between time and concentration difference. Thus, indicating the zero order adsorption on the surface of potato gel. Table 5.17 shows the trend line equation and regression coefficients for above figures and helps in determining the order of reaction.

5.2.2 Fluoride

The data recorded from batch study for Fluoride (Table 5.15) is used to calculate the order for potato gel for Fluoride reduction and 3 plots are plotted for (1) T vs. ΔC, (2) T vs. log ΔC and (3) T vs. 1/ ΔC respectively.

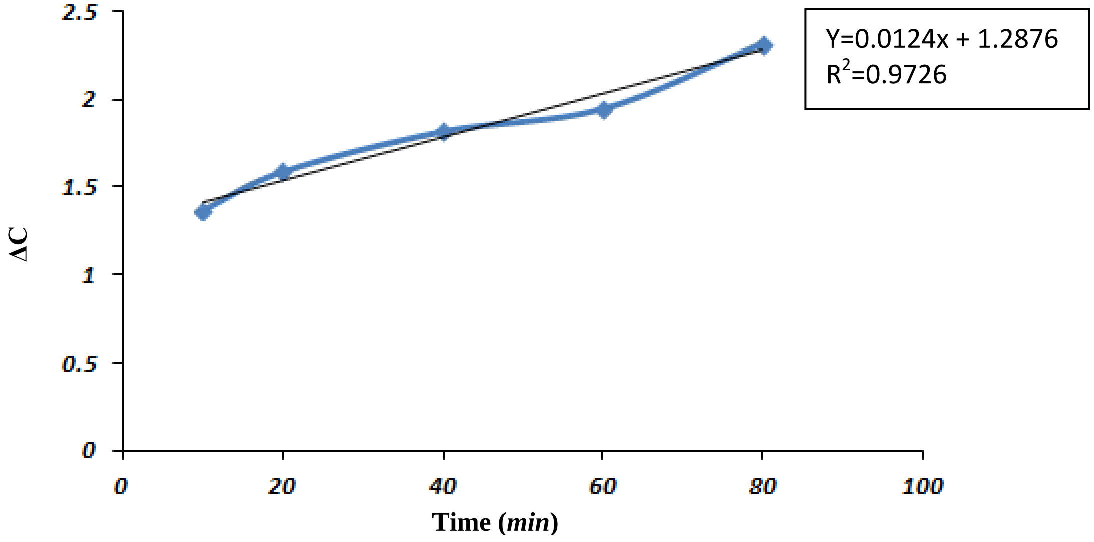

Figure 5.20 : Plot between Time and ΔC for Fluoride

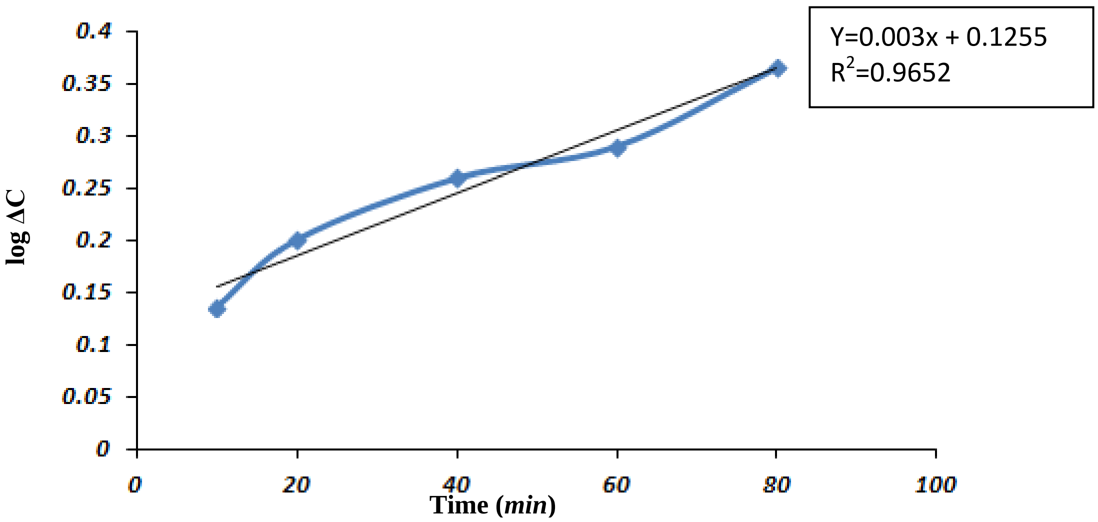

Figure 5.21: Plot between Time and log ΔC for Fluoride

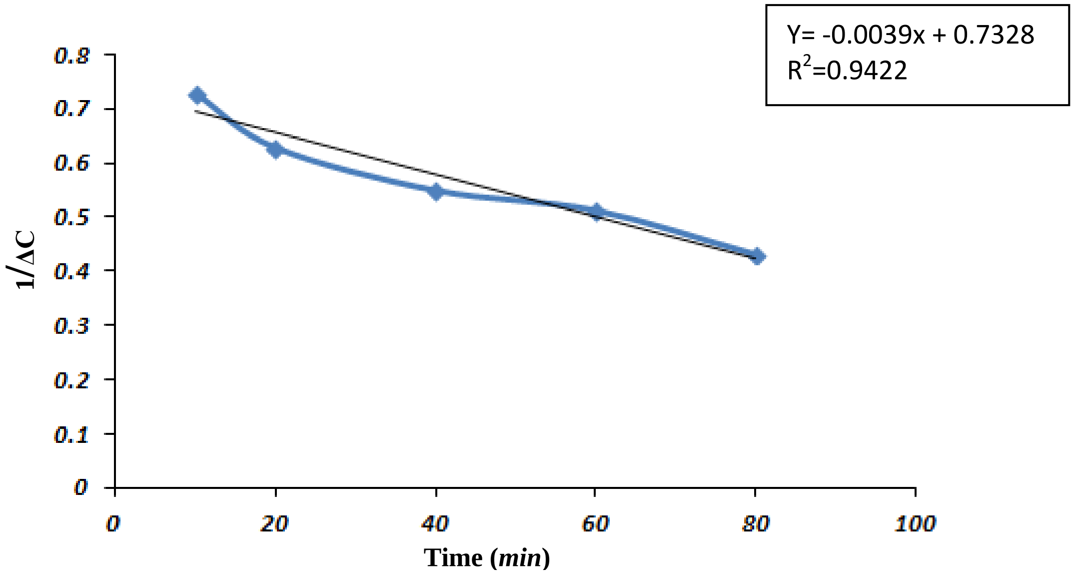

Figure 5.22: Plot between Time and 1/ ΔC for Fluoride

By analyzing the Figure 5.20, Figure 5.21 and Figure 5.22, we find that the straight line pattern is followed in plot between time and concentration difference. Thus, indicating the zero order adsorption on the surface of potato gel. Table 5.17 shows the trend line equation and regression coefficients for above figures and help in determining the order of reaction.

5.2.3 Total Dissolved Solids

The data recorded from batch study for TDS (Table 5.16) is used to calculate the order for potato gel for of TDS reduction and 3 plots are plotted for (1) T vs. ΔC, (2) T vs. log ΔC and (3) T vs. 1/ ΔC respectively.

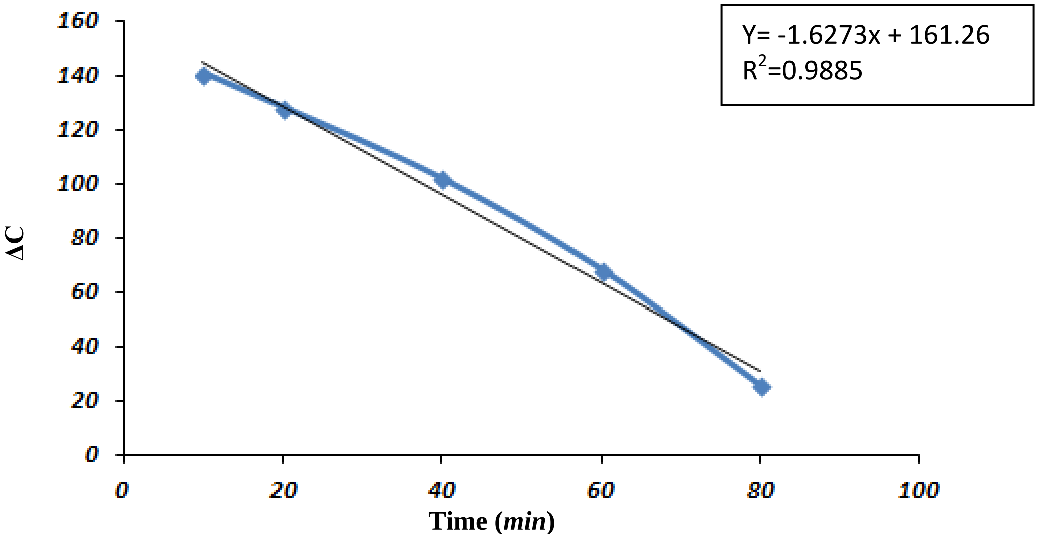

Figure 5.23: Plot between Time and ΔC for TDS

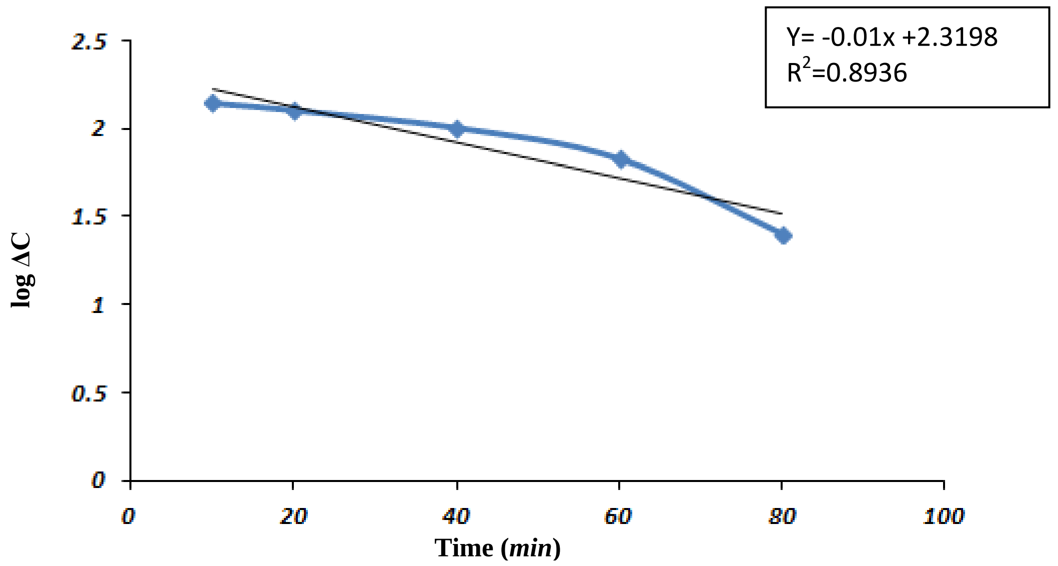

Figure 5.24: Plot between Time and log ΔC for TDS

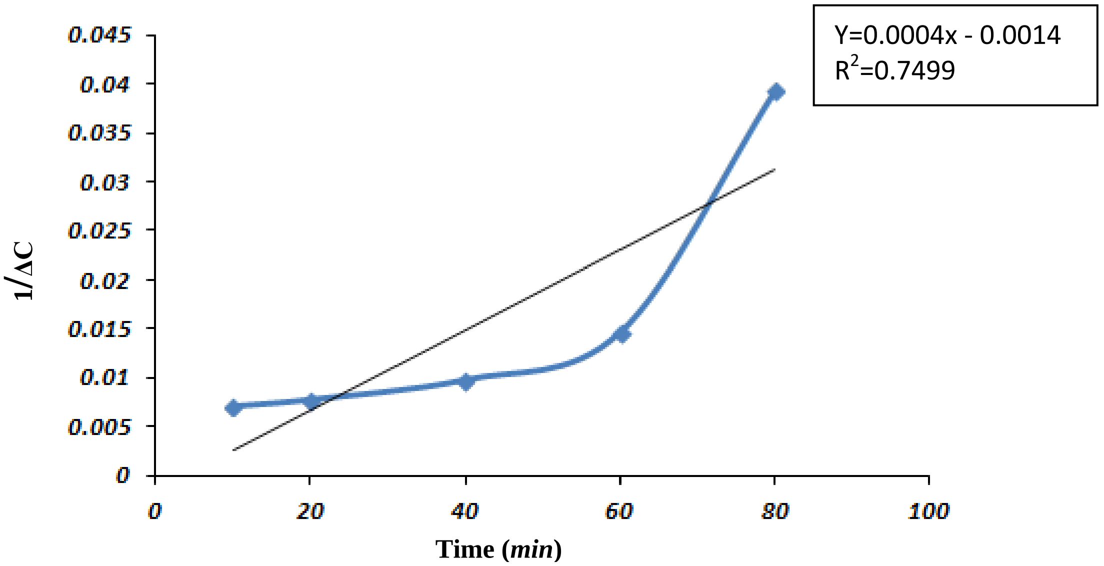

Figure 5.25: Plot between Time and 1/ ΔC for TDS

By analyzing the Figure 5.23, Figure 5.24 and Figure 5.25, we find that the straight line is followed in plot between time and concentration difference. Thus, it is indicating the zero order adsorption on surface of potato gel. Table 5.17 shows the trend line equation and regression coefficients for above figures and help in determining the order of reaction.

Table 5.17: Trend line eqations and R^2 for order determination

Plot type	Trend line equation	Regression coefficient
Nitrate		
Time and ΔC	Y = 0.6845x+63.814	$R^2 = 0.9535$
Time and log ΔC	Y = 0.0033x+1.8186	$R^2 = 0.9243$
Time and 1/ ΔC	Y = -9E-05x+0.0149	$R^2 = 0.8894$
Fluoride		
Time and ΔC	Y = 0.0124x+1.2876	$R^2 = 0.9726$
Time and log ΔC	Y = 0.003x+0.1255	$R^2 = 0.9652$
Time and 1/ ΔC	Y = -0.0039x+0.7328	$R^2 = 0.9422$
TDS		
Time and ΔC	Y = -1.6273x+161.26	$R^2 = 0.9885$
Time and log ΔC	Y = -0.01x+2.3198	$R^2 = 0.8936$
Time and 1/ ΔC	Y = 0.0004x-0.0014	$R^2 = 0.7499$

The examination of various plots and regression coefficient of respective plot suggest that the zero order reaction is taking place on surface of adsorbent for all three different adsorbate.

5.3 Continuous study

The details of column used in the study has been provided in Table 5.18. The bottom and top was packed with cotton for 0.5 *cm* height. In between the cotton layer, potato starch gel balls are filled. 30 *g* material is consumed in filling this space. Peristaltic pump is attached to the column for controlling the inflow water velocity and the experimentation was carried out for different flowrates.

Table 5.18: Details of column used in study

Parameter	**Value**
Height of column	37.5 *cm*
Height of packed material in column	34 *cm*
Dia. of column	3 *cm*

5.3.1 Flowrate optimization

The following steps are followed in optimization of flowrate for Nitrate, Fluoride and TDS.

- The water was pumped into column at different flowrate, starting with 6 *ml/min* to 33 *ml/min*. Outflow water samples were collected and analyzed at different time intervals between 40 *min* to 120 *min*.

- The flowrate of 5 *ml/min* in inlet is not sufficient to pump the water into column so flowrate below 6 *ml/min* has not been experimented. While flowrate above 33 *ml/min* displayed a huge fluctuation in reduction capacity.

Table 5.19: Optimization for flowrate

Sample code	**Contact time (*min*)**	**Volume (*l*)**	**Flow rate (*ml/m*)**	**Inflow concentration (*mg/l*)**	**Outflow concentration (*mg/l*)**	**Reduction (%)**
Flowrate optimization for Nitrate						
PG71	40	4	33	260	11.38	95.62
PG72	50	4	33	260	84.33	67.57
PG73	70	4	33	260	108.52	58.26
PG74	90	4	33	260	76.88	70.43
PG75	120	4	33	260	106.60	59.00
PG76	40	3.4	28	260	9.59	96.31
PG77	50	3.4	28	260	25.94	90.02
PG78	70	3.4	28	260	36.52	85.95
PG79	90	3.4	28	260	40.37	84.47
PG80	120	3.4	28	260	98.95	61.94
PG81	40	0.8	6	260	7.58	97.08
PG82	50	0.8	6	260	18.05	93.06
PG83	70	0.8	6	260	20.27	92.20
PG84	90	0.8	6	260	20.34	92.18
PG85	120	0.8	6	260	22.61	91.30
Flowrate optimization for Fluoride						
PG86	40	4	33	5.30	1.85	65.09
PG87	50	4	33	5.30	1.802	66.00
PG88	70	4	33	5.30	1.91	63.96
PG89	90	4	33	5.30	1.82	65.66
PG90	120	4	33	5.30	1.90	64.15
PG91	40	4	28	5.30	0.36	93.21
PG92	50	4	28	5.30	0.58	89.06
PG93	70	4	28	5.30	0.94	82.26
PG94	90	4	28	5.30	1.36	74.34
PG95	120	4	28	5.30	1.37	74.15
PG96	40	1	6	5.30	0.28	94.72
PG97	50	1	6	5.30	0.27	94.91
PG98	70	1	6	5.30	0.35	93.40
PG99	90	1	6	5.30	0.42	92.08
PG100	120	1	6	5.30	0.59	88.87
Flowrate optimization for TDS						
PG101	40	4	33	600	266.88	55.52
PG102	50	4	33	600	265.68	55.72

PG103	70	4	33	600	271.68	54.38
PG104	90	4	33	600	267.66	55.39
PG105	120	4	33	600	267.48	55.42
PG106	40	4	28	600	223.62	62.73
PG107	50	4	28	600	223.8	62.70
PG108	70	4	28	600	223.8	62.70
PG109	90	4	28	600	232.5	61.25
PG110	120	4	28	600	237.36	60.44
PG111	40	1	6	600	210.00	65.00
PG112	50	1	6	600	211.74	64.71
PG113	70	1	6	600	216.00	64.00
PG114	90	1	6	600	220.14	63.31
PG115	120	1	6	600	221.16	63.14

PG- samples of potato gel

The details are given in Table 5.19 for flowrate optimization for Nitrate, Fluoride and TDS. Following are the observations of the experiment:

- The flowrate experiment showed that reduction in Nitrate varies between 58.26% to 97%. The reduction in Fluoride varies between 64% to 95% and reduction in TDS varies between 54.3% to 65% at different flow rates.
- Higher flowrate has less reduction of Nitrate & displayed the fluctuation with time in reduction and lower flowrate showed the increase in Nitrate reduction and less fluctuation (Figure 5.26). Similar pattern has been displayed by Fluoride (Figure 5.27) and TDS (Figure 5.28).

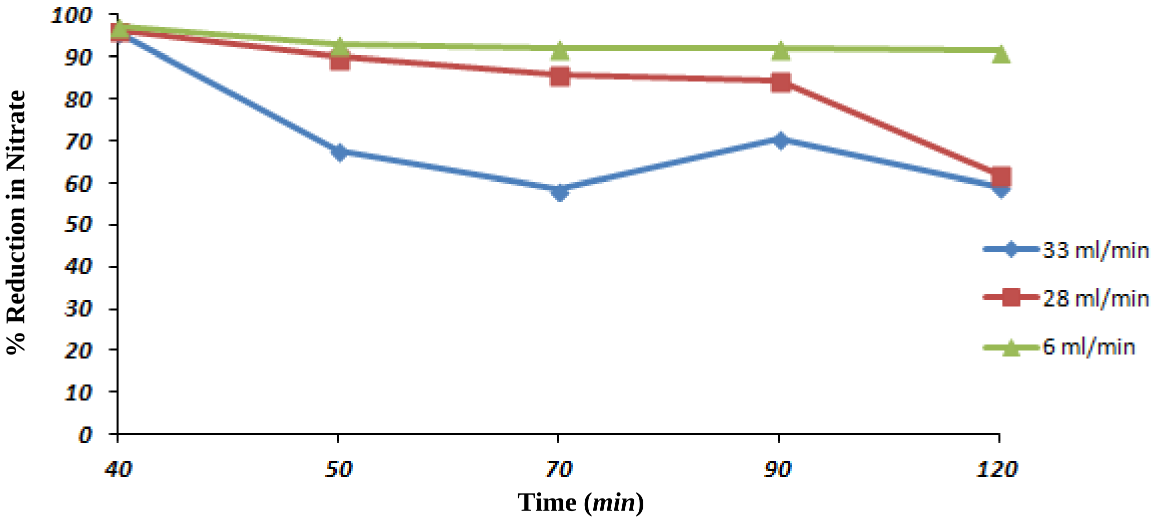

Figure 5.26: Nitrate reduction at different flowrate

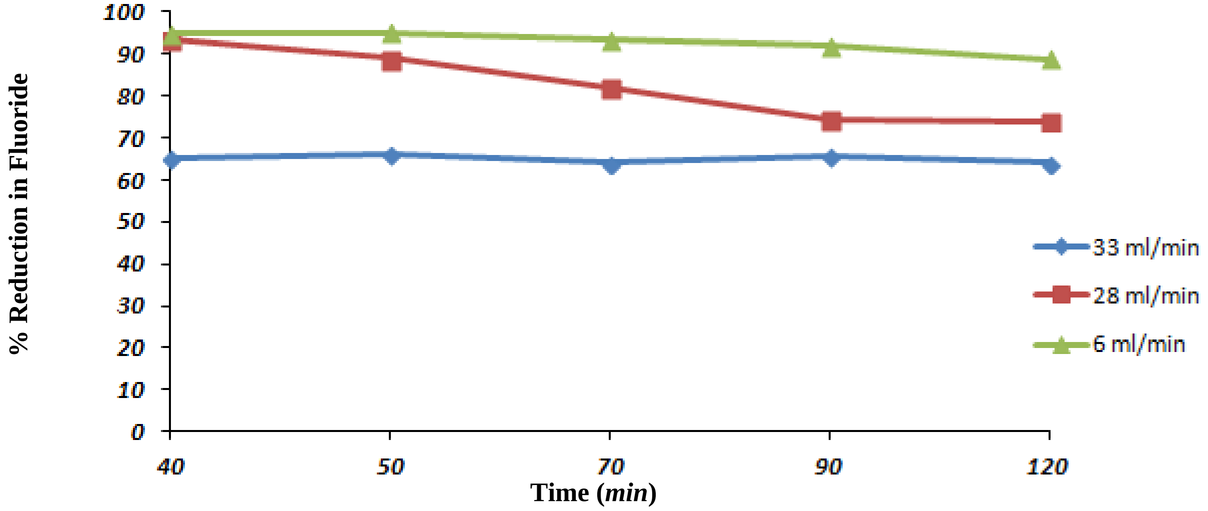

Figure 5.27: Fluoride reduction at different flowrate

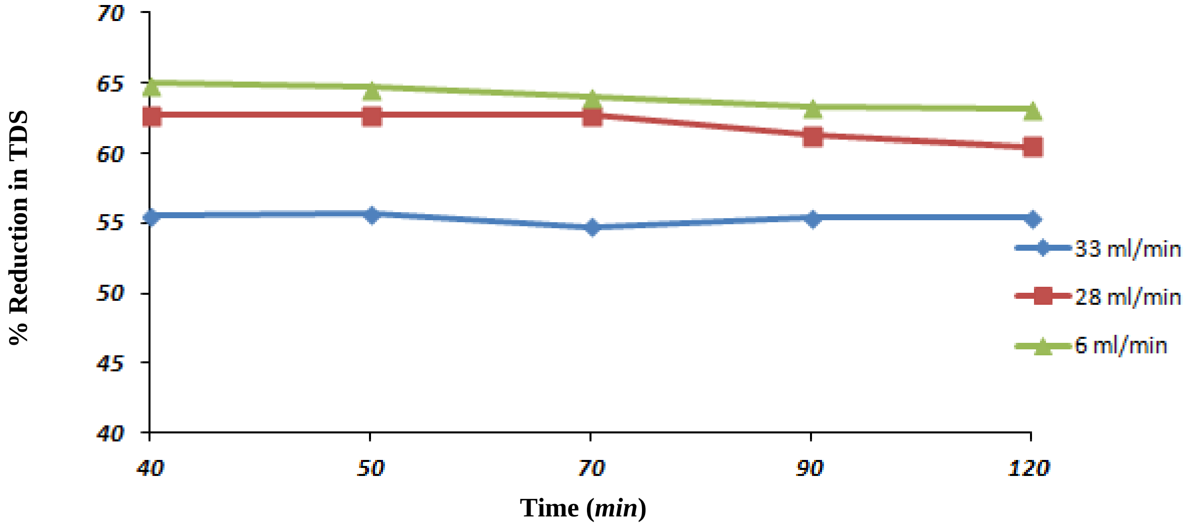

Figure 5.28: TDS reduction at different flowrate

As maximum reduction is observed at flowrate of 6 *ml/min* and reduction remains least fluctuating (steady) with time for all three parameter under study and thus 6 *ml/min* was selected as optimized flowrate for further study.

5.3.2 Column study

Continuous column study has been carried out with optimized parameters. Column is packed with adsorbent and influent has passed through the column at flow rate of 6 *ml/min* for 6 days. Following steps are carried out for the successful running of the experiment.

- Column is packed with cotton in the bottom and top of column and rest of the column space was occupied by the adsorbent (potato gel balls).
- The samples have been collected at an interval of 3 *h* upto 12 *h* and no changes are observed in Nitrate, Fluoride and TDS value in effluent; so the sampling interval is increased to 12 *h* and samples are taken upto 144 *h*.
- It is clear from the study that after 132 *h*, reduction in values of chosen parameters become minimum by adsorbent and it get exhausted. 15 samples are analyzed during 144 *h* run for each parameter. Separate column run has been performed for evaluating the competence of adsorbent for Nitrate, Fluoride and TDS. The details are provided in Table 5.20, Table 5.21 and Table 5.22 respectively for Nitrate, Fluoride and TDS. The picture of setup used has been provided in Annexure 1D.

Table 5.20: Continuous column result for Nitrate reduction

Sample code	**Sampling time (*hour*)**	**Influent conc. of Nitrate (C_o) (*mg/l*)**	**Effluent conc. of Nitrate (C_e) (*mg/l*)**	**Reduction (*%*)**	**Vol. consumed (V) (*l*)**	**C_e/C_o**
PG116	3	260	21	91.92	1.08	0.08
PG117	6	260	21	91.92	2.16	0.08
PG118	9	260	21	91.92	3.24	0.08
PG119	12	260	22	91.54	4.32	0.08
PG120	24	260	33	87.31	8.64	0.13
PG121	36	260	52	80.00	12.96	0.20
PG122	48	260	70	73.08	17.28	0.27
PG123	60	260	95	63.46	21.60	0.37
PG124	72	260	122	53.08	25.92	0.47
PG125	84	260	142	45.38	30.24	0.55
PG126	96	260	168	35.38	34.56	0.65
PG127	108	260	185	28.85	38.88	0.71
PG128	120	260	200	23.08	43.20	0.77
PG129	132	260	204	21.54	47.52	0.78
PG130	144	260	205	21.15	51.84	0.79

PG- samples of potato gel

Table 5.21: Continuous column result for Fluoride reduction

Sample code	**Sampling time (*hour*)**	**Influent conc. of Fluoride (C_o) (*mg/l*)**	**Effluent conc. of Fluoride (C_e) (*mg/l*)**	**Reduction (*%*)**	**Vol. consumed (V) (*l*)**	**C_e/C_o**
PG131	3	5.3	0.56	89.43	1.08	0.11
PG132	6	5.3	0.58	89.06	2.16	0.11
PG133	9	5.3	0.58	89.06	3.24	0.11
PG134	12	5.3	0.66	87.55	4.32	0.12
PG135	24	5.3	0.76	85.66	8.64	0.14
PG136	36	5.3	0.89	83.21	12.96	0.17
PG137	48	5.3	1.25	76.42	17.28	0.24
PG138	60	5.3	1.62	69.43	21.60	0.31
PG139	72	5.3	2.24	57.74	25.92	0.42
PG140	84	5.3	2.89	45.47	30.24	0.55
PG141	96	5.3	3.55	33.02	34.56	0.67
PG142	108	5.3	4.3	18.87	38.88	0.81
PG143	120	5.3	4.81	9.25	43.20	0.91
PG144	132	5.3	4.98	6.04	47.52	0.94
PG145	144	5.3	4.99	5.85	51.84	0.94

PG- samples of potato gel

Table 5.22: Continuous column result for TDS reduction

Sample code	**Sampling time (*hour*)**	**Influent conc. of TDS (C_o) (*mg/l*)**	**Effluent conc. of TDS (C_e) (*mg/l*)**	**Reduction (*%*)**	**Vol. consumed (V) (*l*)**	**C_e/C_o**
PG146	3	600	84	86.00	1.08	0.14
PG147	6	600	89	85.17	2.16	0.15
PG148	9	600	90	85.00	3.24	0.15
PG149	12	600	120	80.00	4.32	0.20
PG150	24	600	170	71.67	8.64	0.28
PG151	36	600	218	63.67	12.96	0.36
PG152	48	600	246	59.00	17.28	0.41
PG153	60	600	290	51.67	21.60	0.48
PG154	72	600	324	46.00	25.92	0.54
PG155	84	600	356	40.67	30.24	0.59
PG156	96	600	395	34.17	34.56	0.66
PG157	108	600	440	26.67	38.88	0.73
PG158	120	600	479	20.17	43.20	0.80
PG159	132	600	483	19.50	47.52	0.81
PG160	144	600	488	18.67	51.84	0.81

PG- samples of potato gel

5.3.2.1 Nitrate reduction

The analysis of samples from column run for Nitrate reduction using potato gel as adsorbent is shown in Table 5.20. Nitrate reduction with time has been plotted and the following observations are depicted in the Figure 5.29.

- It is clear that upto 12 *h*, the reduction in Nitrate remains at 91.92%. From 12th *h* to 120th *h* the Nitrate reduction by adsorbent reduces with time and became constant between 120nd and 144th *h*.
- Between the 12th *h* to 120th *h*, the Nitrate reduction capacity decline from 91% to 23.08%. This portion of graph shows linear relation between Nitrate reduction and time.
- The both ends of the reduction graph have constant extensions attached and shows that initially upto certain time the Nitrate reduction is maximum and in the end it remains at minimum. The overall graph depicted elongated S type shape.

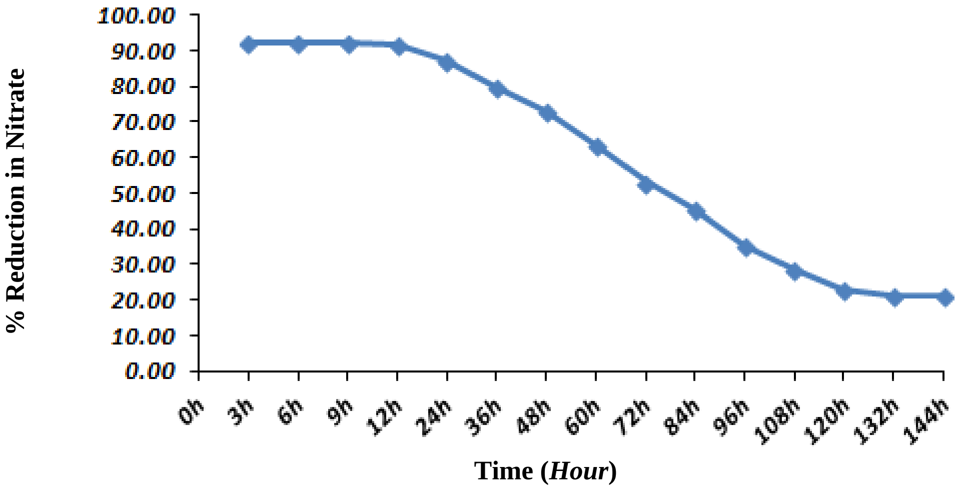

Figure 5.29: Plot for Nitrate reduction for column test

5.3.2.1.1 Breakthrough curve & Thomas model for Nitrate reduction

Breakthrough curve (Figure 5.30) is plotted for the removal of Nitrate by using potato gel as an adsorbent. Initially, reduction of Nitrate in the effluent concentration is more and after some time it started decreasing with a very rapid rate and eventually Nitrate reuction decreases. This would be the ideal breakthrough curve for the adsorption taking place at surface of adsorbent. This adsorption plot also helps in the determination of throughput and exhaustion point (breakthough points).

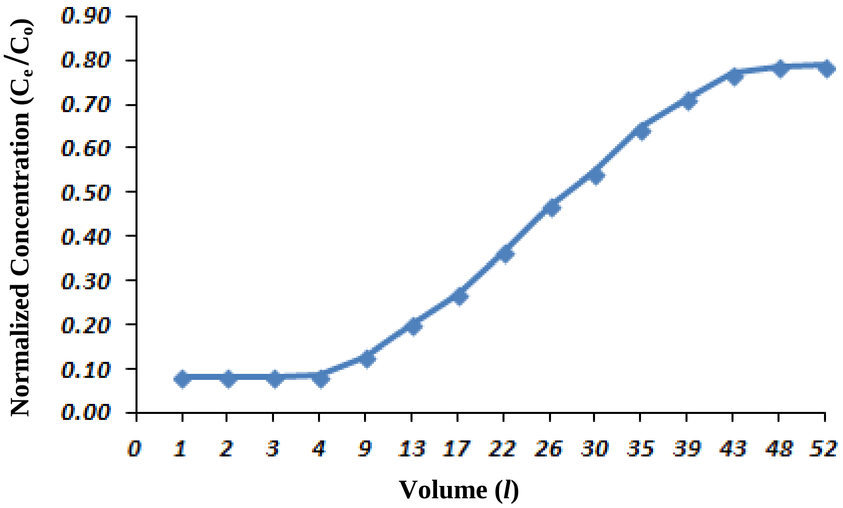

Figure 5.30: Breakthrough curve for Nitrate reduction

After analysing the plot, we found that at 4.32 *l*, the pattern of the graph starts changing so, 4.32 *l* is the throughput volume. At throughput volume, the C_e/C_o ratio found to be 0.08. The breakthrough (throughput) concentration found at this point is 22 *mg/l*. Here in the case of Nitrate, the effulent concentration shows 91.54% reduction and at same time the breakthough takes place.

The volume of exhaustion found to be 43.20 *l* by breakthrough curve. At exhaustion volume, the C_e/C_o ratio found to be 0.77. The exhausting concentration found at this is 200 *mg/l*. Exhaustion of the adsorbant occours when the effluent concentration remains 23.08% of the influent concentration. From Table 5.20 and Figure 5.30, we can say that the breakthrough time for the system is (a) throughput time: 12 hour and the (b) exhaustion time: 120 hour.

The adsorption step should be discontinued when C_e/C_o ratio found to be 0.08. If the adsorption step were to be continued after this time, the outlet solute concentration will rise rapidly, eventually approaching the inlet concentration as entire bed become saturated. If this has occurred no more adsorption can take place by the material.

Thomas adsorption model has been applied for Nitrate reduction for potato gel. Results of adsorption column has follwed Thomas model (Figure 5.31). It is developed using the data mentioned in Table 5.20. The constant derived from Thomas model is indicated in Table 5.23.

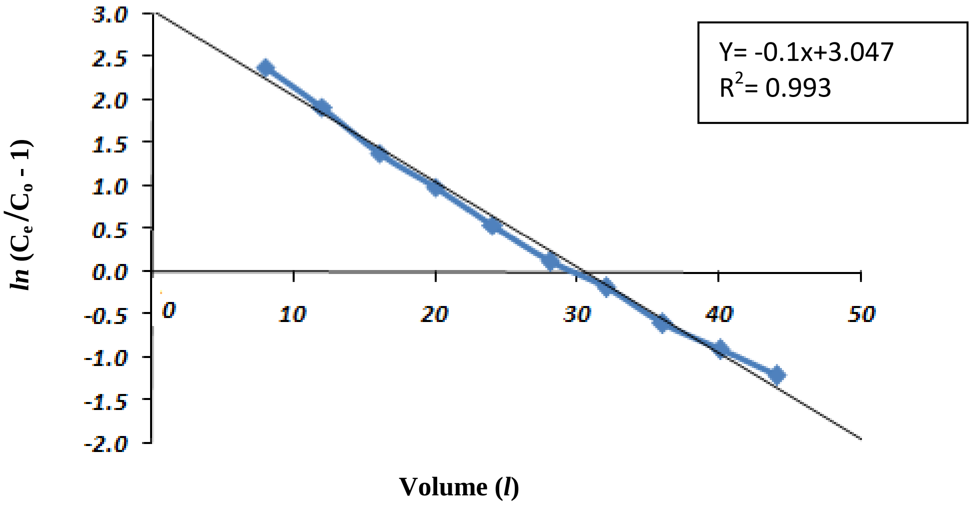

Figure 5.31: Thomas model plot for Nitrate reduction

Table 5.23: Thomas model parameters for Nitrate reduction

Parameter	**Thomas model**
Standard Equation	$\frac{C_e}{C_o} = \frac{1}{1 + \exp[\frac{K_t}{Q}(q_o M - C_o V)]}$
Linear form of standard Equation	$\ln\left(\frac{C_o}{C_e} - 1\right) = \frac{K_t q_o M}{Q} - \frac{K_t C_o}{Q} V$
Trend line equation	Y = -0.1 x+ 3.047
Slope (m)	-0.1
Intercept (c)	3.047
q_o	-0.0003 *g/g*
K_t	4.218 *l/h/g*
R^2	0.993
Equation derived from experiment result	$\frac{C_e}{260} = \frac{1}{1 + \exp[\frac{4.218}{0.36}(-0.0003 * 30 - 260 * V)]}$

5.3.2.2 Fluoride reduction

The analysis of samples from column run for Fluoride reduction using potato gel as adsorbent is shown in Table 5.21. Fluoride reduction with time has been plotted and following observations are depicted from the Figure 5.32.

- It is clear that upto 9 *h*, the reduction in Fluoride was constant and remains at 89.06%. From 9th *h* to 120th *h* the Fluoride reduction by adsorbent reduces with time gradually and became constant between 132nd *h* and 144th *h*.
- Between the 9th *h* to 120th *h*, the Fluoride reduction capacity declines from 87.5% to 9.25%. This portion of graph shows linear relation between Fluoride reduction and time.
- The both ends of the reduction graph have constant extensions attached and shows that initially upto certain time the Fluoride reduction is maximum and in the end it remains at minimum. The overall graph depicted elongated S type shape.

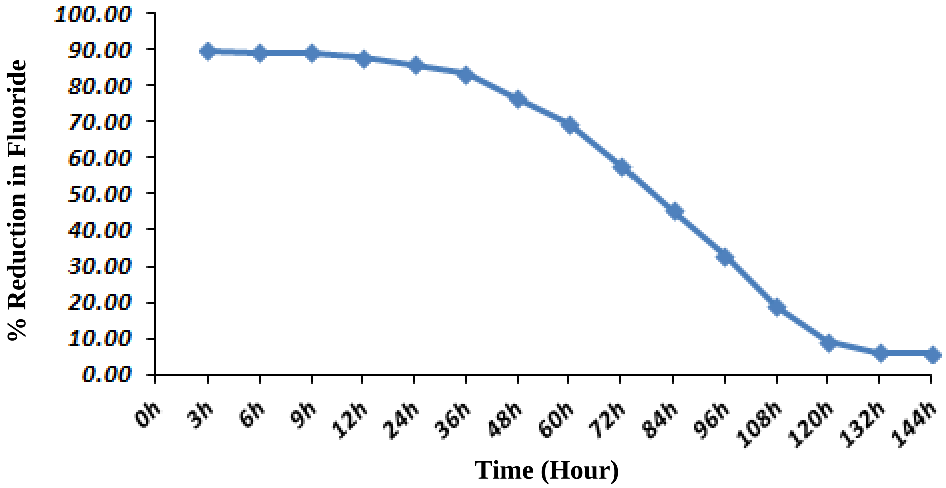

Figure 5.32: Plot for Fluoride reduction for column test

5.3.2.2.1 Breakthrough curve & Thomas model for Fluoride reduction

Breakthrough curve (Figure 5.33) is plotted for the removal of Fluoride by using potato gel as an adsorbent. Initially, reduction is Fluoride in the effluent is more and after some time it started decreasing with a rapid rate and eventually Fluoride reduction decreases. This would be the ideal breakthrough curve for adsorption taking place at surface of adsorbent. This breakthrough curve also helps in determination of throughput and exhaustion points (breakthrough points).

After analysing the plot, we found that at 12.96 *l* the pattern of the graph starts changing so, 12.96 *l* is the throughput volume. At throughput volume, the C_e/C_o ratio found to be 0.17. The breakthrough (throughput) concentration found at this point is 0.89 *mg/l*. Here in the case of Fluoride, the effulent concentration shows 83.21% reduction and at same time the breakthough takes place.

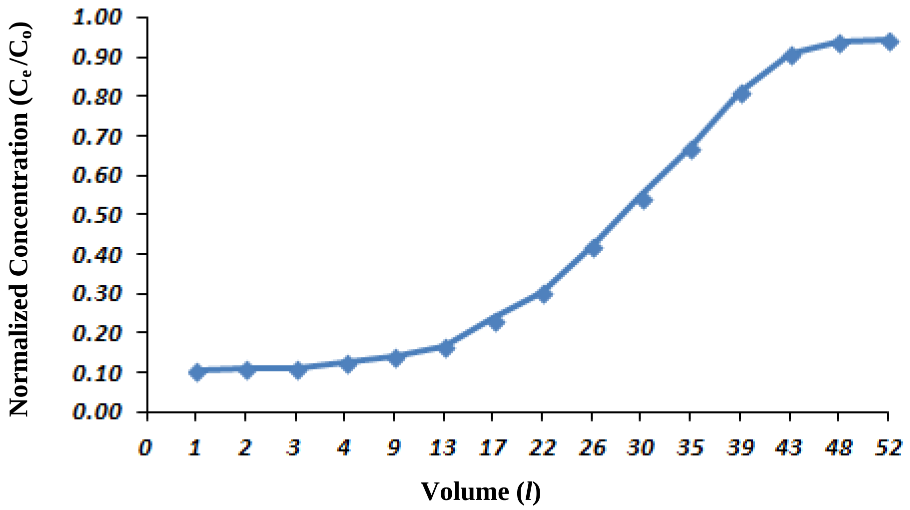

Figure 5.33: Breakthrough curve for Fluoride reduction

The volume of exhaustion found to be 43.20 *l* by breakthrough curve. The exhaustion volume, the C_e/C_o ratio found to be 0.91. The exhauting concentration found at this point is 4.81 *mg/l*. Exhaustion of the adsorbant occours when the effluent concentration remains 9.25% of the influent concentration. From, Table 5.21 and Figure 5.33 we can say that the breakthrough time for the system is (a) throughput time: 36 *h* and the (b) exhaustion time: 120 *h*.

Thomas adsorption model has been applied for Fluoride reduction for potato gel. Results of adsorption column has followed Thomas model (Figure 5.34). It is developed using the data mentioned in Table 5.21. The constants derived from Thomas model is indicated in Table 5.24.

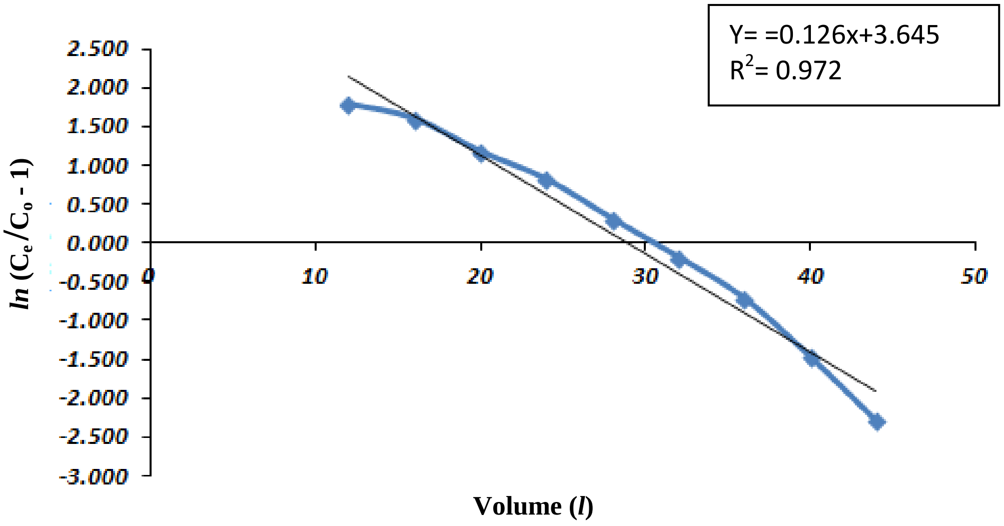

Figure 5.34: Thomas Model plot for Fluoride reduction

Table 5.24: Thomas model parameters for Fluoride reduction

Parameter	**Thomas model**
Standard Equation	$\frac{C_e}{C_o} = \frac{1}{1+\exp[\frac{K_t}{Q}(q_o M - C_o V)]}$
Linear form of standard Equation	$\ln\left(\frac{C_o}{C_e} - 1\right) = \frac{K_t q_o M}{Q} - \frac{K_t C_o}{Q} V$
Trend line equation	Y = -0.126 x+ 3.645
Slope (m)	-0.126
Intercept (c)	3.645
q_o	-0.000006 *g/g*
K_t	247.585 *l/h/g*
R^2	0.972
Equation derived from experiment result	$\frac{C_e}{5.3} = \frac{1}{1+\exp[\frac{247.585}{0.36}(-0.000006*30 - 5.3*V)]}$

5.3.2.3 Total Dissolved Solids reduction

The analysis of samples from column run for TDS reduction using potato gel as adsorbent is shown in Table 5.22. TDS reduction with time has been plotted and following observations are depicted from the Figure 5.35.

- It is clear that upto 9 *h*, the reduction in TDS was constant and remains at 85%. From 9th *h* to 132th *h*, the TDS reduction by adsorbent reduces with time and remains constant after 120th *h*.
- Between the 9th *h* to 120th *h*, the TDS reduction capacity decline from 85% to 20.17%. This portion of graph shows linear relation between TDS reduction and time.
- The both ends of the reduction graph have constant extensions attached and shows that initially upto a certain time the TDS reduction is maximum and in the end it remains minimum.

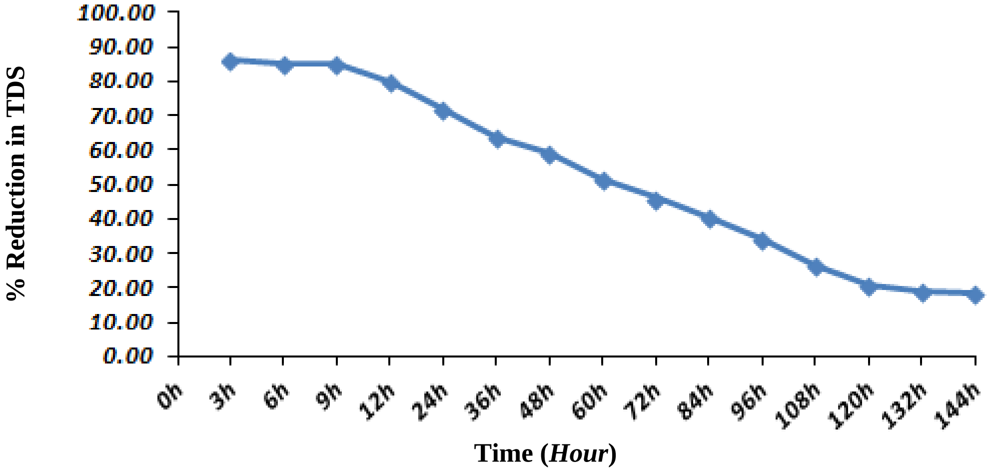

Figure 5.35: Plot for TDS reduction for column test

5.3.2.3.1 Breakthrough curve & Thomas model for TDS reduction

Breakthrough curve (Figure 5.36) is plotted for the removal of Fluoride by using potato gel as an adsorbent. Initially, reduction of TDS in the effluent is more and after some time it started decreasing with a rapid rate and eventually TDS reduction decreases. This would be the ideal breakthrough curve (Figure 5.36) for adsorption taking place at surface of adsorbent. This breakthrough curve helps in determination of throughput and exhaustion point (breakthough points).

After analysing the plot, we found that at 3.24 *l*, the pattern of graph starts changing so, 3.24 *l* is the throughput volume. At throughput volume, the C_e/C_o ratio found to be 0.15. The breakthrough (throughput) concentration found at this point was 90 *mg/l*. Here, in the case of TDS, the effulent concentration shows 85% reduction and at same time the breakthough take place.

The volume of exhaustion found to be 43.20 *l* by breakthrough curve. At the exhaustion volume, the ratio C_e/C_o found to be 0.80. The exhausting concentration found at this point is 479 *mg/l*. Exhaustion of the adsorbant occours when the effluent concentration remained 20.17% of the influent concentration. From Table 5.22 and Figure 5.36 we can say that the breakthrough time for the system is (a) throughput time: 9 *h* and (b) exhaustion time: 120 *h*.

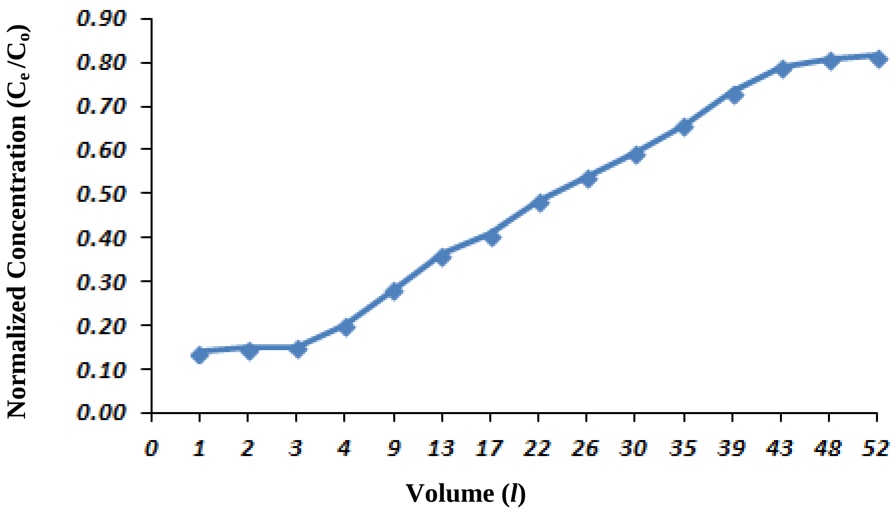

Figure 5.36: Breakthrough curve for TDS reduction

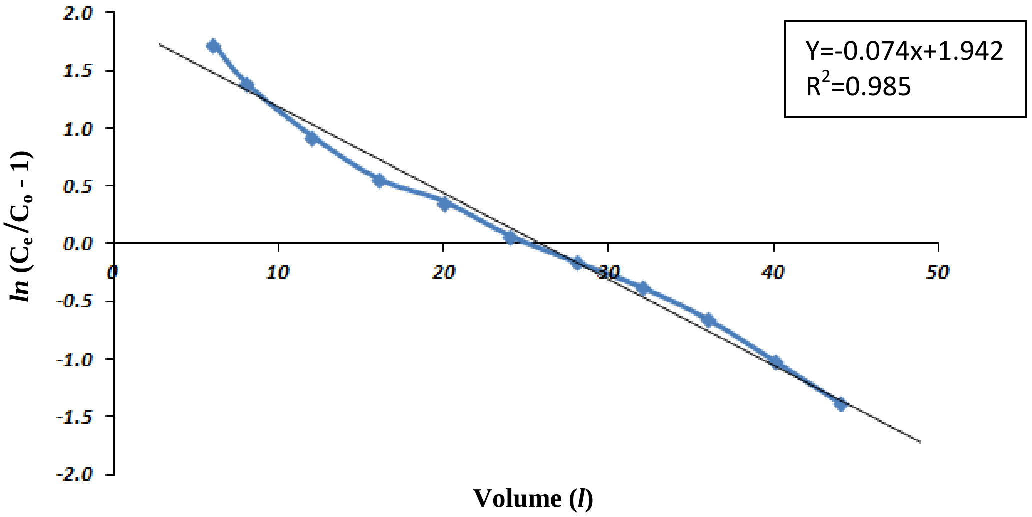

Figure 5.37: Thomas model plot for TDS reduction

Thomas adsorption model has been applied for TDS reduction from potato gel. Results of adsorption column has followed Thomas model (Figure 5.37). It is developed using the data mentioned in Table 5.22. The constants derived from Thomas model is indicated in Table 5.25.

Table 5.25: Thomas model parameters for TDS reduction

Parameter	**Thomas model**
Standard Equation	$\frac{C_e}{C_o} = \frac{1}{1+\exp[\frac{K_t}{Q}(q_o M - C_o V)]}$

Linear form of standard Equation	$\ln\left(\frac{C_o}{C_e}-1\right)=\frac{K_t q_o M}{Q}-\frac{K_t C_o}{Q}V$
Trend line equation	Y= -0.074x+1.942
Slope (m)	-0.074
Intercept (c)	1.942
q_o	-0.0008 *g/g*
K_t	1.1652 *l/h/g*
R^2	0.985
Equation derived from experiment result	$\frac{C_e}{600}=\frac{1}{1+\exp[\frac{1.1652}{0.36}\left(-0.0008*30-600*V\right)]}$

It is found from breakthrough curves that initially the Nitrate, Fluoride and TDS reduction were maximum and upto certain time it remained constant. Then their reduction started declining with time and after reaching exhaustion point, further reduction in Nitrate, Fluoride and TDS is not possible.

The relation between volume fed and the ratio of effluent to influent concentrations (V vs. C_e/C_o) for three parameters (Nitrate, Fluoride and TDS) attained the elongated S type shape. The description of such adsorption graphs are very difficult as change in column condition can change the length of adsorption and which is ultimately reflected by shape of breakthrough curve. The shape of breakthrough curve, show impact or presence of adsorbable, nonadsorbable, and biodegradable organic constituents in water (Metcalf & Eddy, 2002).

5.4 Characterization of Material

The Table 5.26 shows the constituents presents in potato. It is clear that potato has highest percentage of starch (Islam et al., 2002) among all available constituents in it. Thus, starch is providing functional groups over the surface of gel balls which must be responsible for adsorption of Nitrate, Fluoride and TDS present in water.

Further Fourier transformed infrared (FTIR) spectroscopy is carried out under following conditions:

1) Raw potato gel (without any adsorbent process)
2) After Nitrate rich water is used as adsorbate
3) After Fluoride rich water is used as adsorbate

4) After TDS rich water is used as adsorbate

The changes in transmittance from the raw potato gel to other condition of adsorbate passed from it are shown in Figures 5.38, 5.39, 5.40 and 5.41 respectively. These changes in transmittance and change in wave number indicates that adsorption is taken place on the surface (Smith, 1999) of potato gel. The functional groups present in potato gel are indicated in Table 5.27 derived from FTIR.

Table 5.26: Constituents of potato (Islam et al., 2002).

Constituent	**%weight**	**Constituent**	**%weight**
Moisture	50-81	Ash	0.9-1.4
Protein	1-2.4	Carotene (average)	0.004
Fat	1.8-6.4	Thiamine (average)	0.0001
Starch	8-29	Riboflavin (average)	0.0006
Non starch carbohydrate	0.5-7.5	Ascorbic acid (average)	0.012
Reducing sugar	0.5-2.5		

Table 5.27: Wavenumber of functional groups present in potato gel (Smith, 1999)

Functional group	**Wave number (cm^{-1})**
N-H	3250-3400
O-H	2500-3300
C≡N & C ≡C	2210-2260 & 2100-2260
C=O	1700
C=H	1300-1400
C=C	800-900
C-O	900-1000
C-H & C=C	675-900 & 400-450

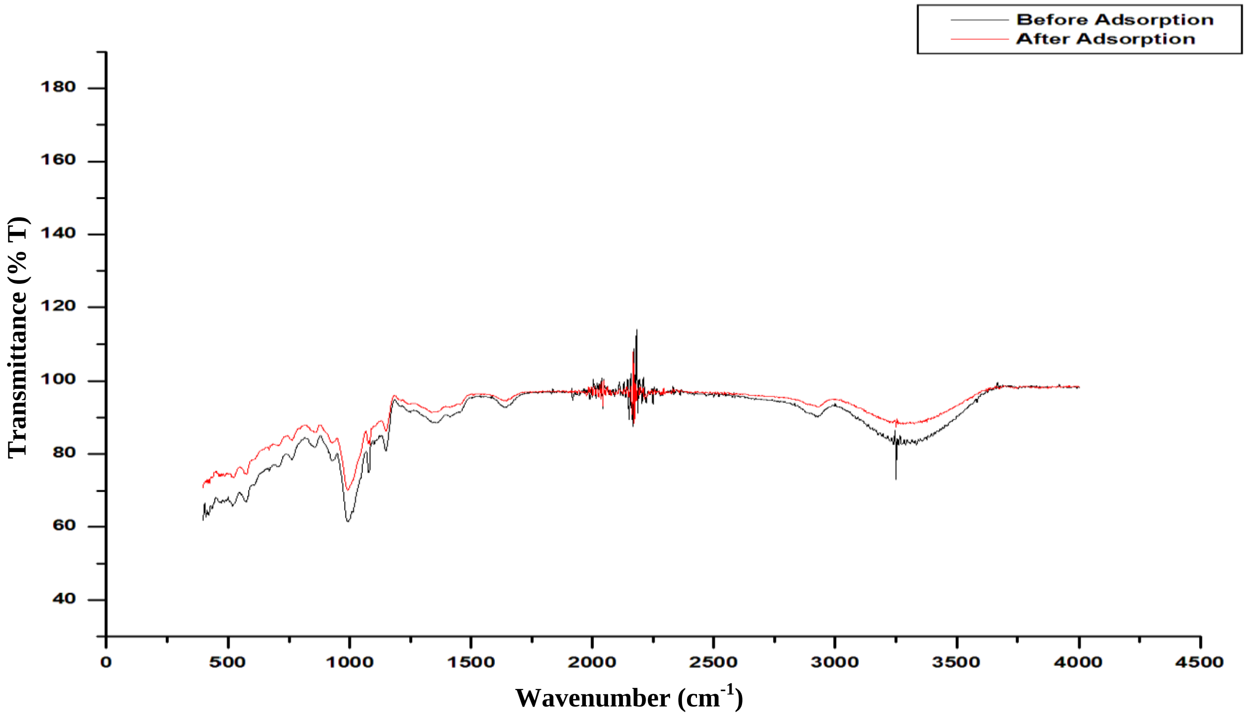

Figure 5.38: FTIR transmittance of potato gel in 2 conditions. (a) Potato gel without any adsorption (b) Nitrate rich water is passed from potato gel

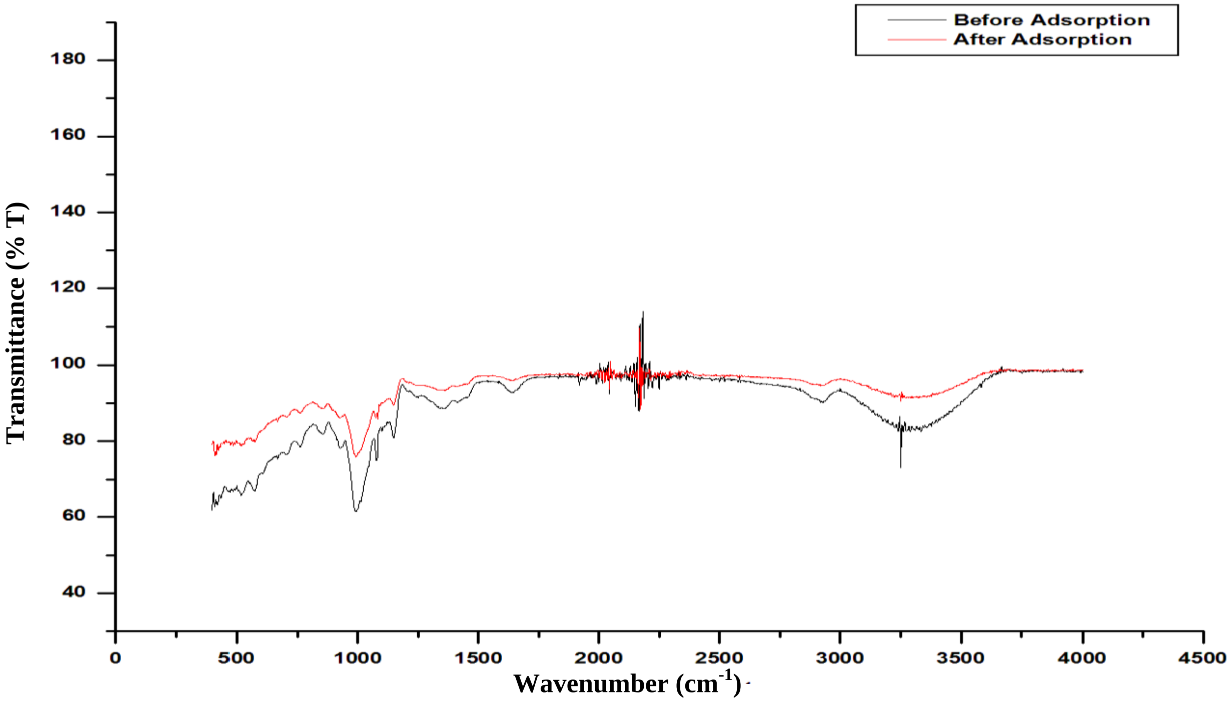

Figure 5.39: FTIR transmittance of potato gel in 2 conditions. (a) Potato gel without any adsorption (b) Fluoride rich water is passed from potato gel

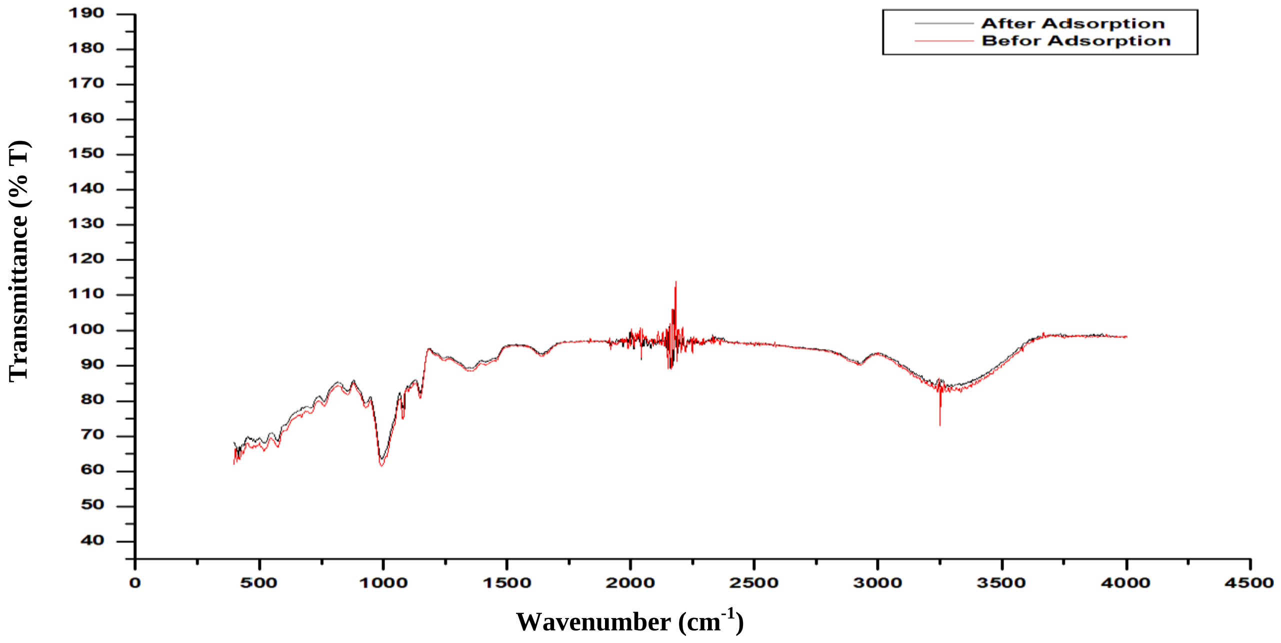

Figure 5.40: FTIR transmittance of potato gel in 2 conditions. (a) Potato gel without any adsorption (b) TDS rich water is passed from potato gel

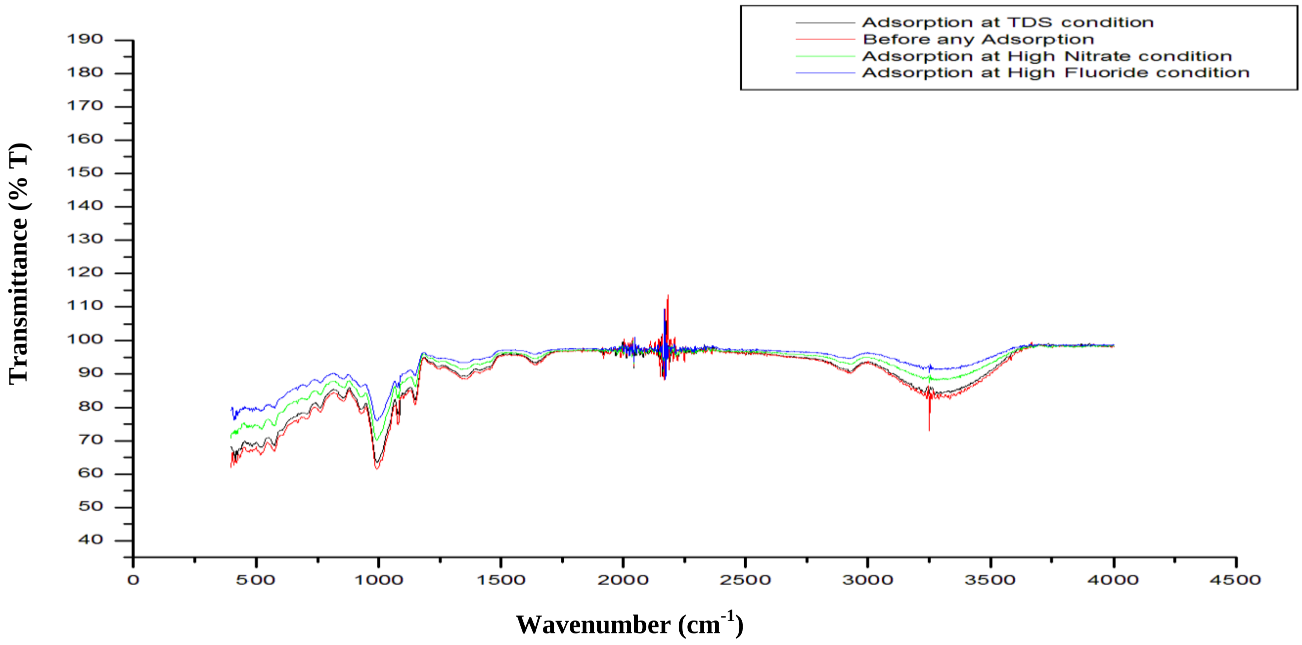

Figure 5.41: FTIR transmittance of potato gel (a) Potato gel without any adsorption (b) High Nitrate, Fluoride and TDS water is passed from potato gel

The FTIR plots (Figure 5.38, Figure 5.39, Figure 5.40 and Figure 5.41) show the gap in transmittance (%T) for different conditions of adsorbent. The shift in the wave number and transmittance suggest that functional groups are present at surface of adsorbent and Nitrate, Fluoride and TDS are captured over the surface.

5.5 Conclusion

It is evident from column study that the use of potato gel in the removal of the Nitrate, Fluoride and TDS has given promising results. The batch study followed the Langmuir isotherm, indicating single layer adsorption for Nitrate and TDS while Fluoride reduction followed Freundlich isotherm indicating multilayer adsorption. Potato gel showed the potential in reduction of these three parameters as column test continued for 144 hour. Potato gel is very effective in the reduction of Nitrate, Fluoride and TDS and it has been observed during the experiment. The zero order adsorption reaction is followed in reduction of three parameters. The FTIR spectroscopy suggests that the adsorption of Nitrate, Fluoride and TDS occurred at the surface of potato gel. Hence, proposed use of potato gel in removal of these three parameters may be an environment friendly.

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6. Conclusions and Future scope

This chapter includes the final outcome of the work and provides the scope for future work.

6.1 Conclusions

The study area (Shekhawati) belongs to arid climatic zone and very scanty rainfall reported in the area. The residents of Shekhawati are totally dependent on groundwater for their domestic needs. This leads to extraction and exploitation of groundwater, which results in lowering of groundwater table and ultimately degrades the quality of water. The quality of water is responsible for many waterborne diseases. In the Shekhawati region, many cases of birth defect and blue baby syndrome have been reported. Dental and skeletal fluorosis with osteoarthritis disease have been increasing in the region.

6.1.1 Groundwater quality and 3D Analysis

The satellite images of study area suggest that Shekhawati region is water scare region as no surface water bodies (rivers, lakes and ponds) exist. The unavailability of surface water promotes the extraction of groundwater in huge quantity for sustaining the life and business in the area. As the groundwater extraction continues from sub-surface region, the water table starts depleting with time.

The wells have been analyzed individually for Nitrate, Fluoride and TDS and categorized in safe zone and rejected zone. It has been observed that the trend of safe zone and rejected zone is reserved during pre monsoon and post monsoon study for Nitrate and Fluoride & TDS respectively. It is observed that Nitrate level in groundwater is reduced during pre monsoon to post monsoon while, Fluoride and TDS have been increased. The water quality index has been determined for the Shekhawati which indicates that 47% and 59% population accessing to safe category of groundwater during pre and post monsoon respectively.

This thesis deals with the 3D block model generation and analysis. The 3D block model is created to see the variation vertically and horizontally for Nitrate, Fluoride and TDS. The characterized data of Nitrate, Fluoride and TDS is interpolated and extrapolated in different layers at various depths. The inverse distance weightage (IWD) method is used to fill the space as it uses the distance and concentration of parameters (Nitrate, Fluoride and TDS) to project the new value of chosen parameter. Code is written with the help of Matlab (ver. 2012), that can interpolate and extrapolate the data for creating the continuous vertical and horizontal layer. It represents the variation of parameters in both directions. The projected data values are grouped in 3 categories (below safe, safe and above safe) and shown the variations in 3 dimensions. It helps in identifying the depth of safe zone and rejected zone.

Plots of depth vs. concentration suggest that, four layers (0-50 *m*, 50-125 *m*, 125-200 *m*, 200-300 *m*) exist between ground level surface and 300 *m* depth. These layers have shown the changes in slope of parametric concentration at 50 *m* depth, 125 *m* depth and 200 *m* depth. 42.85% blocks and 14.28% blocks showed increment in Nitrate during pre and post monsoon respectively. 33.33% blocks and 25% blocks showed increment in Fluoride during pre and post monsoon respectively. 33.33% blocks and 28% blocks showed increment in TDS during pre and post monsoon. From 50 *m* to 125 *m* concentration decreases for all parameters. From 125 *m* to 200 *m* the concentration doesn't vary with depth as it is in its lower range. From 200 *m* to 300 *m* the concentration increases rapidly for all three parameters under study. The shallow depth (0-50 *m*) shows variation in concentration in different blocks identified and this is due to leaching of contaminants through agriculture zone as this variation is in proximity to arable land. While the study area has very deep water table (more than 50 *m*), it is very clear that the host rocks are main reason for presence of higher concentration of Nitrate, Fluoride and TDS in groundwater.

Nitrogen present in calcite and feldspar containing host rock (Gulbrandsen, 1974; William, 1984; Wilson, 2010; Edward and Ford, 1932; Nesse, 2011; White, 2013) reacts with water to form various nitro compounds. It leads to increase in Nitrate concentration in groundwater. Fluorine presents in mica and phosphate containing host rock reacts (Gulbrandsen, 1974; William, 1984; Wilson, 2010; Edward and Ford, 1932; Nesse, 2011; White, 2013) with water to form fluoride in groundwater. Various cations and anions present in shale, chlorite, ferromagnesians, schist may get associated with water and increase the TDS in groundwater (Gulbrandsen, 1974; William, 1984; Wilson, 2010; Edward and Ford, 1932; Nesse, 2011; White, 2013). Clay is associated upto deep levels in few blocks so, clay work as a transporter of Nitrate, Fluoride and TDS beneath the earth to surface or vice versa and easily spread them in very large area (Nora, 1999).

The following points are included indicating novelty, efficiency & limitation, thus concluded as.

- The water quality index indicates that 47% and 59% population accessing to safe category of groundwater during pre and post monsoon respectively.
- Four zones have been identified in subsurface upto 300 m depth.

- Calcite and Feldspar containing rock releases nitro compound in water.
- Mica and Phosphate containing rock releases Fluorine in water.
- Clay work as transporter of Nitrate, Fluoride and TDS among the four layer identified.

6.1.2 Removal of Nitrate, Fluoride and Total Dissolved Solids by proposed material

The reduction of high Nitrate, Fluoride and TDS values from groundwater were achieved by series of experiments and validated by Breakthrough curve and Thomas model (Basmadjian, 1997; Thomas, 1944). The nine natural materials were used for reduction of Nitrate, Fluoride and TDS in water. Two materials (Aloevera gel & Potato gel) have displayed the potential to reduce Nitrate, three materials (Aloevera gel, Amla bark & Potato gel) have shown their potential in reduction of Fluoride and all nine materials (Rice husk, Wheat husk, Banana peel husk, Bagasse, Amla seeds, Coconut coir, Amla bark, Aloevera gel & Potato gel) have reduced the TDS present in water. The potato gel is the only material that has shown reduction in all three chosen water quality parameters (Nitrate, Fluoride and TDS) during experiments. The odour associated with dry flakes of potato is removed by converting potato into gel. Four parameters (Time, Weight, Concentration & Flowrate) are optimized through batch and continuous study for reduction of Nitrate, Fluoride and TDS using potato gel as adsorbent. The isotherm plots indicate that Nitrate and TDS reduction have followed the Langmuir model while Fluoride reduction has followed the Freundlich model. The single layer adsorption is suggested by Langmuir and multi layer adsorption by Freundlich (Foo and Hameed, 2010).

Adsorption column test was performed for 144 *h*. The result of this test shows that potato gel as adsorbent has reduced Nitrate, Fluoride and TDS. The breakthrough curve helped in determining throughput and exhausted volume of the process for these three parameters. The shape of breakthrough curve also suggested the presence of adsorable, nonadsorable and biodegradable organic constituents in groundwater (Metcalf and Eddy, 2002). Notably, 92%, 89% and 86% reduction in Nitrate, Fluoride and TDS has been observed during the experiment. The experimental results suggest that zero order bio-adsorption reaction takes place in potato gel and the eight functional group (N-H, O-H, C≡N & C ≡C, C=O, C=H, C=C, C-O, C-H & C=C) found to be present in potato gel must be responsible for the adsorption of Nitrate, Fluoride and Total Dissolved Solids as suggested by the FTIR studies.

The following points are included indicating novelty, efficiency & limitation, thus concluded as.

- The application of potato has been found in water purification. It might be cheap and more affordable material for water treatment.
- 92%, 89% and 86% reduction in Nitrate, Fluoride and TDS has been observed in water.
- Being a organic material, potato gel has potential of self contamination.

The main research contribution are as:

- The social impact of water quality is identified.
- The application of potato in form of gel is identified in reduction of Nitrate, Fluoride and TDS.

The parameters exceeding the prescribed limit can cause the health hazard and remedies are given based on experimental results. To find the limitation is added in future work plan and efficency can be tested in real condition which is also added in future work plan. The novelty is that source rock is found for the higher concentration of fluoride, nitrate and TDS in groundwater. The second novelty includes the identification of application of potato in treatment of water. The result concluded are only based on experiments. The study area is affected by higher concentrations of Nitrate, Fluoride and TDS. The population is poor who can't afford the costly instrument for water purification. For such habitants the potato gel technique can be demonstrated and they at their household can reduce the concentration of Nitrate, Fluoride and TDS in drinking water. This is how the practicality of work is correlated with field problem.

6.2 Further scope of the work

There is possibility to undertake following work in future as an extension of this study.

1. 3D physical model with more numbers of layers with greater details can be created over the availability of suitable data.

2. Development of the low cost water treatment device for domestic purpose using the adsorbent studies in this work for reduction in above said contaminants could be done after the pilot plant study which is based on laboratory experiments.

3. Sensitivity analysis of various parameter involved in treatment of water will be carried out. Limitation and efficiency of this treatment material may be found.

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Annexure 1

This annexure contain the picture of work undertaken during the thesis and major instruments used in analysis of samples.

Annexure 1A: Picture during sampling time

Annexure 1B: Picture of Lab work

Annexure 1C: Picture of material used

RH- Rice Husk, WH- Wheat Husk, BH- Banana peel Husk, CC- Coconut Coir, SH- Bagasse, AS- Amla seed, AB- Amla Bark, AG- Aloevara Gel, PG- potato gel

Annexure 1D: Picture of instruments used during Thesis work

(a)Bio-adsorption column study (b) Peristaltic pump (c) UV Spectrophotometer (d) FTIR

Annexure 1E: Specification of UV Spectrophotometer

Optical design	Double beam with and reference cuvette position; creny Turner Monochromator
Spectral Bandwidths(s)	1 *nm*
Light source	Xenon flash lamp
Detector	Dual silicon photodiodes
Scan ordinate modes	Absorbance, % transmittance, % reflectance, Kubelka Munk, log(1/R), log(Abs), Abs*Factor, Intensity
Wavelength	150-1100 *nm*

Annex 1F: Specification of peristaltic pump

Model number	RH-P110S-50
RPM	0.5-49.5
Flowrate	6-3000 *ml/hr*
Tubing	3 *cm* dia (with 2 *mm* wall thickness)
Pressure	Upto 2 *kg/sq.cm*.
Power source	230 V, 50 Hz, AC
Motor	DC stepper motor
Temp range	0-50 °C
Dimentions	125x225x290 *mm* (HxWxD)
Weight	7 *kg*. (approx)
No of channels	1

Annex 1G: Specification of Spectroquant

Parameter	Nitrate	Fluoride
Catalog no	1.09713.0001 1.09713.0002	1.14598.0001 1.14598.0002
Range	1.0-25.0 *mg/l* NO3- If higher, dilute the sample	0.10-2.00 *mg/l* F- 1.0-20.0 *mg/l* F-

Annex 1H: Specification of FTIR

Wavelength range	8300- 350 cm^{-1} optimized, proprietary KBr beamsplitter 7800-225 cm^{-1} with CsI beamsplitter option
Spectral resolution	0.4 cm^{-1} for 3028 cm^{-1} band in Methane
Wave number precision	0.008 cm^{-1} at 2000 cm^{-1}
Wave number accurancy	0.02 cm^{-1} at 2000 cm^{-1}
Optical system	Sealed and desiccated optical unit. Vibration isolated baseplate
Interferometer	Improved rotary Michelson interferometer for fast scanning, self compensating for dynamic alignment changes due to a tilt and shear, incorporating high reflectivity, first surface aluminum coated optics
Detectors	DTGS (standard) Liquid nitrogen cooled mercury cadmium telluride (MCT) detector (option)

This annexure contain the tables representing the list of sampling town/village, their chemical analysis and WQI.

Annexure 2A: List of villages and towns included in sampling

S No.	Location Name	Sample ID	S No.	Location Name	Sample ID
Jhunjhunu					
1	Mandawa	J01	17	Chanana	J17
2	Patoda	J02	18	Chidawa	J18
3	Bhisau	J03	19	Pilani	J19
4	Jhajhar	J04	20	Dheendhawa	J20
5	Chelasi	J05	21	Kazi	J21
6	Nuwa	J06	22	Kalota	J22
7	Luna	J07	23	Kharkhada	J23
8	Malsisar	J08	24	Garakheda	J24
9	Bhedgi	J09	25	Surajgarh	J25
10	Bugala	J10	26	Dudhwa	J26
11	Patushri	J11	27	Dabla/Jilo	J27
12	Bhudan ka Baas	J12	28	Rawa	J28
13	Mandrela	J13	29	Bohana	J29
14	Gudha	J14	30	Udika	J30
15	Devpura	J15	31	Panthroli	J31
16	Khed	J16			
Sikar					
32	Nechawa	S01	42	Lakshmangarh	S11
33	Lasol	S02	43	Harshwa	S12
34	Morwada	S03	44	Hetamsar	S13
35	Garoda	S04	45	Lavanda	S14
36	Dhannani	S05	46	Data Ramgarh	S15
37	Chuwas	S06	47	Katiwa	S16
38	Dhadhan	S07	48	Harshnath	S17
39	Khud	S08	49	Sikar	S18
40	Ghond	S09	50	Kolida	S19
41	Jajhod	S10	51	Dabdi	S20
52	Khachariawas	S21	62	Khandela	S31
53	Dukia	S22	63	Diwarala	S32

54	Goriyan	S23	64	Thoi	S33
55	Piprali	S24	65	Cheeplata	S34
56	Bandhal	S25	66	Maunda Tarla	S35
57	Khatu	S26	67	Ajeetgarh	S36
58	Lohargarl	S27	68	Hatideah	S37
59	Khoti	S28	69	Deepawas	S38
60	Ringus	S29	70	Raipura	S39
61	Hanspur	S30	71	Wampura	S40
Churu					
72	Sampar	C01	100	Ladidiyo	C29
73	Sanpurbada	C02	101	Maalaksar	C30
74	Marwanchota	C03	102	Baniyasar	C31
75	Usury	C04	103	Rosasar	C32
76	Badsar	C05	104	Saiwa	C33
77	Amarsar	C06	105	Jaitasar	C34
78	Tamapur	C07	106	Chappar	C35
79	Eleyasbada	C08	107	Momasar	C36
80	Chargah	C09	108	Bandhnau	C37
81	Kiliyatpurbada	C10	109	Near Bandhnau	C38
82	Methopana	C11	110	Hariyasar	C39
83	Jhakh	C12	111	Bukansar Bada	C40
84	Inwara	C13	112	Sadasar	C41
85	Kunwarpalsar	C14	113	Gusail Dhani	C42
86	Rirri	C15	114	Lodsar	C43
87	Upan	C16	115	Badawar	C44
88	Sherchota	C17	116	Panihara	C45
89	Mungiabadsar	C18	117	Bhojasar	C46
90	Nachnichota	C19	118	Golasar	C47
91	Bailla	C20	119	Mangesar	C48
92	Badsar Munda	C21	120	Bholasar	C49
93	Sarothiya	C22	121	Sardarsahar	C50
94	Sandawa	C23	122	Khejda	C51
95	Khana	C24	123	Gajpura	C52
96	Ketasar	C25	124	Rattusar	C53
97	Sattasar	C26	125	Chariyan	C54
98	Pattandesar	C27	126	Meenasar	C55
99	Ghandisar	C28	127	Gusaisar	C56
128	Daudsar	C57	146	Kailash	C75
129	Dadraiyo	C58	147	Dheerawas chota	C76

130	Ribia	C59	148	Sisraali	C77
131	Chadsar	C60	149	Sithone	C78
132	Chadsar	C61	150	Changai	C79
133	Karnisar	C62	151	Bayen	C80
134	Bilyurampura	C63	152	Khanti Baas	C81
135	Amarasar	C64	153	Daukwa	C82
136	Molisar	C65	154	Bungi	C83
137	Rampura	C66	155	Sidhmukh	C84
138	Bikasee	C67	156	Ramsara	C85
139	Lakhanwas	C68	157	Ramsara	C86
140	Pithana	C69	158	Nimma	C87
141	Sahawa	C70	159	Harpalu	C88
142	Kadwasar	C71	160	Laseri	C89
143	Churu	C72	161	Jorhdi	C90
144	Bharoosar	C73	162	Jhumpa	C91
145	Gundaas	C74	163	Biroon Dhani	C92

Annex 2B: Samples results for pre and post monsoon

		Pre Monsoon			**Post Monsoon**		
Sr	**Sample ID**	**Nitrate** *(mg/l)*	**Fluoride** *(mg/l)*	**TDS** *(mg/l)*	**Nitrate** *(mg/l)*	**Fluoride** *(mg/l)*	**TDS** *(mg/l)*
1	C01	5	0.21	230	35	0.59	3200
2	C02	5	0.21	230	6	0.14	200
3	C03	5	0.21	230	6	0.14	200
4	C04	5	0.21	230	6	0.14	200
5	C05	765	1.49	1350	25	0.77	1920
6	C06	740	1.18	1620	14	0.95	2040
7	C07	5	0.21	230	6	0.14	200
8	C08	5	0.21	230	6	0.14	200
9	C09	5	0.21	230	6	0.14	200
10	C10	5	0.21	230	6	0.14	200
11	C11	5	0.21	230	6	0.14	200
12	C12	630	1.43	1320	22	0.97	1960
13	C13	70	0.93	1340	159	0.58	1280
14	C14	103	1.6	1650	18	0.81	600
15	C15	5	0.21	230	24	0.66	1040
16	C16	5	0.21	230	6	0.14	200

17	C17	5	0.21	230	6	0.14	200
18	C18	5	0.21	230	6	0.14	200
19	C19	5	0.21	230	6	0.14	200
20	C20	5	0.21	230	29	0.65	2120
21	C21	81	1.61	660	30	0.4	640
22	C22	210	0.33	3000	260	0.46	2680
23	C23	45	0.41	790	3	0.31	200
24	C24	5	0.21	230	5	0.1	180
25	C25	48	0.27	570	64	0.85	1520
26	C26	158	0.48	570	4	0.13	280
27	C27	33	0.23	270	16	0.6	340
28	C28	247	1.25	2160	35	0.59	3200
29	C29	5	0.21	230	32	1	2800
30	C30	550	2.14	1590	15	0.66	1240
31	C31	138	0.66	2250	18	0.52	2000
32	C32	67	0.8	2220	11	0.23	250
33	C33	5	0.21	230	165	0.64	760
34	C34	67	0.35	3300	66	0.22	4400
35	C35	116	0.32	840	77	0.71	1360
36	C36	85	0.59	2700	20	0.54	440
37	C37	10	0.24	295	87	0.55	640
38	C38	150	0.1	2040	567	0.12	2000
39	C39	54	1.4	1380	127	0.67	2480
40	C40	5	0.21	230	9	0.3	360
41	C41	5	0.21	230	6	0.14	200
42	C42	5	0.57	4500	65	1.8	13600
43	C43	131	1.02	1320	244	8.4	3400
44	C44	790	0.43	8700	215	3.52	1360
45	C45	525	0.69	3900	395	0.92	3280
46	C46	280	0.58	2280	73	0.57	2320
47	C47	34	0.96	1170	73	1.2	1960
48	C48	575	1.7	1800	657	1.4	1800
49	C49	213	0.51	3600	655	0.73	4400
50	C50	5	0.17	90	11	0.26	520
51	C51	250	0.58	6300	337	0.6	7200
52	C52	5	0.21	230	83	0.73	4800
53	C53	30	0.49	1200	211	0.63	1120
54	C54	765	2.03	8400	304	21	2880
55	C55	675	2.07	8400	265	21	1560
56	C56	36	1.46	930	72	1	1800

57	C57	101	0.49	1590	170	0.41	1240
58	C58	730	0.31	3600	271	0.34	3600
59	C59	5	0.21	230	39	4.5	4400
60	C60	675	1.28	3600	815	1.5	3720
61	C61	5	0.21	230	13	0.27	285
62	C62	16	0.2	195	684	1.4	5200
63	C63	62	0.73	1950	82	0.63	2080
64	C64	78	0.62	1860	26	0.74	1920
65	C65	142	0.51	2700	136	1.1	3200
66	C66	108	0.39	4500	803	3.4	2240
67	C67	90	0.99	840	2	0.23	140
68	C68	234	1.03	2700	19	0.28	400
69	C69	36	0.23	900	11	0.3	440
70	C70	153	0.81	3300	381	1.2	1760
71	C71	121	1.85	6600	502	0.86	3600
72	C72	138	1.1	2190	266	1.6	2720
73	C73	70	0.56	11400	857	0.44	6800
74	C74	600	8.3	9600	160	0.88	760
75	C75	80	0.61	2020	255	0.86	2080
76	C76	96	13.6	1560	253	2.6	1200
77	C77	20	0.15	840	1803	1	500
78	C78	88	0.65	4500	149	6.8	840
79	C79	42	0.94	720	215	2.6	1801
80	C80	330	1.44	3600	143	5.6	880
81	C81	53	1.66	7200	61	2.9	1640
82	C82	95	0.33	2220	235	0.35	3120
83	C83	7	0.39	330	3	0.32	180
84	C84	175	2.24	2490	85	0.66	1240
85	C85	22	1.95	2130	4	0.71	600
86	C86	18	0.56	3600	3	0.69	560
87	C87	59	0.25	4200	85	0.85	1680
88	C88	50	0.43	8700	45	1.8	3560
89	C89	294	1.75	5100	216	3	6000
90	C90	178	0.74	2100	2	0.22	1600
91	C91	96	0.93	1020	73	1	8800
92	C92	53	0.54	2430	6	0.87	1480
93	J01	18	6.47	1740	60	0.65	1240
94	J02	530	0.76	2790	853	0.59	2800
95	J03	142	2.05	1950	46	1.2	2600
96	J04	70	0.24	570	100	0.37	680

97	J05	98	0.31	1050	63	0.93	760
98	J06	58	1.79	960	70	0.91	880
99	J07	78	4.08	2250	153	1	2280
100	J08	172	4.48	3600	207	2.6	4400
101	J09	8	0.27	300	108	0.34	520
102	J10	28	0.56	480	49	0.4	480
103	J11	36	0.98	960	50	0.63	1000
104	J12	2	0.23	660	11	0.4	920
105	J13	49	2.85	1740	60	1.2	1720
106	J14	135	2.21	1080	65	0.4	440
107	J15	30	0.55	450	51	0.92	880
108	J16	214	0.53	540	146	0.32	640
109	J17	44	0.38	660	71	0.23	330
110	J18	39	0.44	960	35	0.63	800
111	J19	7	0.16	160	195	0.65	760
112	J20	78	0.53	480	57	0.2	760
113	J21	131	1.44	900	202	0.56	1160
114	J22	2	0.34	540	14	0.37	720
115	J23	52	0.4	510	76	0.28	560
116	J24	31	0.77	450	49	0.46	480
117	J25	57	0.82	1700	74	0.55	920
118	J26	81	0.49	480	64	0.55	1080
119	J27	30	0.53	690	153	0.67	920
120	J28	11	2.18	1590	43	0.4	80
121	J29	40	0.43	1700	117	0.49	1120
122	J30	48	0.89	1020	390	0.28	920
123	J31	15	0.9	630	111	1.6	1920
124	S01	42	3.46	1770	181	0.93	2120
125	S02	15	1.63	570	83	0.77	680
126	S03	60	2.38	1590	589	1.4	1000
127	S04	455	1.8	1740	48	0.71	1720
128	S05	82	2.85	1560	64	0.17	920
129	S06	43	3.29	2340	120	2.9	1560
130	S07	126	2.94	3300	58	0.9	2480
131	S08	55	1.46	540	61	0.51	520
132	S09	67	1.99	1080	48	0.44	440
133	S10	32	1.31	630	50	0.28	1120
134	S11	130	4.45	1230	128	0.8	880
135	S12	38	2.9	960	74	1.1	920
136	S13	37	4.84	2100	68	1.8	1440

137	S14	405	1.93	1530	517	0.92	1520
138	S15	125	0.23	1860	225	0.18	1800
139	S16	5	0.21	230	60	0.21	520
140	S17	140	0.35	900	298	0.35	960
141	S18	55	0.43	780	48	0.2	480
142	S19	15	1.57	390	59	0.23	520
143	S20	22	0.81	660	188	0.2	1240
144	S21	12	1.12	510	23	0.33	440
145	S22	50	27.7	1740	62	0.24	440
146	S23	55	0.3	600	14	0.17	640
147	S24	5	0.15	330	37	0.13	400
148	S25	5	0.21	230	75	0.33	560
149	S26	18	0.71	510	14	0.36	600
150	S27	5	0.26	390	37	0.12	200
151	S28	10	0.39	510	64	1.8	760
152	S29	38	0.65	660	54	0.68	840
153	S30	14	1.63	660	93	1	880
154	S31	2	4.08	510	251	0.73	1160
155	S32	45	0.43	660	38	1.1	680
156	S33	7	1.48	450	35	0.95	320
157	S34	2	0.56	300	151	0.34	800
158	S35	19	1	450	63	0.28	400
159	S36	5	0.21	230	45	0.43	320
160	S37	17	1.45	870	264	0.72	1440
161	S38	130	2.17	1200	242	0.45	1200
162	S39	30	0.74	720	40	0.56	480
163	S40	14	1.34	1050	125	0.42	680

Annexure 2C: WQI during pre and post monsoon

Name	***Pre Monsoon WQI***	***Post Monsoon WQI***	***Name***	***Pre Monsoon WQI***	***Post Monsoon WQI***
C01	12.20	92.37	C41	12.20	10.89
C02	12.20	10.89	C42	91.37	314.81
C03	12.20	10.89	C43	141.70	424.07
C04	12.20	10.89	C44	739.74	260.15
C05	622.28	67.63	C45	469.22	367.70
C06	601.37	65.48	C46	258.30	105.41

C07	12.20	10.89	C47	66.02	113.41
C08	12.20	10.89	C48	493.70	547.78
C09	12.20	10.89	C49	229.11	574.74
C10	12.20	10.89	C50	8.98	22.59
C11	12.20	10.89	C51	303.07	382.96
C12	520.44	70.52	C52	12.20	157.70
C13	94.85	152.00	C53	53.11	188.96
C14	139.35	41.33	C54	751.78	739.85
C15	12.20	49.78	C55	686.00	688.96
C16	12.20	10.89	C56	74.61	105.56
C17	12.20	10.89	C57	112.20	155.70
C18	12.20	10.89	C58	607.63	268.30
C19	12.20	10.89	C59	12.20	202.22
C20	12.20	71.26	C60	588.44	699.04
C21	106.78	41.78	C61	12.20	20.38
C22	212.89	247.48	C62	19.55	624.44
C23	55.61	12.44	C63	94.65	109.41
C24	12.20	8.93	C64	102.56	67.70
C25	51.06	91.63	C65	161.52	178.52
C26	137.20	10.52	C66	163.67	707.70
C27	34.06	30.85	C67	102.67	8.93
C28	246.74	92.37	C68	241.22	26.96
C29	12.20	92.59	C69	46.78	22.15
C30	481.46	46.44	C70	186.33	338.22
C31	154.39	58.22	C71	240.74	450.96
C32	104.41	17.43	C72	163.17	277.93
C33	12.20	149.11	C73	254.30	757.93
C34	112.41	127.11	C74	788.89	150.74
C35	107.04	95.48	C75	106.48	242.67
C36	121.07	34.15	C76	399.33	265.19
C37	17.66	87.33	C77	32.15	804.44
C38	147.33	456.00	C78	154.63	275.48

C39	94.11	150.30	C79	64.00	247.05
C40	12.20	19.33	C80	336.44	245.04
C81	196.15	136.96	J31	41.61	149.78
C82	114.70	233.85	S01	137.50	190.07
C83	19.35	12.33	S02	56.83	89.93
C84	220.91	98.30	S03	123.83	484.07
C85	95.13	28.74	S04	406.04	80.00
C86	85.78	26.89	S05	150.07	66.52
C87	119.26	109.85	S06	143.96	179.33
C88	191.59	132.67	S07	213.67	104.30
C89	341.67	326.67	S08	82.19	65.19
C90	183.30	33.04	S09	111.85	52.67
C91	108.78	222.96	S10	63.31	61.93
C92	91.76	48.44	S11	215.69	127.26
J01	186.11	79.56	S12	108.59	94.59
J02	455.98	691.63	S13	169.96	114.37
J03	183.24	104.07	S14	368.39	428.74
J04	66.69	93.63	S15	128.70	200.67
J05	96.98	80.00	S16	12.20	57.78
J06	98.74	86.74	S17	126.48	244.52
J07	185.94	173.56	S18	63.30	48.00
J08	286.96	284.44	S19	52.50	57.48
J09	16.93	96.22	S20	45.30	164.37
J10	41.19	53.19	S21	42.28	31.70
J11	64.44	67.70	S22	681.59	58.59
J12	17.59	32.37	S23	57.41	24.81
J13	128.63	99.78	S24	12.54	36.96
J14	167.11	64.37	S25	12.20	72.22
J15	41.94	72.89	S26	37.61	28.37
J16	179.30	125.93	S27	15.98	33.41
J17	52.04	63.20	S28	24.57	100.07
J18	54.67	53.26	S29	53.59	69.11

J19	11.41	171.56	S30	57.59	105.78
J20	77.56	59.33	S31	100.65	221.48
J21	144.04	181.41	S32	53.89	63.93
J22	18.04	30.59	S33	45.57	52.37
J23	55.91	71.85	S34	18.93	132.74
J24	47.57	54.52	S35	43.80	59.56
J25	88.78	82.37	S36	12.20	48.22
J26	78.89	77.63	S37	59.31	235.56
J27	45.50	143.56	S38	164.52	209.26
J28	83.09	42.07	S39	50.67	50.07
J29	67.52	116.22	S40	57.65	113.26
J30	72.33	310.44			

Annexure 2D: Constituients of litholog at SGWB wells and distance from sampling well.

Sr. No.	Location	Layer change at depth in modelled data	Litholog (SGWB)	Distance from sampling location
1	Bidoli	0-50 *m* (Layer 1) 50-125 *m* (Layer 2) 125-200 *m* (Layer 3)	0-75 *m* (sand fine to medium grained) 75-84 *m* (quartzite)	8 *km* N of S26
2	Johara		0-114 *m* (fine sand to medium grained sand) 114-120 *m* (Quartzite/ feldspar/ biotite)	3 *km* S of S29
3	Mundru		0-30 *m* (fine sand/kankars/clay) 30-60 *m* (Wuartz/Muscovite) 60-90 *m* (Schist)	6 *km* W of S32
4	Khandela		0-33 *m* (fine sand/kankars) 33-54 *m* (Phyllite) 54-110 *m* (Gneisses/Feldspar/ Mica)	7.5 *km* SE of S28
5	Neem ka Thana		0-20 *m* (fine sand/kankars/ clay) 20-110 *m* (Quarzite/ Biotite schist)	7 *km* SE of S35
6	Bhukana		0-90 *m* (fine sand/kankars/ clay) 90-98 *m* (Granite)	3 *km* W of J17
7	Gudhagorji		0-78 *m* (fine sand/kankars) 78-88 *m* (Granite)	7 km SW of J16
8	Barau		0-82 *m* (fine sand/kankar) 82 -100 *m* (Granite)	6 *km* N of J21
9	Bhodan		0-15 *m* (fine sand/clay) 15-85 *m* (Phyllite) 85-110 *m* (Granite)	7 *km* S of J27
10	Muradpur		0-15*m* (fine sand/clay) 15-54 *m* (Quartzite) 54-85 *m* (Phyllite) 85-110 *m* (Granite)	7 *km* NW of J26
11	Kerot		0-6 *m* (fine sand/clay) 6-45 *m* (Quartzite) 45-92 *m* (Granite)	4 *km* SW of S35
12	Ponk		10-50 *m* (fine sand/clay) 50-70 *m* (quartzite) 70-74 *m* (granite)	5 *km* N of J14
13	Kalakhari		0-30 *m* (fine sand/kankar)	6 *km* NE of

			30-37 *m* (Phyllite)	J27
14	Seegra		0-90 *m* (sand/clay/kankar) 90-92 *m* (Granite)	8 *km* NW of J11
15	Khasoli		0-54.85 *m* (sand/kankar/clay) 54.85-98.80 *m* (medium grain sand with kankar predominated) 98.80-102.15 *m* (Granite)	5 *km* SE of C66
16	Chandgothi		0-57.92 *m* (fine sand/clay) 57.92-93.91 *m* (clay with kankars) 93.91-115.29 *m* (Sandstone/ feldspar /quartz) 115.29-117.12 *m* (Granite/ feldspar)	7 *km* SE of C79
17	Adsar		0-144.92 *m* (sand/clay/kankar) 144.92-189.90 *m* (clay) 189.90-192.34 *m* (coarse sand/feldspar/ferromagnesians)	7.5 *km* S of C27
18	Dhirwas		0-53.95 *m* (sand/clay/kankar) 53.95-66.39 *m* (clay/kankar) 66.39-75.80 *m* (Sandstone/ shale) 75.80-78.58 *m* (sand/kankar) 78.58-119.54 *m* (Sandstone)	7 *km* W of C69
19	Sahwa		0-77.11 *m* (sand/kankar/clay) 77.11-102.45 *m* (Sandstone)	3 *km* E of C64
20	Billun		0-36.57 *m* (sand/clay/kankar) 36.57-109.79 *m* (Sandstone with mica and shale)	3 *km* S of C57
21	Dhirdesar		0-51 *m* (sandy clay with kankar) 51-58 *m* (medium grained sand) 58-75.60 *m* (sandy clay with kankar) 75.60-79.60 *m* (Sandstone) 79.60-91.0 *m* (kankar)	5 *km* S of C65

Journals

- Development of a low cost potato gel system for Nitrate removal from water. Singhal A, Gupta R, Singh A N, Shukla P, Sharma A. (2016). Res. Jour. of Chem. & Env. 20 (9), pp. 10-18.
- Assessment of Groundwater Quality Using GIS and Various Water Quality Indices. A Case Study of the Shekhawati Region of Rajasthan, Northwest India. Gupta R, Singhal A and Singh A N. (2016). European Journal of Scientific Research. 141 (4), pp. 427-444.
- Plant Indicators of Salinity in Shekhawati Region of Rajasthan, India. Singh A N, Singhal Anupam and Gupta Rajiv. (2014). Frontiers in Geosciences. 2(2), pp. 18-22.
- Land Use/Land Cover Information at Various Scales of Remote Sensing Data of Jhunjhunu District, Rajasthan. Singh A N, Singhal Anupam and Gupta Rajiv. (2014). Journal of Remote Sensing & GIS. 5(1), pp. 43-54.
- A small discussion on microwave application for groundwater exploration: A review. Singh A N, Singhal Anupam and Gupta Rajiv. (2013). IJGG. 3(3), pp. 474-485.

Conferences

- Land use/ Land cover information from various classification methods of Shekhawati region of Rajasthan. A. N. Singh, Deepthi G. V. and Anupam Singhal. ICEEOT – 2016, IEEE Conference at DNI college of Engineering Chennai, Tamil Nadu, India, held at 3-5th March 2016 (978-1-4673-9939-5/16/$31.00 ©2016 IEEE)
- Assessment of groundwater salinity using GIS and Vulnerability of population: A study of Shekhawati region of Rajasthan, India. A. N. Singh, Anupam Singhal, Rajiv Gupta and Anuradha Devi. National Conference on Recent Advancements in Minerals & Water Resources, 5-6 Dec 2015, Govt. Science College, Rewa, pp. 61.
- A Study on Industrial Waste as a Fertilizer. Anuradha Devi, Anupam Singhal, Rajiv Gupta, S.K. Verma and A.N.Singh. 5th Annual conference on Advances in Biotechnology (Biotech – 2015), Indian Institute of Technology Kanpur, India, 13th to 15th March 2015.
- Utilization of copper tailing and spent pickling liquor for improving the fertility of soil.Anuradha Devi, Anupam Singhal, S.K Verma, Rajiv Gupta, A N Singh, Prasad Panzade and Martina Fernandes. 4th International Conference in Advances in Biotechnology held on 10-11 March 2014 (Biotech 2014), BITS Pilani Dubai campus, Dubai, pp 48-50.

Arun N. Singh birth place is Pauri Garhwal which was once capital of British India for Garhwal region.
The date of birth is 14 November 1983. He completed his B.Sc. in Geology, Physics and Mathematics from HNB Garhwal University, Srinagar, India in 2002. He has completed M.Sc. in Remote Sensing & GIS application from Bundelkhand University, Jhansi, India in 2005. In 2011 he have done certificate course from ITC Netherlands (University of Twenty) in Applied Geophysics.
He has diverse exposure in geosciences. His first worked as a project assistant at BIET-Jhansi and used to train the school student on using the GPS. After that he worked as GIS analyst & Project Controller at Jordan in a Mining and exploration organization. There he was managing the Gold exploration program running in African continent. He worked at senior management level during the exploration work. In his third job he returned back to India and worked for a NGO and lead their Rural development program. At present he is working as a Project Fellow at Dept. of Civil Engineering, BITS-Pilani, India. Here his work is concentrated on characterization of groundwater and finding the source of contamination of groundwater in the Shekhawati region of Rajasthan

Brief biography of Supervisor

Dr. Anupam Singhal birth place is Saharanpur. The date of birth is 25 Oct., 1969. He had completed B.E. in Civil Engineering and M.E. in Environment Engineering from IIT-R, Roorkee, India in 1992 & 1994 respectively. In year 2006, he was awarded with PhD from IIT Roorkee in Hazardous Waste Management. He has diverse exposure in environmental engineering projects. He has worked as environmental engineer in industry & consultancy organization for eight years. He has designed many treatment plant for Water & Wastewater and Air pollution control systems and consultant in industry and consultancy organization. He has also carried out many EIA studies. Presently, he is working as Associate Professor in Dept. of Civil Engineering at BITS-Pilani. He is working on various projects funded by Govt. agencies. He has published many research papers in international/national journals/conferences of repute.

Brief biography of Co-Supervisor

Dr. Rajiv Gupta completed his B.E. and M.E. in Civil Engineering from BITS-Pilani India in 1983 and 1989 respectively. In 1995, he was awarded with PhD. In Fluid Structure Interaction from BITS-Pilani, India. Presently, he has been working as a senior Professor at Dept. of Civil Engineering at BITS-Pilani, India. In his last 3 decades of teaching and research, he has authored a number of books and course development material and published more than 150 research papers in India and abroad. His fields of interests are Energy- Water conservation, GIS and RS and Concrete Technology. He is executing various projects related to water domain of worth approx. 6 crores.

Comments of Dr B K Dubey.

1. The use of term 3D model for the kind of work presented in the relevant section of the thesis is misleading in the view of this author. What you have done is the 3D representation of the data that you have collected and its relationship with soil properties. Usually when we say model, we expect to see a predictive model where we can use the collected data from field, use of mathematical equation and predict the future contaminant concentration. In my view a disclaimer on this regards should be added to avoid confusion. I leave this to the discretion of the doctoral supervisory committee.

   Reply: *A three-dimensional representation of a phenomina or thing or of a proposed structure, typically on a smaller scale than the original is termed as model. Herbert, 1982; suggest that the representing the data in 3D is also a modeling (physical models). With IDW technique, interpolation, extrapolation is done with limited dataset. Thus, in my opinion, it is a 3D modelling. But in present time, more emphasis is given on numerical approach. We have changed it to 3D analysis instead of 3D modeling.*

2. The low cost sustainable material for treatment is identified as potato gel for all three contaminants studied. What is the cost per unit of treatment? How you envision implementing this technology in the field scale? Please include a discussion along this line in the thesis.

   Reply: *The cost calculation for potato gel treatment system as follows-*
   Cost of potato = Rs. 10/Kg
   Labour charges= Rs. 300/day
   Electricity used=5 unit= Rs40
   Total expense to make gel from 1kg potato= Rs 50 (10+40)and get 500 gm of gel
   Cost of treatment= Rs 50 / 100 lt = Rs 0.5/lt.

   If we go for commercial level production then the cost will reduce.

   We are planning to modify the old candle filters technology to implement it in field. Either the potato gel is filled in between the candles or mixed with other material to make a filteration medium. This is added in future scope of the work.

3. Refer to the observation of the contamination in wells pre and post monsoon (first presented as part of abstract in the bullet points), the trend for Nitrate is reverse of what is presented for Fluoride and TDS but no explanation is provided.

   Reply: *The increase in number of wells in safe category of Fluoride and TDS may indicate the dilution of minerals (Biotite and Mica) in water that results due to good rainfall during the monsoon time of the sampling year (ie. 2012). While the decline in* *wells in safe category of Nitrate might be linked with leaching of nitrate compounds from agricultural area in few pockets.*

4. Paragraph next to bullet points (refer #3 above), refers to presence of minerals being cause of contamination, which minerals?

   Reply: *The name of minerals are given in section 4.5, being causing the contamination . Botite & Mica for Fluoride while Feldspar & Calcite for Nitrate. TDS due to presence of cation, anion & organic material in soil strata* (Gulbrandsen 1974, Wilson 2010, white 2013).

5. There are few English language issues, suggest a good read by a language expert if possible.

   Reply: *The lingual mistakes are corrected with help of experts in language dpartment.*

6. Table 1.2, what about low dose of Fluoride?

   Reply: *Low levels of fluoride intake help to prevent dental caries (WHO, 1996.)*

7. Section 1.2, third paragraph: what causes the odour?

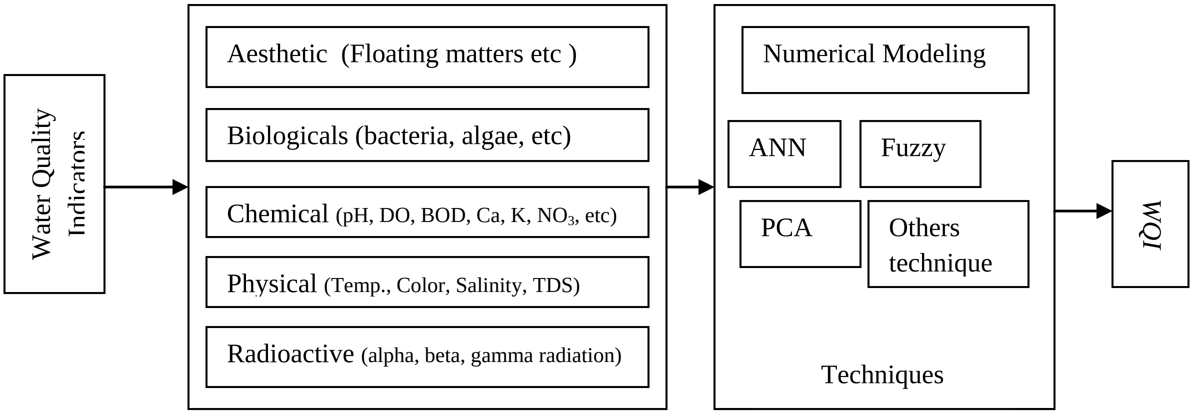
   Reply: *Iron bacteria are found in groundwater having high levels of iron produce specific smell (http://www.water-rightgroup.com/blog/common-reasons-why-your-water-stinks/). Sometimes sulfur rich water produces the odour due to release of* H_2S*. Barium and cadmium are naturally occurring metals found in natural deposits that can make a specific smell in water if these mineral host rock are present in aquifer (https://www.watertechonline.com/why-does-water-have-a-bad-taste-or-odor-1/). Thus, Some times if heavy dose of chemical get mixed in water which can induce their specific smell in water and keeping it is open can release the gases traped and odour may be removed.*

8. Section 2.2, 3D modeling, no mathematical model presented.

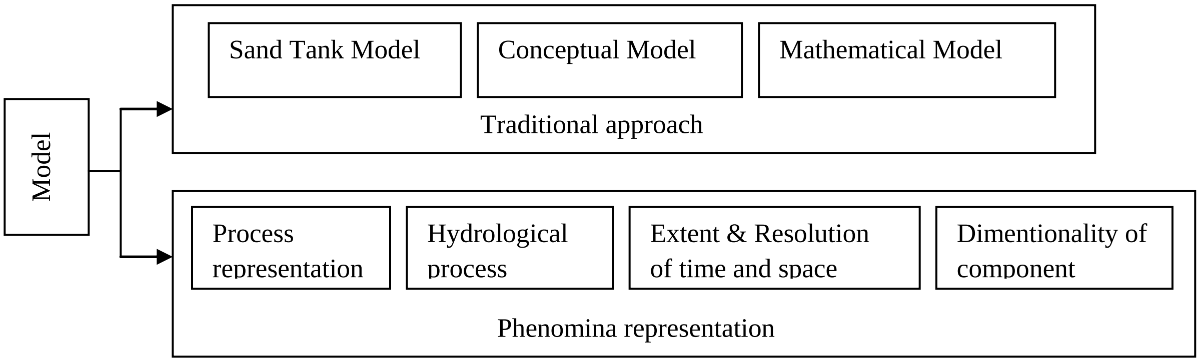
   Reply: *Herbert, 1982; suggest that the representing the data in 3D is also a modeling (physical models). We have also done mathematical modeling in Matlab (ver 2012) and used interpolation function (interp1,* scatteredInterpolant, plot, grid *) for modeling, then only we are able to produce the continous surface. Points are displayed in various layers for categorization as well. The outcome of this modeling is in form of graphs for easier understanding of phenomena.*

9. The literature review chapter will benefit if few summary tables and schematics are presented summarizing the information from different literature sources. I like the fact that it is a detailed review, but gets difficult to follow in absence of few summary tables/figures.

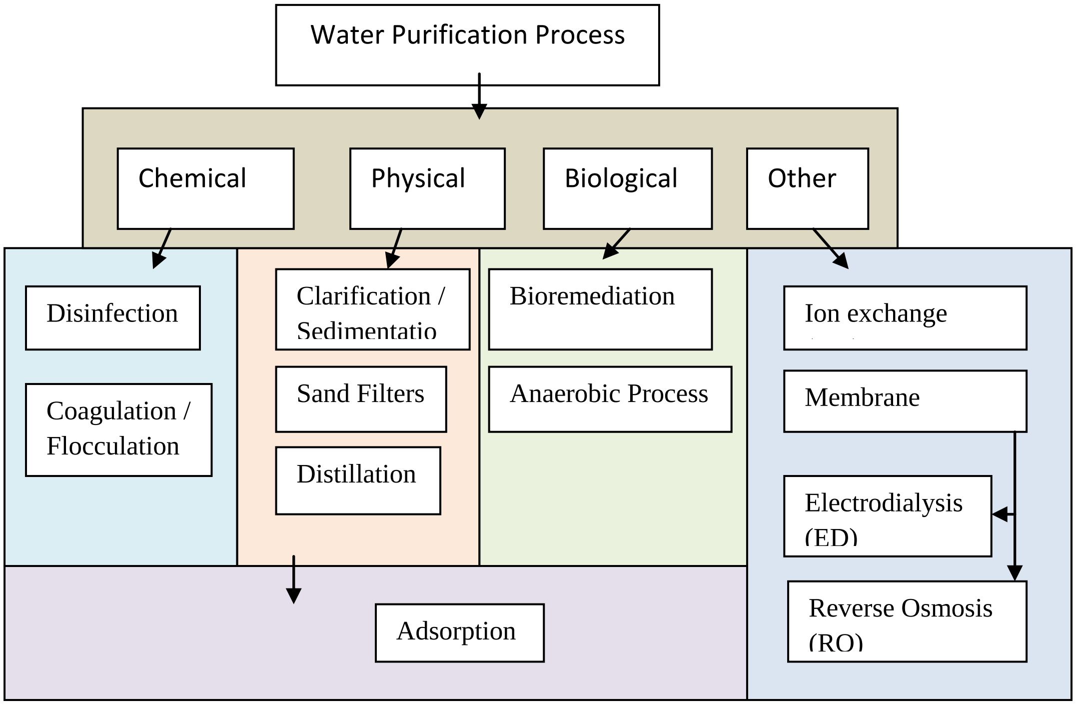
   Reply: *The graphical representation of general summary is added in respective sections.*



Water Quality



Modeling



Water treatment

Comments of Dr T I Eldho

1. Use either "groundwater" or "ground water"
   Reply: *Changes are made to groundwater.*

2. Page 7-1.2 Gaps in present research-pl. rename as research gap.
   Reply: *Change done.*

3. Page 8- in lines 5-8 ".. a new purification process should be designed, …" could author achieve this?. If so, in conclusion chapter- clearly mentioned with details.
   Reply: *Purification technique is not designed in the work but the new material is found. It was proposed initially to develop the technique, but later work on problem leads to identification of material. Modification in sentence is done.*

4. Page 8- in objective: author mentioned 3D modeling- however, what author did is only "3D analysis"- no modeling in term of groundwater transport modeling, is not done. Hence in all places it should be changed as 3D analysis -instead of 3D modeling (as it creates confusion and impression that author carried out 3D modeling).
   Reply: *Changes done.*

5. Few references given in the thesis are missing in reference list. eg. page 16- ref. alobaidy et al., 2010; page 41- ren et al., 2015; chapter 3- who 2005 etc-. check for all reference and add in reference list appropriately!.
   Reply: S*uch problem in reference is solved.*

6. Chapter 2- Give literature review in chronological order!.
   Reply: T*he literature review is provided in such a manner so that the continuity in reading be maintained. The procedure followed for literature review is accepted procedure in many reputed journals.*

7. Provide the latest literature on topic.
   Reply: *There are few latest literature references in this work exist.*

8. Chapter 3- page 62- explain the relevance of EC and sampling time?
   Reply: *The basic idea behind this graph is to represent the overall ionic concentration in the study area. The ionic concentration is related to electric conductivity, directly. So, in absence of parameters data in study area, EC is used. As the trend of EC is rising during time of sampling indicates that the ion responsible for rise in conductivity are on higher side.*

9. Chapter 3- page 63, 64, 68- "3D modeling"- change to "3D analysis".
   Reply: *Change done*.

10. Chapter 3 - give references when eq. and procedure from literature are given.
    Reply: *ref. are mentioned*.

11. Chapter 3- page 72- (b) T vs Log Delta C?
    Reply: *Typing error and it is corrected*.

12. Chapter 3- it will be nice, if climatic, geological and geomorphologic details of the study area are given!.

    Reply: *In this work more emphasis is given on treatment of water so such information seems to be of no use with it, thus these details are avoided. Climatic detail is provided in chapter 4: 4.1*.

13. In all chapters, plz cheak whether the listed references are quoted in the text.
    Reply: *Corrected*.

14. Chapter4/5/6- change "3D modeling" to 3D analysis – in term of groundwater modeling, author did not do any modeling. It is only data analysis and interpretation through interpolation/extrapolation. This can not be called as 3D modeling. Plz make changes wherever it is written!.

    Reply: *A three-dimensional representation of a phenomina or thing or of a proposed structure, typically on a smaller scale than the original is termed as model. Herbert, 1982; suggest that the representing the data in 3D is also a modeling (physical models). With IDW technique, interpolation, extrapolation is done with limited dataset. Thus, in my opinion, it is a 3D modelling. We have changed it to 3D analysis instead of 3D modeling.*

15. Chapter 4- page 89- 3 categories of distribution in Fig 4.3, 4.4- but only 2 are visible/legends given!.

    Reply: *It is a typing error and problem is removed*.

16. Chapter 4: Fig 4.6/4.8- what is the range for 4th colour.
    Reply: *Only 3 colour and range are given.in legend No 4th colour exist in these fig.. If such problem exist then, it might be due to printing*.

17. Page 92/93 - change arial to areal.
    Reply: *Changes done*.

18. Page 99 onwards- change "3d modeling" to "3D analysis".

    Reply: *Changes done*.

19. Chapter 5- page 130/131- clearly mention the difference between "batch study" and "column study".

    Reply:

    Under the batch processing model, a group of one or more work, will perform a specific set of tasks t*hat does not require a user to control it.*

    Column study is a numerical model that simulates one-dimensional advection and dispersion of a reactive solute originating from a contaminant spill. It models the processes of transport, sorption and reaction in the aqueous and sorbed phases of a solute.

    Column is a continous study.

20. Chapter 5- give section on "experimental procedure" - give step by step procedure used in study.

    Reply: *The experimental procedure is given in chapter 3. To avoid repetition, it is not provided in chapter 5*.

21. Chapter 5- Give a clear section on experimental plan with complete explanation- so that it is the type of experiments conducted, its relevance to field problem and interpretations.

    Reply: *Experimental plan is provided in chapter 3*. To avoid repetition, it is not provided in chapter 5.

22. Give appropriate photographs and explain.

    Reply: *Photos are given in Annexure with appropriate heading*.

23. In Page 157- why 6ml/min to 33 ml/min – explain.

    Reply: *It is mentioned in chapter 5 under section 5.3.1 itself. The range of pumps is 0.1-50 ml/min. If flowrate is less than 6 ml/min then the backflow of water occur in column (flowrate less than 6 ml/min is not sufficient to pump water into column). While flowrate above 33 ml/min, displayed a huge fluctuation in reduction capacity (the result are very fluctuating above this flowrate during the studied time).*

24. Give a separate section with sensitivity of various parameters and elaborate the outcome!.

    Reply: *No such study was carried out during experimentation. Added in future work plan.*

25. What are the limitation of the study?-. Explain briefly.
    Reply: *Added in future work.*

26. What are the applications.
    Reply: *Higher values to nitrate, fluoride and TDS can be reduced in drinking water in prone area. It will help in keeping the health hazards away which will be caused by these three parameters.*

27. How we can use "potato gel" in large scale - for treatment.
    Reply: *Medium of potato gel can be used either standalone or in combination with other material for treatment of water in large scale. We are experimenting with potato gel and ceremic plates for treatment of water at large scale.*

28. Chapter 6 – not written properly!.
    Reply: *Rewritten.*

29. Chapter 6- Rewrite as summary and conclusions- give brief summary as 6.1, 6.2 conclusions.
    Reply: *Summary is given chapterwise in respective chapters. The general conclusion are mentioned here.*

30. Conclusions should be given pointwise (as given here!).
    Reply: *To keep the continuity, the paragraphs approach is taken*. Specific findings are given pointwise.

31. Give detailed conclusions with application, general conclusions, experiments based conclusions, novelty, efficiency, limitations etc.'
    Reply: A*dded.*

- *The water quality index indicates that 47% and 59% population accessing to safe category of groundwater during pre and post monsoon respectively.*
- *Four zones have been identified in subsurface upto 300 m depth.*
- *Calcite and Feldspar containing rock releases nitro compound in water.*
- *Mica and Phosphate containing rock releases Fluorine in water.*
- *Clay work as transporter of Nitrate, Fluoride and TDS among the four layers identified.*

- *The application of potato has been found in water purification. It might be cheap and more affordable material for water treatment.*
- *92%, 89% and 86% reduction in Nitrate, Fluoride and TDS has been observed in water.*
- *Being a organic material, potato gel has potential of detoration.*

  The parameters exceeding the prescribed limit can cause the health hazard and remedies are given based on experimental results. To find the limitation is added in future work plan and efficency can be tested in real condition which is also added in future work plan. The novelty is that source rock is found for the higher concentration of fluoride, nitrate and TDS in groundwater. The second novelty includes the identification of application of potato in treatment of water. The result concluded are only based on experiments.

32. Practically correlate with field problems and elaborate and give recommendations/ conclusions.

    Reply: *The study area is affected by higher concentrations of Nitrate, Fluoride and TDS. The population is poor who can't afford the costly instrument for water purification. For such habitants the potato gel technique can be demonstrated and at their household, they can reduce the concentration of Nitrate, Fluoride and TDS in drinking water. This is how the practicality of work is correlated with field problem.*

33. What are the research contribution from the present study. Provide a section in chapter 6.3 and explain with respect to objectives set.

    Reply: The contribution from present study are:

    - *The social impact of water quality is identified.*
    - *3D modeling help in identification of source rock causing increment in concentration of Nitrate, Fluoride and TDS.*
    - *The batch and continous study parameters are optimised for biosorption study.*
    - *The application of potato in form of gel is identified in reduction of Nitrate, Fluoride and TDS.*