ADSORPTIVE REMOVAL OF FLUORIDE FROM WATER BY SURFACE MODIFIED LATERITE SOIL

A DISSERTATION

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Requirement for the award of degree

Of

MASTER OF TECHNOLOGY

In

CHEMICAL ENGINEERING

(With specialization in industrial pollution abatement)

By

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CANDIDATE'S DECLARATION

I hereby declare that the work presented by me in this thesis entitled " ADSORPTIVE REMOVAL OF FLUORIDE FROM WATER BY SURFACE MODIFIED LATERITE SOIL" in partial fulfilment of the requirements for the award of the degree of Master of Technology in Chemical Engineering with specialization in Industrial Pollution Abatement(IPA),submitted to the Department of Chemical Engineering, Indian Institute of Technology , Roorkee is an authentic record of my original work carried out under the guidance of Dr. P. Mondal , Assistant Professor , Department of Chemical Engineering , IIT Roorkee.

Date14/06/2013

Place: IIT ,Roorkee. Pragya Mishra.

CERTIFICATE

This is to certify that the above statements made by the candidate is correct to the best of my knowledge and belief.

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(PRAGYA MISHRA)

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ABSTRACT

Fluoride (F^-) contamination in groundwater has been recognized as one of the serious problems worldwide . Fluoride is classified as one of the contaminants of water for human consumption by the World Health Organization (WHO) , which causes large-scale health problems. Elevated fluoride concentrations in the groundwater occur in various parts of the world. Fluoride is generally released into the groundwater by slow dissolution of fluorine-containing rocks eg granite, basalt, etc. Industries like glass, semiconductor , etc also discharge effluents containing high concentrations of fluoride. High concentration of fluoride could be toxic to mankind in several ways and thus removal of fluoride is required to control fluoride concentrations within the limit.

Among several treatment technologies applied for fluoride removal, adsorption process has been explored widely and offers satisfactory results. In this study we have studied fluoride removal using surface modified laterite soil as it serves as a low cost, easily available and a highly effective adsorbent. Laterite soil was brought from Burdwan district of West Bengal. It was washed with distilled water several times , crushed and sieved to get a particle size range of 250 to 350 microns. It was then treated with 2N HCl followed by treatment with 1N NaOH .The adsorbent i.e acid treated laterite soil , so developed was used for removal of fluoride and further the batch process is optimised by varying the particle size ,adsorbent dose , pH , fluoride concentration and time of contact.

The acid base treatment is done to enhance the absorption characteristics .In this process 81% removal of fluoride was reported The adsorption efficiency of the acid base treated laterite was compared with acid treated laterite . Acid base treated laterite was further impregnated with $FeCl_3$ and the efficiency increases to 85%.From EDX analysis it is clear that iron is the main component responsible for fluoride removal. The equilibrium data obtained through batch mode was fitted to Langmuir, Freundlich and Tempkin isotherm. The Tempkin isotherm fits better to the equilibrium data. Fluoride adsorption on acid base treated laterite follows pseudo second order kinetics .Column studies are done so as to study the defluoridation capacity of the adsorbent in continuous mode. The effect of flow rate , fluoride concentration and bed height is studied.

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NOMENCLATURE

C_o	Initial fluoride concentration
C_e	Concentration of adsorbate solution at equilibrium(mg/l)
K_F	Freundlich constant(1/mg)
K_L	Constant related with free energy of adsorption (1/mg)
K_T	Tempkin isotherm constant (1/mg)
K_f	Pseudo first order rate constant (min-1)
K_s	Pseudo second order rate constant (g/ mg min)
1/n	Heterogeneity factor,dimensionless
q_t	Amount of adsorbate adsorbed per unit amount of adsorbent at time t(mg/g)
q_e	Amount of adsorbate adsorbed per unit amount of adsorbent at equilibrium time (mg/g)
K_{id}	Intra-particle diffusion rate constant
SSE	Sum of square of errors
BET	Brauner-Emmett-Teller
FTIR	Fourier Transform Infrared
XRD	X ray diffraction

CHAPTER 1

INTRODUCTION

1.1 GENERAL

Fluoride is highly reactive nature it does no exist in the elemental state. The occurrence of high concentration of fluoride in groundwater is seriously injurious to mankind. According to the standards set by World Health Organization (WHO) the permissible level is 1.5 mg/L for drinking water.[Zhang et al.,2005; Amini et al.,2008].

The impact of fluoride in drinking water can be positive or negative to mankind .It depends on the concentration and the duration of its exposure. An excess of fluoride intake can cause structural and biochemical changes in muscles and tissues .Most commonly caused diseases are dental carries mostly among children, [Mahramanlioglu et al.,2002] brittle bones ,cancer ,osteoporosis etc. [Chinoy,1997; Harrison,2005;]. One of the most common symptom of excess fluoride ingestion is reflected by mottling of teeth in case of mild cases and embrittlement of bones and neurological disorder in extreme case[Fan et al., 2003:Bhatnagara et al.,2011].

The excessive concentration of fluoride in drinking water and its adverse impact on human health have increased the need of defluoridation studies. Treatment of waste water containing fluoride ion has been done using various methods like ion exchange ,membrane filteration , precipitation , electrocoagulation and flocculation, and adsorption have been used for fluoride removal. Amongst these methods adsorption is the most effective and widely used method because it has low maintenance cost. It is applicable for fluoride removal in at very low concentrations and it is universal. In recent years, considerable attention has been focused on the study of fluoride removal using natural ,synthetic and biomass materials such as activated alumina, calcite, fly ash, chitosan beads, attapulgite, red mud, chitosan beads , alum sludge, hydrated cement ,etc.**[**Hua et al.,2008;Bhatnagara et al.,2011**]**

1.2 SOURCES OF FLUORIDE

The various sources of fluoride are

Fluoride containing rocks

Fluoride is largely distributed in the geological environment in the form of minerals like eg fluorite, biotites, topaz etc. Fluoride containing rocks are one of the major sources of fluoride ion. Fluoride ions present in these rocks gets dissolved in water and hence fluoride enters the ground water. [Abe et al.,2004;Banks et al., 1995; Edmunds etc al.,2005; Apambire et al.,1997; Reddy et al.,2003; Shen et al.,2003].The figure 1.1below shows a comparison of the amount of fluoride released by different types of rocks.

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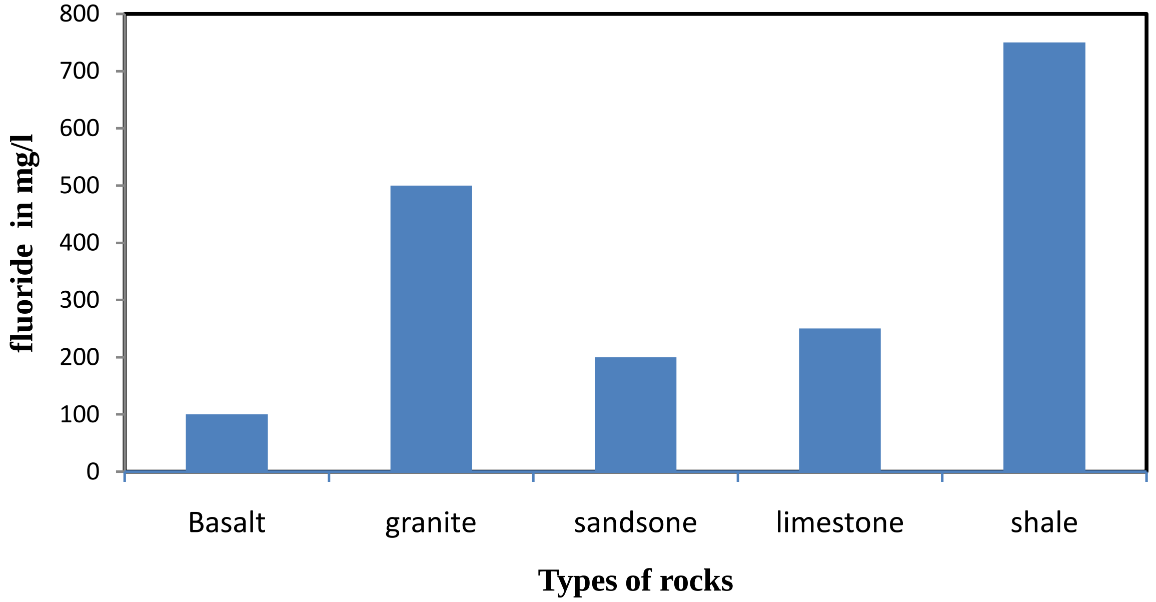


Figure 1.1: Comparison of the amount of fluoride released by various types of rocks.[Jacks et al.,2005].

Industries releasing fluoride

Fluoride ion is also released from a number of industries like glass, ceramic, electropalating ,brick and iron work ,etc which have a very high fluoride concentrations ie ten to thousands of mg/l of fluoride.[Bhatnagara et al.,2011].

1.3 PROPERTIES OF FLUORIDES:

Fluoride is a highly reactive and hence it does not occur in free state.The various properties of fluoride are listed in the table below.

Table1.1. Properties of fluoride[web 1]

Property	**Value**
Physical state	Pale yellow green coloured gas
Melting point	-219 °C
Boiling point	-188 °C
Density	$1.8*10^{-3}$ g/cm^3 at 20 °C
Water solubility	42 g/litre at 10 °C
Atomic mass	18.998403 g/mol

1.4 EFFECT OF FLUORIDE ON HUMAN HEALTH

The effect of fluoride on human health depends on the concentration and duration of its exposure. Fluoride in drinking water could be beneficial to human health if it is in a very small concentration and harmful if the concentration exceeds the permitted value.

On the other side , an excess of fluoride can cause

1) Mottling of teeth in mild cases
2) brain damage, brittle bones, osteoporosis
3) embrittlement of bones and neurological disorder in extreme cases

Besides these there are reports which also indicate that fluoride maty also interfere with DNA synthesis and can cause structural and biochemical changes in muscles and nerves.

[Bhatnagara et al., 2011].Concentration of fluoride in drinking water and its impact on human health are listed in the table 1.2 below:

Table 1.2:Concentration of fluoride in drinking water and its impact on human health(Jacks et al.,2005)

Concentration of fluoride (mg/l)	**Effect on human health**
Nil	Limited growth and fertility
<0.5	Dental caries
0.5-1.5	Promotes dental health and prevents tooth decay
1.5-4.0	Dental fluorosis(mottling and tooth decay)
4.0-10.0	Dental fluorosis, skeletal fluorosis (pain in neck bones and back)
>10.0	Crippling fluorosis

Table 1.3 : Various forms of fluorosis(Jacks et al.,2005)

Type	**Effect**
Dental fluorosis	• Affects teeth and its common in children • Teeth become yellow • The disease has mostly cosmetic implication and has no treatment
Skeletal fluorosis	• It affects the bones and skeleton • Neck, hip, shoulder and knee joints are effected commonly • Not easily detectable • In severe cases complete rigidity of joints occurs
Non-skeletal manifestations	• Soft tissues of the body are affected

	• Symptoms include gastro intestinal complaints, loss of appetite pain in stomach, constipation followed by diarrhea, muscular weakness and neurological manifestations. • Cardiac problems, still birth , male infertility

Prevention of fluorosis

- **Using alternate water resources**
  It includes the use of surface water, rain water and low fluoride groundwater.
- **Improving the nutritional status of food**
  Adequate calcium intake
  Vitamin C ingestion.
- **Defluoridation**
  Removing excess fluoride from drinking water using different techniques.(Jacks et al.,2005)

1.5 PERMISSIBLE AMOUNT OF FLUORIDE

According to World Health Organization (WHO) guidelines the permissible concentration of fluoride in drinking water is 1.5 mg/L.(Zhang et al.,2005)

1.6 FLUORIDE CONTAMINATION IN INDIA

High concentration of fluoride have been reported in India ,China ,Bangladesh ,Morocco, Kenya and other parts of the world.(Chinoy et al.,1991).In India excess of fluoride ion is common in some of the semi arid regions given below

1 areas of Rajasthan,

2 southern Punjab

3,Gujarat ,Karnataka and Tamil Nadu etc

Some areas of Andhra Pradesh have reported such high concentration as 5 mg/l. A broad survey report of the country shows that fluoride concentration varies from 5 to 50 mg/l and about millions of people in rural areas consume unsafe drinking water and fall prey to several diseases especially fluorosis.(web 2)

CHAPTER 2

LITERATURE REVIEW

2.1 LATERITE SOIL

Laterite soils are rusty and red in colour and are found in various parts of the country. The word "laterization " means prolonged and intensive chemical weathering producing a variety in thickness, grade, chemistry and mineralogy. The common features of laterite are as follows:

- It is rich in iron and aluminium.
- Formed in hot and humid areas especially in the land areas between the tropics of Cancer and Capricorn.
- Used in waste water treatment especially for removal of phosphorous and heavy metals like chromium, cadmium, lead ,etc. It is also used for removal of arsenic and fluoride.(web 3) **.**

Table 2.1: Showing important constituents of laterite soil (EDX analysis)

Constituent	Atomic %	Weight %
IRON	32.33	12.88
ALUMINIUM	6.14	5.08
SILICATES	10.23	8.13

Work done by different authors on different methodologies for fluoride removal

1) **Tembhurkar and Dongre., [2006]** studied the application of activated charcoal of commercial grade for removal of fluoride. Batch experiments were performed and the effect of major parameters like pH, dose of adsorbent, rate of stirring, contact time and initial adsorbate concentration on fluoride removal efficiency were optimized. It was observed that fluoride removal is possible from pH 2 to 8 with a maximum fluoride removal efficiency of 94% at pH 2 at optimum conditions. The percentage of fluoride removed depended on pH, adsorbent dose and contact time at a given initial solute concentration. Equilibrium data was fitted to both Langmuir and Freundlich isotherm and the kinetics of the process was determined. Langmuir isotherm fitted better to the adsorption data.
2) **Meenakshi and Maheshwari., [2006]** studied the applicability of membranes for the defluoridation of water. The membrane separation process causes the disinfection and treatmenrt of water in a single step. Membrane also removes pollutants, pesticides,microorganisms and inorganic and organic micropollutants ,etc. The process is highly simple, reliable, highly efficient though somewhat expensive compared to other options. Life of membrane is long and process operates with minimal manpower. Not only fluoride but other ions are also removed. Remineralization of water was required after treatment so as to add the other essential components. Maintenance is low and water quality is ensured.
3) **Tahikt et al.,[2007].** A study was performed in Morocco, a fluoride affected region to investigate the harmful effect of fluoride on teeth and skeleton .NF400 and NF 90 was used for fluoride removal .The fluoride removal operations were performed on underground water and the major parameters like pressure, initial fluoride content and volume reduction factor was studied. While NF400 gave satisfactory result for lower values of initial fluoride content, the NF90 membrane rejected fluoride and other ions

6)Viswanathan et al.,[2009] studied the defluoridation of fluoride by modification of Chitosan beads (CB).It was observed that Chitosan beads have very low defluoridation capacity (DC) but on modification by introduction of COOH and NH3+ groups via carboxylation and protonation the DC value increases for raw chitosan from 52 mgF -/kg to 1800 mg F^-/kg for protonated cum carboxylated chitosan beads (PCCB).The suitability of PCCB was tested using water sample from fluoride endemic area .The sorbent lowered fluoride from 2.33 mg/l to the required level. About 0.5 g of PCCB was used for a 50 ml of sample, for 30 min at room temperature.It was also noticed that PCCB also removed other common ions but this did not effect the reduction of fluoride to the tolerance value. Equilibrium data was fitted to both Langmuir and Freundlich isotherm and the kinetics of the process was determined .Freundlich isotherm fitted better to the adsorption data. It followed the pseudo second order kinetics thus intra particle diffusion could be accounted as one of the major reasons responsible for fluoride removal.

2) **Chen et al., [2010].** A new adsorbent was developed using granular ceramic which is stable Al-Fe surface complex for removal of fluoride from water. Physical properties such as Particle size ,pore size, surface roughness of the granular ceramic were determined using BET, SEM and EDS. Batch experiments were performed and the effect of major parameters like pH , dose of adsorbent,rate of stirring, contact time and initial adsorbate concebtration on fluoride removal efficiency were optimized. Equilibrium data was fitted to both Langmuir and Freundlich isotherm and the kinetics of the process wa determined .Freundlich isotherm fitted better to the adsorption data. It followed the pseudo second order kinetics thus intra-particle diffusion could be accounted as one of the major parameters responsible.Effect of anions.Phosphate and Sulfate and cations i.e calcium and Magnesium were studied.While the adsorption of fluoride increased with the concentration of cations it decreased with an increase in the concentration of the anions.it was ensured that water quality was maintained and no aluminium or ferric ions were leached out.

3**)Malakootian et al.,[2011].** Pumice was used for fluoride removal from the synthetic water. Batch experiments were performed and the effect of major parameters like pH , dose of adsorbent,rate of stirring, contact time and initial adsorbate concebtration on fluoride removal efficiency were optimized. It was noted that at neutral pH ,time 3 hrs ,20 mg/l of pumice and with 2 mg/l of initial fluoride dose the adsorption process was 87.75 efficient.A case study was also performed on the Kuhbonan water keeping pH 7, time 3 hrs the adsorption process was 74.64 % efficient Equilibrium data was fitted to both Langmuir and Freundlich isotherm and the kinetics of the process was determined .Freundlich isotherm fitted better to the adsorption data. It followed the pseudo second order kinetics thus intra particle diffusion could be accounted as one of the major parameters responsible .Thus it was shown that pumice is a low cost and highly efficient adsorbent for fluoride removal.

5)Ganvir and Das ,[2011] An attempt was made to develop a user friendly defluoridation method using low cost, abundantly available and highly efficienrt adsorbent. For this purpose surface modified RHA was used .It was coated with aluminium hydroxide and it was found that the adsorption capacity was directly increased with the amount aluminium hydroxide coated . Adsorption capacity was found to be between 9 and 10 for RHA. For aluminium hydroxide coated RHA adsorption capacity was 15.08 mg/g for batch mode and 9.5 mg/g for column mode. Process was found to be pH depended with 5 as the best pH. A filteration unit was designed to treat 1250 l of 5 mg/l of fluoride tap water at a flowrate of 5L/h to lower the fluoride value to the permissible limit.

Table 2.2: Statistical data showing areas affected and problems faced due to fluoride contamination.

Serial No	Reference	Statistical Data	
		Region Affected by fluoride contamination	Problems faced due to high fluoride content .
1	Jacks et al.,2005	• In India about 14 states and 150,000 villages suffer from fluoride contamination. • The problem is more pronounced in the states of Andhra Pradesh,Bihar ,Gujarat,Tamil Nadu, Madhya Pradesh, Rajasthan,Uttar Pradesh,etc.	• About 62 million people are at risk of fluorosis. • In Nagaur district Rajasthan about 25% population suffers from dental fluorosis and 10 % from skeletal fluorosis.
3	Ganvir and Das, 2011	• Endemic fluorosis occurs in at least 25 countries across the globe. • In China 28 provinces are affected by fluoride contamination. • In Sri Lanka,Dissanayake fluoride concentration upto 10 mg/l have been reported in ground water	• About 62 million people are at risk of fluorosis across the globe. • Over 6 million children are suffering from dental fluorosis , skeletal fluorosis and non- skeletal

		in dry zone. • In India 19 states have reported health problems due to high fluoride contamination	fluorosis.
4	Maiti et al.,2011	• High fluoride contamination have been reported especially in countries like China ,Iran,Joran, India,Pakistan ,Thailand and Japan.	• Dental, Skeletal and non skeletal fluorosis have been reported.
5	Tembhurkar and Dongre., [2006]	• Excessive fluoride contamination have been reportedby many countries like India, Sri Lanka,China, Rift Valley countries in East Africa, Turkey, and parts of South Africa. • In India 19 states have reported health problems due to high fluoride contamination.	• An intake of 6 mg/day of fluoride leads to multi – dimensional health problems like dental, skeletal and non skeletal fluorosis .

2.2 VARIOUS METHODOLOGIES FOR FLUORIDE REMOVAL

Due to an increase in human activities excess of fluoride is being emitted .Industries discharge effluents highly loaded with fluoride .The excess of fluoride is harmful in many ways thus there is a need to bring down the fluoride level to the safe limit .For this purpose the treatment of water is done using a number of methodologies .Some of the common methodologies are coagulation and precipitation, ion exchange, electrochemical methods, nano filteration ,membrane separation ,adsorption, etc

Electrochemical removal of fluoride

PAOA-modified carbon felt electrodes were taken in a continuous flow reactor .The effect of various parameters like the inlet flow rate, initial fluoride concentration, voltage and pH was studied. The process was operated under a wide pH range. It was observed that PAOA-modified carbon felt electrode reactor is a highly efficient and promising system for removal of fluoride from contaminated water. [Cui et al.,2012].

Fluoride removal by nano filteration

Nanofilteration is a very advanced separation method. Carbon nano tubes are used for this purpose [Bhatnagara et al.,2011]. .Advantages of CNT are

1) small size and large surface area

2) high mechanical strength and remarkable electrical conductivities

3) CNTs use latest technology

4) They opearate in wide pH range

5) They have high defluoridation capacity

A study was performed in Morocco, a fluoride affected region to investigate the harmful effect of fluoride on teeth and skeleton .NF400 and NF 90 was used for fluoride removal .The fluoride removal operations were performed on underground water and the major parameters like pressure, initial fluoride content and volume reduction factor was studied. While NF400 gave satisfactory result for lower values of initial fluoride content, the NF90 membrane rejected fluoride and other ions.[Tahikt et al.,2007].

Fluoride removal by Bio-sorbents

The defluoridation can also be done by using biosorbents like cellulose, chitosan etc.The defluoridation was done by modification of Chitosan beads (CB).It was observed that Chitosan beads have very low defluoridation capacity (DC) but on modification by introduction of COOH and NH3+ groups via carboxylation and protonation the DC value increases for raw chitosan from 52 mg F^-/kg to 1800 mg F^- /kg for protonated cum carboxylated chitosan beads (PCCB).The suitability of PCCB was tested using water sample from fluoride endemic area .The sorbent lowered fluoride from 2.33 mg/l to the required level. About 0.5 g of PCCB was used for a 50 ml of sample, for 30 min at room temperature.It was also noticed that PCCB also removed other common ions but this did not effect the reduction of fluoride to the tolerance value. Equilibrium data was fitted to both Langmuir and Freundlich isotherm and the kinetics of the process was determined .Freundlich isotherm fitted better to the adsorption data. It followed the pseudo second order kinetics thus intra particle diffusion could be accounted as one of the major reasons responsible for fluoride removal [Viswanathan et al.,2009] .

Table 2.3 : A comparison of various methodologies for fluoride removal

Serial No	Name of the methadology	Work done, advantages and disadvantages	Efficiency of the process	Reference
1	Electrochemical	• PAOA-modified carbon felt electrodes were taken in a continuous flow reactor. • The effect of various parameters like the inlet flow rate, initial fluoride concentration, voltage and pH was studied. • The process was operated under a wide pH range(pH 5-9). • The process was highly promising and reliable. • It was a little expensive.	• Highly efficient the breakthrough capacity was found to be 10 mg/g.	Cui et al.,2012

2	Membrane Separation	• the disinfection and treatmenrt of water in a single step. • Life of membrane is long and process operates with minimal manpower. • The process is highly reliable. • Other common ions are also removed. • Remineralization of water was required after treatment so as to add the other essential components. • Maintenance is low and water quality is ensured	• Removal efficiency of different types of membranes for fluoride removal lies between 90 - 100%	Meenakshi and Maheshwari., [2006]
4	Nano-filteration	• NF400 and NF 90 was used for fluoride removal. • pH 7.58 for NF400 and pH 7.04 for NF90 • flow rate 750 for NF400 and 700 for NF90 • major parameters like pressure, initial fluoride content and volume reduction factor was studied.	• NF400 rejected 95% fluoride for fluoride conc of 20 ppm and NF 90 rejected 85% fluoride for fluoride conc of 20 ppm	Tahikt et al.,[2007]

		• While NF400 gave satisfactory result for lower values of initial fluoride content, the NF90 membrane rejected fluoride and other ions.		
5	Adsorption	• Various adsorbents have been studied like RHA,activated charcoal,laterite. • Major parameters like pH , time, adsorbent dose , adsorbate concentratio were studied. • The process is found to be highly effective. • It is less expensive.	• Adsorption capacity of coated RHA was found to be 15.08 mg/g for batch mode and 9.5 mg/g for column mode.	• Ganvir and DAS,[2011] • Tembhurkar and Dongre.,[2006] • Sarkar et al.,[2006]

Adsorption

Adsorption is a mass transfer process between the solute in the liquid phase to the adsorbent in the solid phase .Among the various methods for fluoride removal adsorption has been widely explored Advantages of the adsorption process are

1) high defluoridation capacity

2) lower operating cost

3) selectivity

4) easy handling nature
5) simplicity of the process

The efficiency of the process depends on nature of adsorbent, selectivity towards target species, loading capacity and affinity towards adsorbent.(Maiti et al.,2011).The table below lists the different types of sorbents and their properties.

Table 2.4 Various Types of sorbents used for adsorption of fluoride.[Bhatnagara et al.,2011]

Type of sorbent	**example**	**properties**
Aluminium base sorbents	alumina	1)Inexpensive and highly efficient. 2) They require careful handling as aluminium is a neurotoxin
Industrial based	Fly ash,alum	1)high defluoridation capacity in batch mode 2) these materials have been found to be inexpensive
Carbon-based adsorbents	Charcoal, activated carbon	1)lower defluoridation capacity in batch mode. 2)surface modification is done to enhance defluoridation capacity
Natural materials	bauxite, laterite, palygorskite, bentonite and kaolinite	1)contain gibbsite or aluminium oxides 2)Laterite soil high defluoridation capacity in batch mode 3)difficult regeneration 4)low efficiency under high fluoride concentration

Nano sorbent	Carbon nano tubes	1)latest technology 2)operate in wide pH range 3)high defluoridation capacity
Agricultural based sorbents	Calcium chloride, aluminium chloride , aluminium impregnated corn cobs etc	1)inexpensive 2)renewable 3)eco-friendly 4) lower defluoridation capacity in batch mode 5) surface modification is done to enhance defluoridation capacity

Among the different types of sorbents available laterite is inexpensive, abundantly available and has high defluoridation capacity. The table below shows the work done on laterite as an adsorbent for fluoride removal.

Table 2.5 : Work done on laterite.

Serial No	**Reference**	**Work done**
1	**Sarkar et al.,2006**	• Studied the kinetics and mechanism of fluoride removal using laterite. • The effect of major parameters like pH, fluoride dose , time, adsorbent dose and temperature was studied . • Raw laterite from Bankura district of West Bengal of with particle size 500 microns

		was used. • The equilibrium data satisfied both Freundlich and Langmuir isotherm. • Adsorption process follows Pseudo first order kinetics. • The process was found to be 78.2% efficient for 500 micron particles at pH 6.8. fluoride dose 10 ppm,temperature 303 K , time 195 min and maximum fixation capacity as .8461 mg/g.
2	**Sarkar et al.,2006**	• Studied the design and operation of fixed bed column for the remival of fluoride from water. • Raw laterite from Bankura district of West Bengal of with particle size 500 microns was used. • Operational parameters like the bed height,volume, concentration and flow rate of the feed solution were optimised for the column reactor. • For a column with diameter .6 cm and height 60 cm ,initial fluoride dose 20 ppm ,bed height 20 cm column capacity was found to remain 68 % after five cycles.

3	**Maiti et al.,2011**	• Studied the chemically treated laterite as promising fluoride adsorbent for aqueous system and kinetic modelling. • Laterite soil from local place of Kharagpur was collected and chemically treated • The effect of major parameters like pH, fluoride dose , time, adsorbent dose and temperature was studied. • Laterite was treated at pH 6.5 with 6N HCl for 3 hours. • Optimal pH range was found to be 3-5. • The equilibrium data satisfied both Freundlich and Langmuir isotherm . • Adsorption process follows shrinking core model. • The Qmax for Langmuir model was found to be 37.9 mg/g at 305 K.
4	**Gomoro et al.,2012**	• Studied the removal of fluoride using thermally treated laterite • The effect of major parameters like pH, fluoride dose , time, adsorbent dose and temperature was studied. • RGS i.e red gullale soil from Adiss Ababa of particle size in the range 170-320 microns and thermally treated at 400,500,550,600 and 800 °C were used. • The maximum capacity of 47 mmol/kg

		was obtained for RGS fired at 500 °C.
5	**Wambu et al.,2012**	• Studied the fluoride adsorption onto acid treated laterit mineral from Kenya • The effect of major parameters like pH, fluoride dose , time, adsorbent dose and temperature was studied. • Laterite soil with particle size less than 1000 microns and treated with 0.1 N HCl for 30 min was used**.** • The equilibrium data satisfied both Freundlich and Langmuir isotherm. However Freundlich isotherm fits better to the adsorption data. • The effect of other ions like nitrate, chlorate,sulphate,chloride and phosphate was also studied and it was found that nitare ion has positive impact on fluoride removal. • It was noted that at high conc and high temperature physisorption with intra-particle diffusion of Fluoride dominated whereas at low surface coverage ion exchange mechanism dominated • Maximum adsorption capacity was found to be 10.5 mg/g.
6	**Vithanage et al., 2012**	• Studied the modelling and sorption of fluoride on to iron rich laterite.

		• Laterite obtained from south western parts of Sri lanka was used. • The effect of major parameters like pH, fluoride dose , time, adsorbent dose and temperature was studied. • The equilibrium data correlated to Freundlich isotherm. • Surface complexation modelling shows that both iron and aluminium ion account for adsorptive removal of fluoride.

2.3 OBJECTIVE :-

The aim of the present work is to develop a low cost adsorbent for the removal of fluoride from water in presence of other ions. Point wise objectives are as follows:

1. Assessment of fluoride removal capacity of naturally available laterite soil in batch reactor.
2. Kinetic and equilibrium modeling of the process.
3. Assessment of fluoride removal capacity of naturally available laterite soil in column reactor using surface modified laterite.

CHAPTER 3

ADSORPTION MODELLING

To understand the adsorption process and to quantify the adsorption phenomenon both kinetic and adsorption models are applied.

3.1 Equilibrium modelling

The different types of isotherms models are used to explain equilibrium adsorption.

Freundlich isotherm

The Freundlich isotherm is derived by assuming a heterogeneous surface with a non-uniforn distribution of heat of adsorption over the surface. Non-linear Freundlich adsorption isotherm for monolayer adsorption is given by:

$$q_e = K_f \times C_e^{1/n}$$

or

$$\ln q_e = \ln K_f + 1/n \ln C_e$$

where :

- K_f is the Freundlich constant (l/mg)
- **1/n** is the heterogeneity factor

Langmuir Isotherm

According to Langmuir adsorption theory monolayer adsorption takes place on homogeneous sorption sites of equal energy. The Langmuir adsorption isotherm equation is given below:

$$q_e = K_L q_m C_e / (1 + K_L C_e)$$

or

$$C_e / q_e = C_e / q_m + 1/K_L \, q_m$$

Where

- q_e is the amount of solute adsorbed per unit weight of the adsorbent at equilibrium (mg/g)

- **C_e** is the equilibrium concentration of the solute in the bulk solution(mg/l)
- **q_m** is the maximum monolayer adsorption capacity (mg/g)

K_L is the Langmuir contant related to the adsorption energy(l/mg)

Tempkin Isotherm

According to Tempkin Isotherm

- It considers the interaction between the molecules already adsorbed and to be adsorbed
- Free energy of adsorption is a function of the surface coverage as the rate of adsorption decreases as the adsorbed surface coverage increases.

$$q_e=RT/b \ln(K_T\ C_e)$$

or

$$q_e=B_1 \ln K_T + B_1 \ln C_e$$

where

- **$B_1=RT/b$, b** is the tempkin energy constant (j/mole)
- **K_T** is the tempkin constant

3.2 KINETIC AND DIFFUSION MODELS

Pseudo First order

These are derived based on the residual adsorption capacity of the adsorbent i.e the rate of adsorption is based on the residual adsorption capacity of the adsorbent at any point of time.

$$dq_t/dt=K_f(qe-qt)$$

where

- q_t is the amount of adsorbate adsorbed at time t (mg g^{-1}) ,
- qe is the adsorption capacity at equilibrium (mg g^{-1})
- K_f is the pseudo first order rate constant
- t is the contact time

The integration of the above equation with initial $q_t = 0$ gives the following expression

$\log(q_e - q_t) = \log q_e - K_f t/2.303$

K_f is the pseudo first order rate constant which is determined from the plot of $\log(q_e - q_t)$ against time t.

Pseudo Second order

The pseudo-second order model is represented as

$dq_t/dt = K_s(qe-qt)^2$

where Ks is the pseudo second order rate(g/mg min).Integrating above equation and noting that $q_t = 0$ at t=0, the following equation is obtained:

$q_t = t\ Ks\ q_e^{\ 2}(1 + t\ Ks\ qe)$

The initial sorption rate, h (mg/g min), at t=0 is defined as: $h = Ks\ q_e^{\ 2}$

Bangham Equation

Bangham equation is given as

$\log(\ \log Co/\ (Co - q_t\ m)) = \log(k_o\ m/2.303V) + \alpha \log(t)$

Where V is the volume of the solution(ml) and $\alpha(<1)$ and k_o are constants.

Inter particle diffusion study

The adsorbate transport process from the solution phase to the surface of the adsoebent occurs in several step. The overall adsorption process may be controlled by many factors such as pore diffusion, external or film diffusion, surface diffusion and adsorption on the pore surface, or a combination of one or more step.

According to Weber and Morris, the transient uptake of the solute varies almost proportionately with $t^{½}$ for most adsorption process.The intra particle diffusion model is given as

$q_t = K_{id}\ t^{\ 0.5} + C$

where K_{id} (mg/g min $^{0.5}$) is the rate constant for intra particle diffusion.[Maiti et al.,2011]

CHAPTER 4

MATERIAL and METHODS

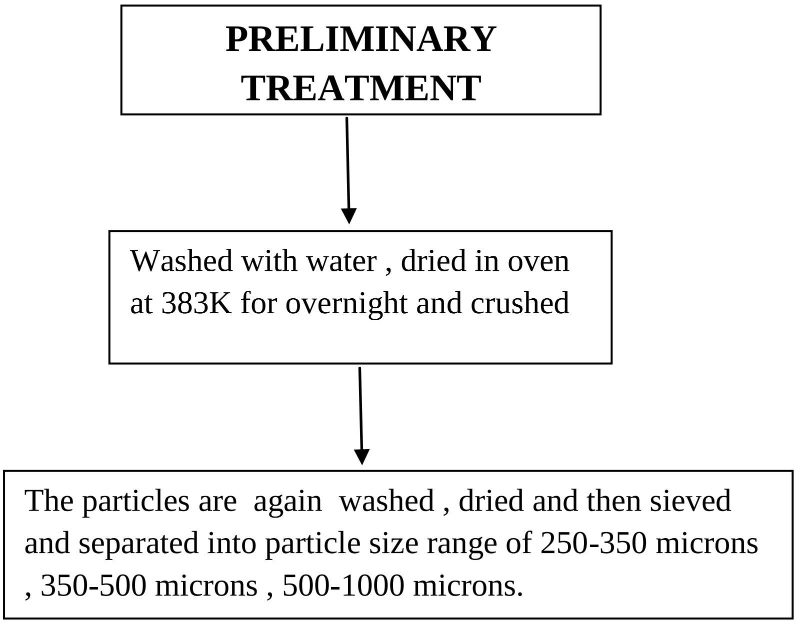
In the present study laterite soil has been utilised for the removal of fluoride from synthetic fluoride solution. Experimental details of the study have been presented in this chapter. All the chemicals that were used were of A.R grade.

4.1 LATERITE SOIL

Laterite soil was brought from the Burdwan district of West Bengal. It was treated for surface modification and used as an adsorbent.

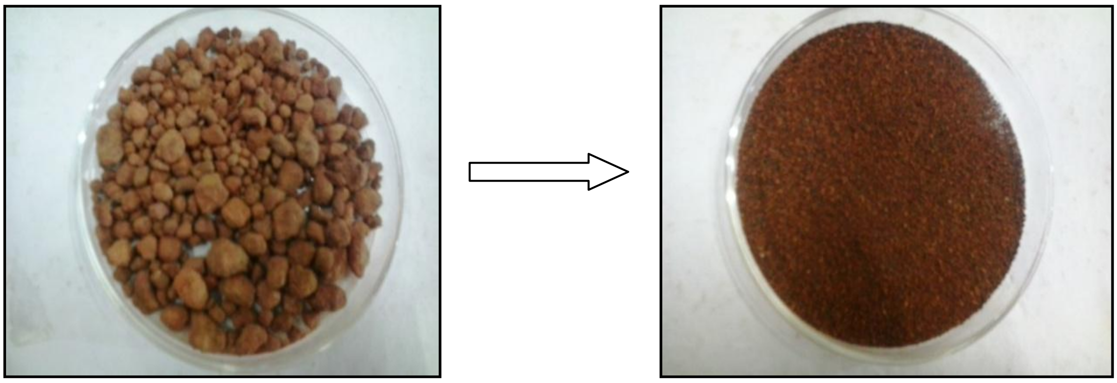
4.2 PREPARATION OF THE ADSORBENT

The laterite soil was washed with water several times and crushed to get particle size in the range of 250 microns to 2000 microns. It was again washed with water several times and dried in oven overnight at 383K **.**Dried laterite particles were sieved and separated into various particle size ranges i.e 250-350 microns, 350-600 microns, 600-1000 microns. Acid treatment was performed on each of the particle size range.



Washed with water , dried in oven at 383K for overnight and crushed

The particles are again washed , dried and then sieved and separated into particle size range of 250-350 microns , 350-500 microns , 500-1000 microns.



Raw laterite brought from Burdwan district of West Bengal

Laterite after Preliminary Treatment

Figure 4.1 Preliminary treatment of raw laterite and laterite before and after preliminary treatment

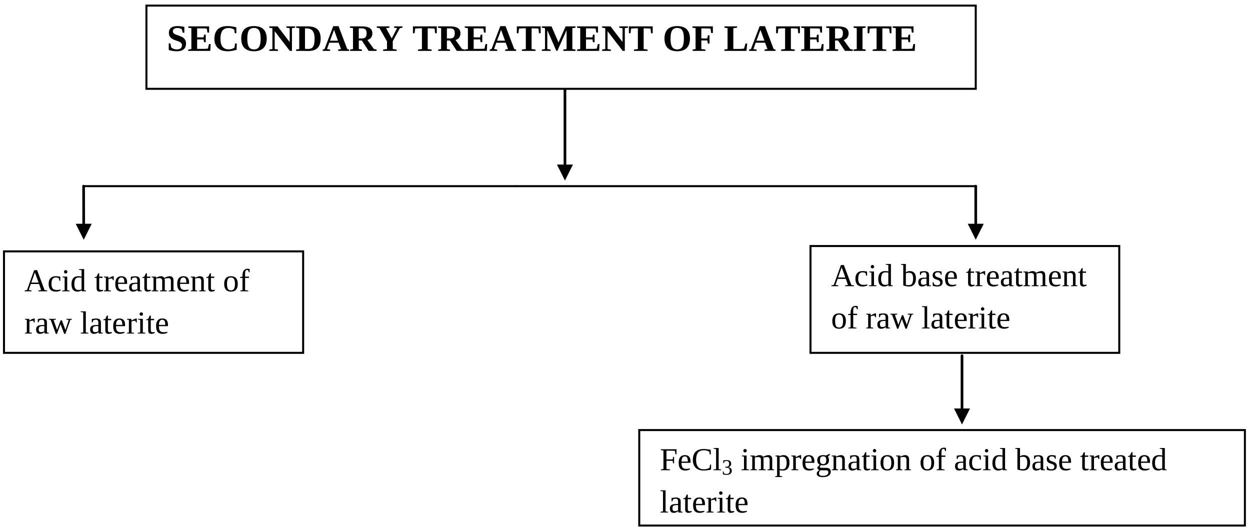
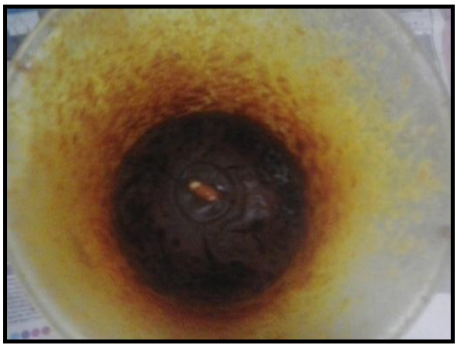


Figure 4.3 Scheme for secondary treatment of laterite

Showing experimental set up for acid treatment



Laterite after acid treatment

Laterite after acid base treatment(250-350) microns

Laterite after acid base treatment(350-500) microns

Laterite after acid base treatment(500-1000) microns

Figure 4.3 Images of laterite sample after secondary treatment of laterite

4.3 ACID TREATMENT PROCEDURE

4.3.1 Acid base treatment

For the acid treatment, 50 grams of laterite was weighed and a 200 ml of 2N HCl solution (prepared from HCl 35.5 % w/v) was added to it . The mixture was heated at 80 °C for 6 hours and after that 200 ml distilled water was added to it and after that 1N NaOH solution (prepared using NaOH pellets of A.R grade) was added to it at room temperature under constant stirring and the final pH of the mixture was adjusted to 6.5.The mixture was kept undisturbed for 24 hrs and the clear liquid was decanted from the top and the mixture was again washed with water and filtered using Wattman filter paper and the filtrate was discarded and the residue i.e solid mass was kept in oven to dry at 383K**.** The dried mass was the acid base treated laterite. [Maiti et al., 2011].

4.3.2 Acid treatment method

About 50 g samples of raw laterite was treated with 0.1 N HCl for 30 , 60, 120, 240 min. Since there was no increase in fluoride uptake by the adsorbent after 30 min treatment it was selected for comparison.[Wambu et al, 2012]

4.3.3 $FeCl_3$ impregnation of acid base treated laterite:

About 20 g of the acid base treated laterite was treated with 200 ml of Ferric chloride solution which contains about 2.5% of Fe^{3+} ions. The final pH was set to 12 by the addition of 1N NaOH solution. For $FeCl_3$ impregnation the solution was heated in water bath and the temperature was maintained at 383K .Heating was done so as to evaporate all the water present in the solution. After that it was dried at 393K for 24h and then washed with millipore water .Washing was done till all the liquid became free from iron. No colour change of wash liquid on addition of $AgNO_3$ and KSCN solution confirmed the absence of chloride ion and ferric ions in the wash liquid, respectively[Mondal et al.,2007].

4.4 TECHNIQUES FOR CHARACTERIZATION OF THE ADSORBENT

The techniques for characterization of the laterite soil have been described below:

Density

The bulk density of the laterite is determined by the MCA bulk density meter.

Surface area

Braunauer-Emmett-Teller (BET) method is used for the determination of the surface area of the sample. This method is based on adsorption of gas on a surface. The amount of gas adsorbed on the surface at a given pressure is used for the surface area determination.

XRD

X-ray diffraction analysis of treated laterite particles before adsorption and after adsorption was done using Phillips diffraction unit. Copper was used as the target material while nickel was used as the filter media and K radiation was maintained at 1.542 10^{-10} m**.** Beyond basic identification XRD can also provide additional information. If the sample is a mixture of two or more components, XRD data can also be analysed for the determination of the proportion of the different minerals which are present in the mixture. Other information so obtained could also include possible deviations of the minerals from their ideal composition(Presence of solid solutions and their element substitutions),The degree of crystallanity of the minerals present, the structural state of the minerals (for deduction of information about temperatures and (or) pressures of formation), and also the degree of hydration for minerals which contain water in their structure.

TGA

The thermo gravimetric analysis (TGA ,Perkin Elmer , Japan) of treated laterite particles is carried out in the temperature range 25 C to 1000 C. It measures the amount and rate (i.e velocity) of change in the mass of a given sample as a function of time or temperature in a controlled atmosphere. These measurements are done for the determination of the thermal and oxidative properties as well as compositional properties.

The technique can be used for the analysis of

1) multi- component Systems

2) the effect of reactive or corrosive atmosphere

3) thermal stability , oxidative stability

4) estimated life time of the product

5) decomposition kinetics of the material

6) moisture and volatile content of the material

FESEM

FE-SEM stands for Field Emission Scanning Electron Microscopy (Quanta 200 F, Netherland) shows the morphological characteristics of the laterite soil. Electrons are liberated from the field emission source and accelerated at a high voltage in a high vaccum column. These electrons strile the surface of the object and secondary electrons, back scattered electrons are emitted.A detector detects the intensity of the secondary electrons and generates electronic signals which are the amplified and transformed to produce a digital image that can be seen on a monitor.

4.5 PREPARATION OF THE SYNTHETIC SOLUTION

Synthetic fluoride solution was prepared using NaF(molecular weight 41.99 g/mol). One liter of the NaF solution was prepared by adding 1 gram of NaF to 1000 ml distilled water and it was used as the stock solution and appropriate dilutions were done to prepare fluoride solutions of different concentration.

4.6 ANALYTICAL MEASUREMENTS

SPANDS METHOD

The SPANDS calorimetric method was used for the analytical measurement of the fluoride sample .It utilizes the reaction between zirconium dye and the fluoride. Fluoride reacts with the dye and forms a colourless complex anion (ZrF_6^-). As the amount of fluoride increases the, the intensity of the colour so produced decreases.[APHA,1999]

SPANDS solution: About 958 mg of the SPANDS, sodium 2-(parasulfophenylazo)-1, 8-dihydroxy-3, 6-napthalene disulfonate, was dissolved in 500 ml of distilled water . Thi s solution is stable for one year if kept in shade i.e protected from direct sunlight.

Zirconyl acid reagent: About 133 mg of Zirconyl chloride octahydrate $ZrOCl_2.8H_2O$ was weighed. It was dissolved in 25 ml of distilled water , 350 ml of concentrated HCl (9.7 N) was added to the solution. The final mixture was diluted with distilled water and the volume was made upto 500 mL.

Acid zirconyl-SPANDS reagent:

Equal volumes of SPANDS solution and Zirconyl-acid-reagent were taken and then mixed. The combined reagent so formed so formed is stable for at least 2 years.

Reference solution: The reference solution was made by adding 10 ml of SPANDS solution to 100 ml of distilled water .And the 7 ml of concentrated HCl (9.7 N) diluted to 10 ml was added to the diluted SPANS solution .The reference solution is stable for one year. It is used for setting the instrument reference point or zero point.

Preparation of the standard curve

Fluoride solutions of different concentration like 0.0563, 0.113, 0.225, 0.337, 0.45 mg F^-/L were prepared by diluting suitable quantities of standard fluoride solution to 50 ml with distilled water. And then add 10 ml of mixed acid-zirconyl SPANDS reagent .The mixture was then added to each of the solution earlier prepared and mixed well. The reference solution was used to set the instrument i.e UV Spectrophotometer to zero absorbance .The absorbance readings of the standards were used to plot a graph between the concentration of fluoride in milligrams and absorbance with λ_{max} as 575 nm .The caliberation curve is shown below in figure 4.4.

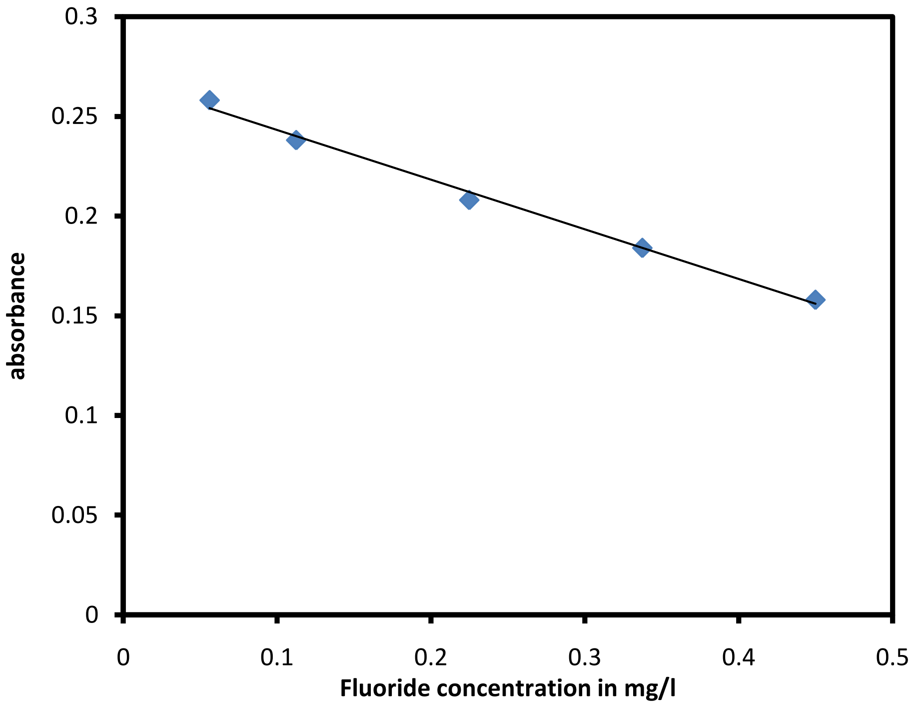


Figure 4.4 Calibration curve between absorbance and concentration of fluoride in milligrams

4.7 EXPERIMENTAL PROCEDURE

Batch experiments were performed so as to study the effect of major parameters like pH , mass of the adsorbent m , initial fluoride dose C_0 and time t. For each experimental run about

50 ml of fluoride solution known concentration and known amount of adsorbent were taken in a 50 ml stoppered conical flask at 30 C. The pH and time were accordingly adjusted .The mixture was agitated at constant speed of 150 rpm. Samples were tested at appropriate time intervals and analysed for the residual fluoride concentration by SPANDS method using UV spectrophotometer.

Parameter studied

1) **pH** :The pH of the solution was varied from 2 to 10 by adding either dilute aqueous solutions of HCl (0.1 N) or NaOH (0.1N).
2) **Adsorbent dose**: The adsorbent dose was varied from 0.25 g to 0.125 g in a 50 ml fluoride solution of known concentration
3) **Fluoride dose**: The fluoride dose was varied from 5.625 ppm to 45 ppm.
4) **Time** :The time was varied from 15 min to 360 min.

Table 4.1 Experimental procedure.

<table>
<tr><th>Parameters</th><th colspan="9">Values</th></tr>
<tr><td>pH</td><td colspan="2">2</td><td colspan="2">4</td><td colspan="2">6</td><td colspan="2">8</td><td>10</td></tr>
<tr><td>Adsorbent dose (g)</td><td colspan="2">0.025</td><td colspan="2">.05</td><td colspan="2">.075</td><td colspan="2">0.1</td><td>0.125</td></tr>
<tr><td>Fluoride dose (ppm)</td><td colspan="2">5.625</td><td colspan="2">11.25</td><td colspan="2">22.5</td><td colspan="2">33.75</td><td>45</td></tr>
<tr><td>Temperature K</td><td colspan="2">293</td><td colspan="2">298</td><td colspan="2">303</td><td colspan="2">313</td><td>323</td></tr>
<tr><td>Time (min)</td><td>15</td><td>30</td><td>45</td><td>60</td><td>120</td><td>180</td><td>240</td><td>300</td><td>360</td></tr>
</table>

The reaction was carried till fluoride laterite system attained equilibrium. The equilibrium data so obtained was used for the generation of adsorption isotherms and for the determination of kinetics of the process. The residual fluoride concentration was determined by dilution of the fluoride to the appropriate level followed by analytical measurement via SPANDS method.

Batch tests were carried out to study the adsorptive capacity of the adsorbent i.e acid base treated laterite, acid treated laterite and thermally treated laterite .The adsorbent with the maximum adsorption capacity was used for characterization and optimization of the adsorption process. Blank experimental runs with only different amounts of the adsorbents in 50 ml of double distilled water, were conducted simultaneously at similar conditions to account for any colour leached by the adsorbents or adsorbed by glass conatainers. The percentage removal of fluoride and the amount of fluoride adsorbed on the surface of the adsorbent i.e equilibrium uptake of fluoride, q_e (mg/g) was calculated using the following relationships

Percentage Removal=$100\times(C_o-C_e)/ C_o$

Amount adsorbed, $q_e = V\times(C_o-C_e)/m$

Where:

- C_o is the initial fluoride concentration (mg/l)
- C_e equilibrium concentration of fluoride
- V is the volume of sample(ml)
- m is the mass of the adsorbent (mg)

4.8 CONTINUOUS MODE STUDY

For continous study a column reactor was used and the optimised values of pH , temperature were taken from batch experimental study.

Column Reactor

The column reactor used in the present study had diameter of 3 cm and height about 60 cm. The figure 4.5 in the next page shows the column used in the present study.

Figure 4.5 :Column reactor.

Adsorbent

Acid treated laterite soil was used as adsorbent**.** The particle size used was 1700-2500 microns.

Experimental Program

The effect of various parameters such as flow rate, fluoride dose, volume, bed height of laterite soil and time were studied. The effect of various parameters like flow rate ,fluoride dose and bed height on the removal of fluoride were studied for the column reactor .Values of the parameters used in the present study are listed in table 4.2.

Table 4.2: Experimental Program for column reactor

Parameters	**Values**				
Flow rate (ml/min)	21.74	43.48	65.72	89.96	108.7
Fluoride dose(ppm)	11.25	22.5	33.75	-	-
Bed Height(cms)	15	30	45	-	-

CHAPTER 5

RESULTS AND DISCUSSION

The experimental results are given in detail in this chapter.

5.1 CHARACTERIZATION OF THE ACID BASE TREATED LATERITE SOIL

Characterization includes bulk density, BET surface area, XRD , DTA-TGA, FESEM , EDX.

5.1.1 BULK DENSITY

The bulk density of the acid base treated laterite was found to be 1352 kg/m^3

5.1.2XRD

The d spacing values of the X-ray spectra of acid base treated laterite before and after adsorption shown in figure 5.1 and figure 5.2.Indicate the presence of pure goethite for values of 24.7 , 38.7, 42.8, 62.5 and a slight shift in peaks indicates substitution of Fe atoms by other available atoms present in the system like aluminium.XRD peaks at 31.1, 24.3 ,59.0 and 81.7 indicate the presence of silicon oxide. Further value of 41.6, 47.9 ,53.7 ,62.7, 71.1 and 74.1 correspond to weak crystalline compounds ferrihydrite and haematite.

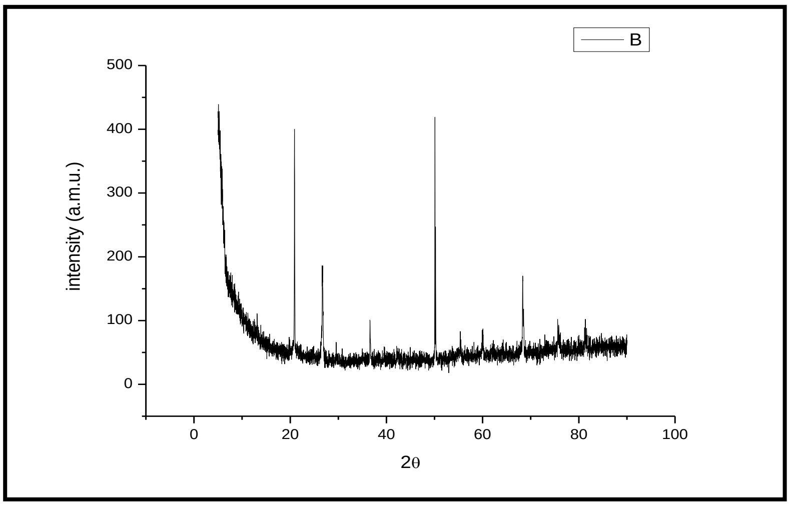


Figure 5.1 XRD image of acid base treated laterite before adsorption

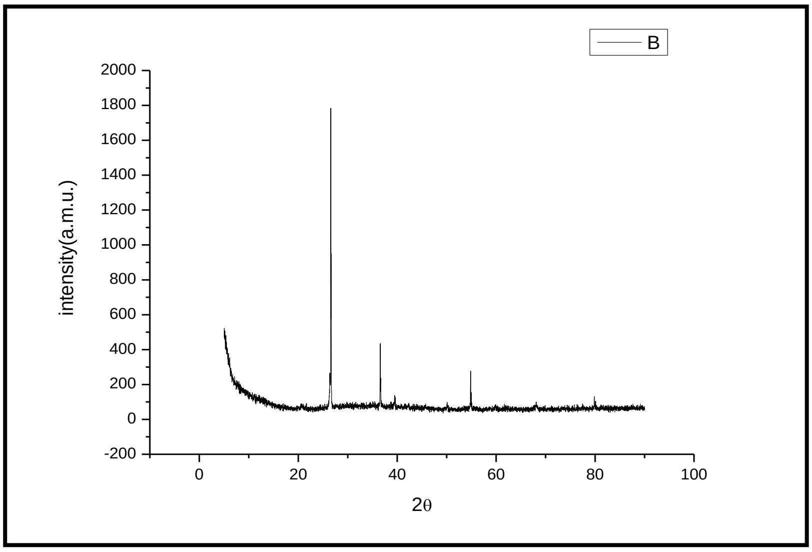


Figure 5.2 :XRD image of acid base treated laterite after adsorption

5.1.3 BET SURFACE AREA

The BET surface area values of the acid treated laterite before adsorption and after adsorption are given in the table 5.1.It was observed that BET surface area increases after acid treatment from 11.1206 m^2/g for raw laterite to 26.6720 m^2/g for acid base treated laterite as the volatile matter is removed after acid treatment.

Table 5.1 : BET surface area values and pore volume values for raw and treated laterite before and after adsorption.

Type	**Parameter**	**Value**
Raw laterite after preliminary treatment.	BET surface area	11.1206 m^2/g
	PORE volume	0.016550 cm^3/g
Acid treated laterite before adsorption	BET surface area	26.6720 m^2/g
	PORE volume	0.027892 cm^3/g
Acid treated laterite after adsorption	BET surface area	6.6291 m^2/g
	PORE volume	0.011026 cm^3/g

5.1.4 TGA

The TGA analysis for raw laterite and acid base treated laterite soil was done and the results are shown in the figure 5.3 and 5.4. The TGA analysis was done between the 298 K to 1298K. For raw laterite about 6% weight loss occurs between 298K to 773K which could be because of oxidation of silica and carbonaceous compounds. A weight of loss 1% between 773 K to 1298 K.

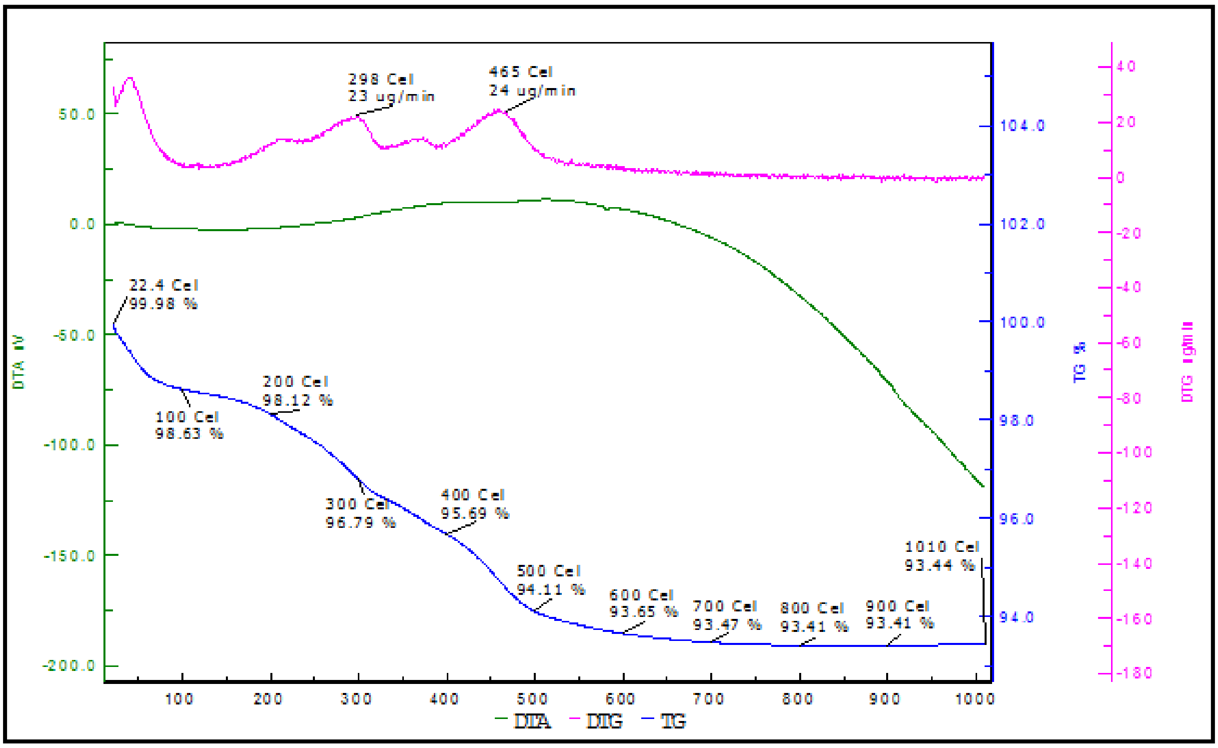


Figure 5.3 TGA analysis of raw laterite.

For acid base treated laterite about 6% weight loss occurs between 298 K to 773 K which could be because of oxidation of silica and carbonaceous compounds. A weight loss of 1 % between 773 K to 1298 K.

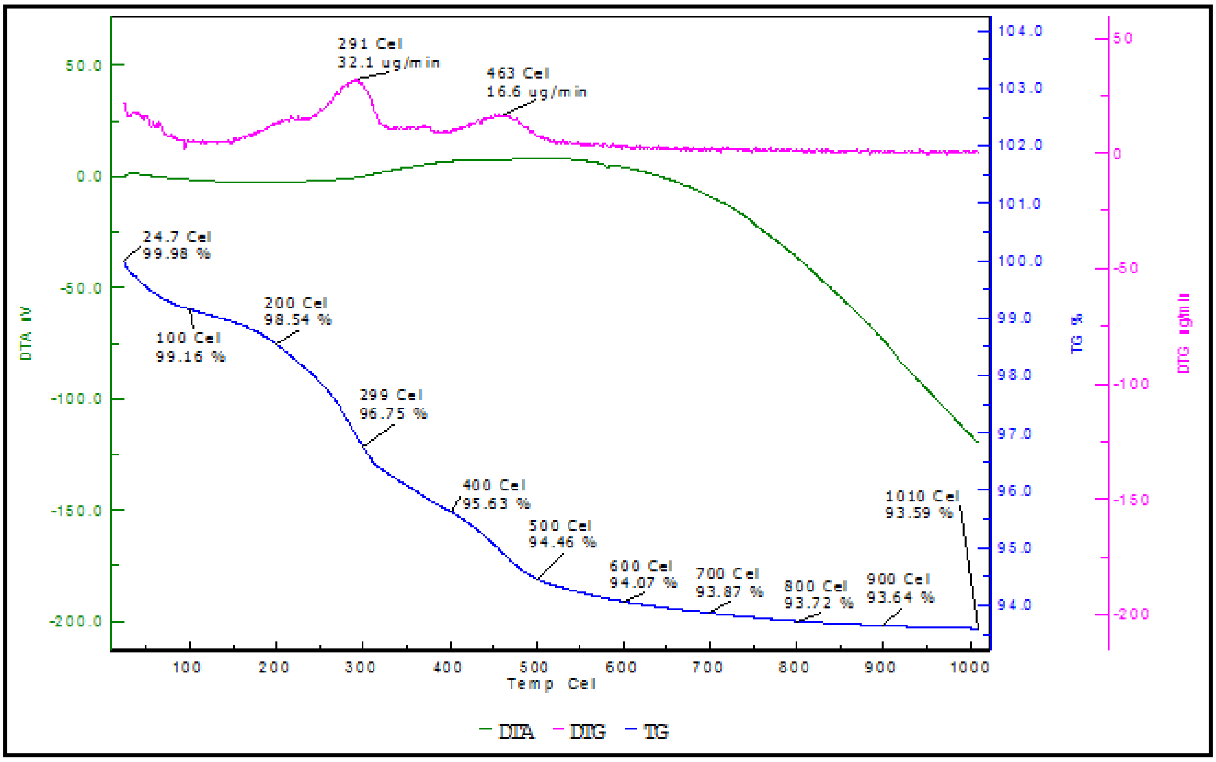


Figure 5.4 TGA Analysis of acid base treated laterite soil.

FESEM

The figures 5.5 , 5.6 , 5.7 , 5.8 ,5.9 , 5.10 and 5.11 shows FESEM images of raw laterite and treated laterite.

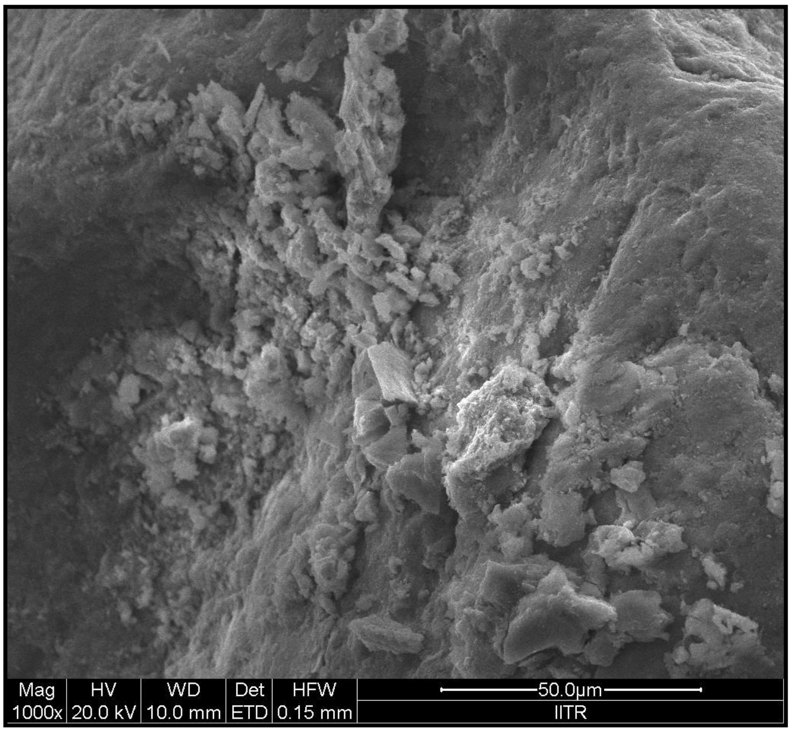


Figure 5.5 FESEM image of raw laterite

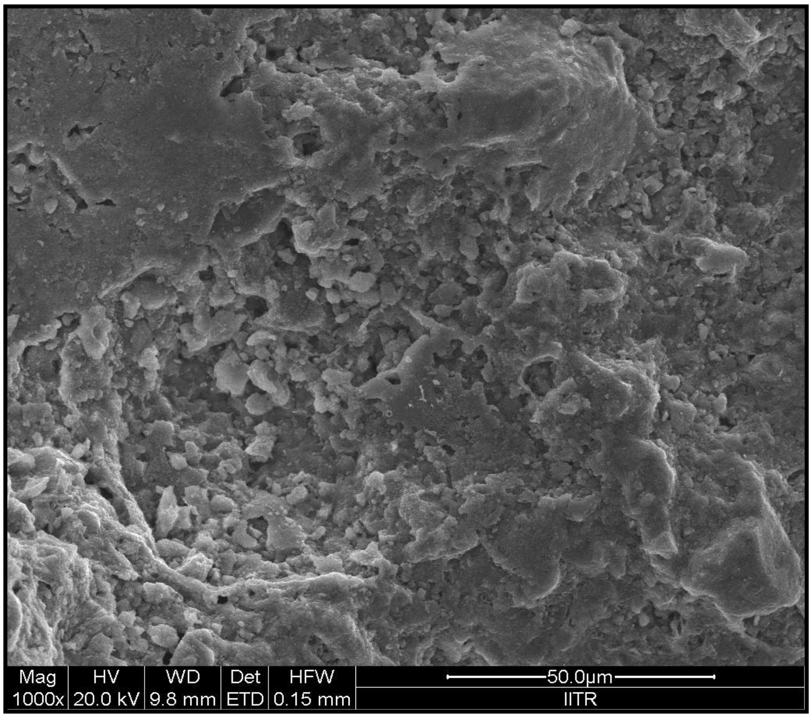


Figure 5.6 FESEM image of acid base treated laterite before adsorption

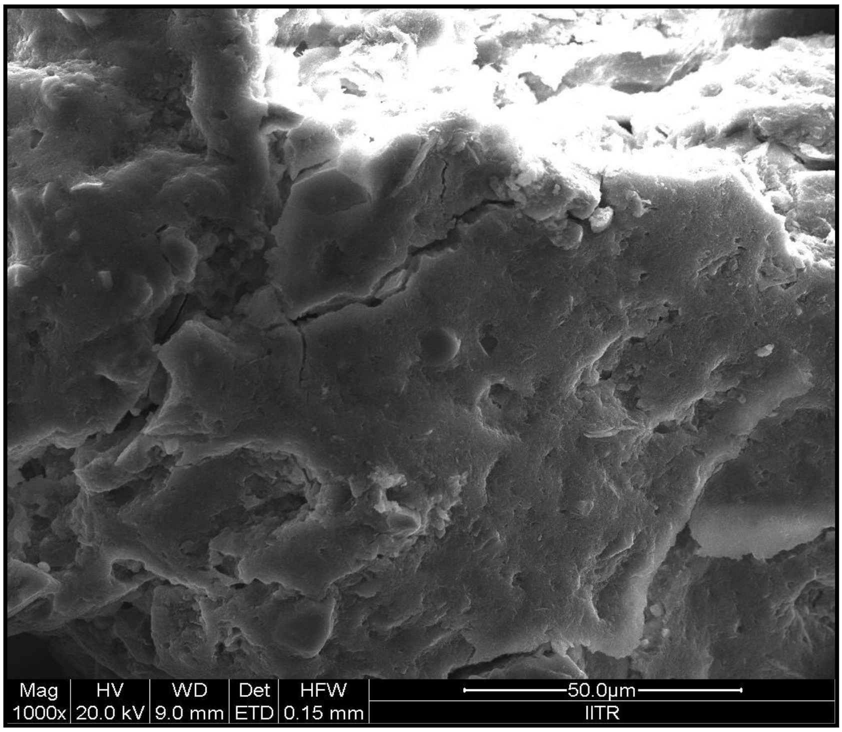


Figure 5.7 FESEM image of acid base treated laterite after adsorption

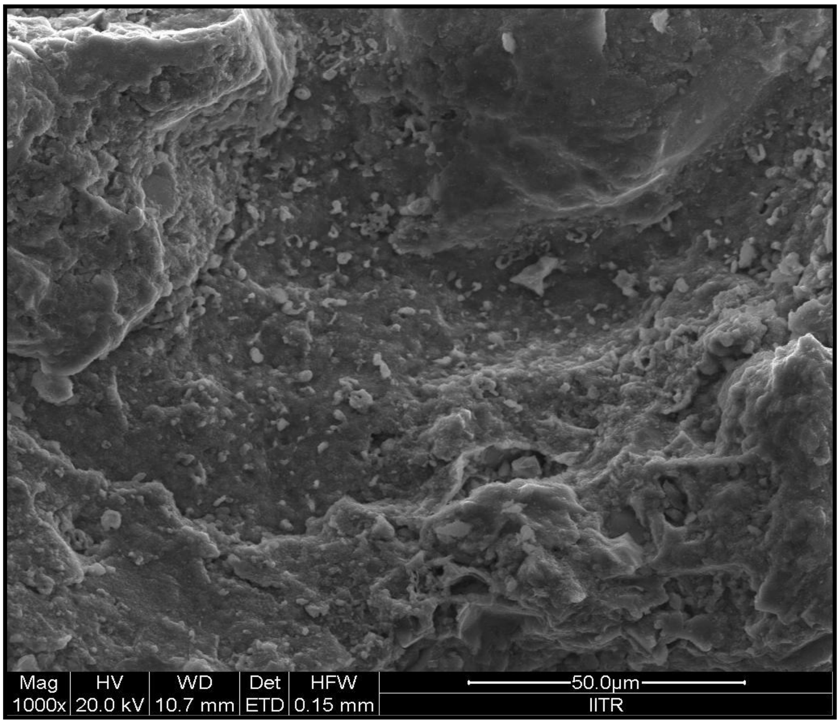


Figure 5.8 FESEM image of acid treated laterite

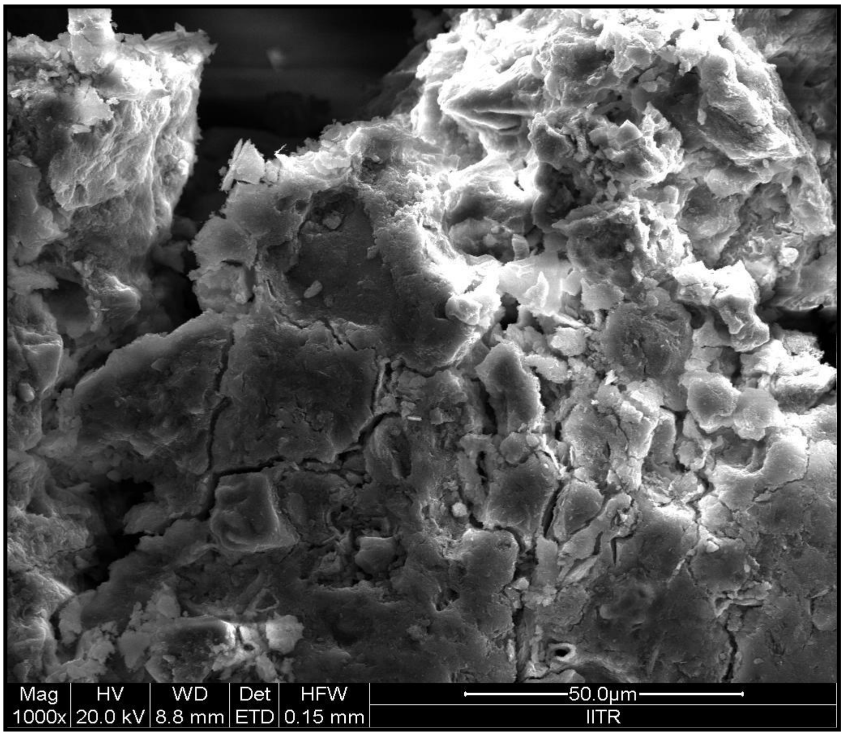


Figure 5.9 FESEM image of acid treated laterite after adsorption

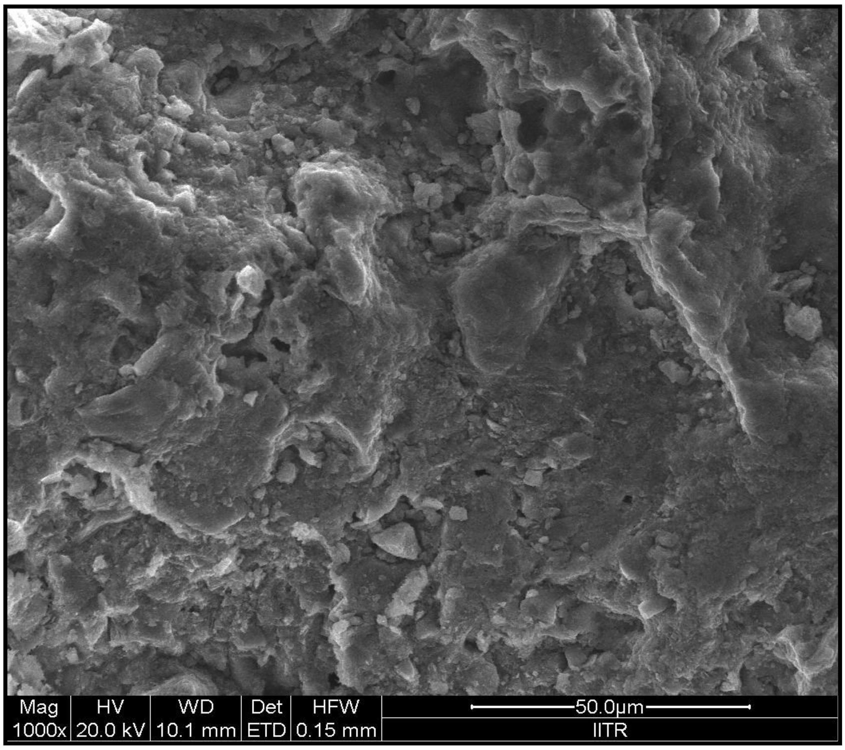


Figure 5.10 FESEM image of $FeCl_3$ impregnated acid base treated laterite before adsorption

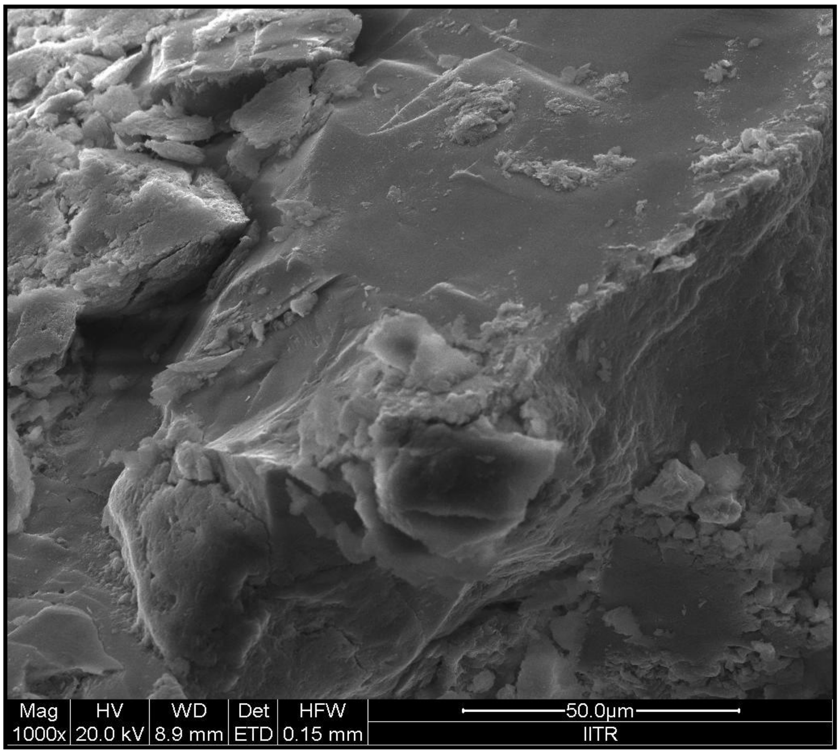


Figure 5.11 FESEM image of $FeCl_3$ impregnated acid base treated laterite after adsorption.

Table 5.2 EDX of Raw Laterite

Element	Weight%	Atomic%
C K	6.79	12.62
O K	43.55	60.75
Al K	6.14	5.08
Si K	10.23	8.13
Mn K	0.41	0.17
Fe K	32.23	12.88

Table 5.3 EDX of acid base treated laterite before adsorbtion

Element	Weight%	Atomic%
C K	6.94	12.60
O K	45.97	62.66
Al K	5.14	4.15
Si K	10.59	8.22
Mn K	0.33	0.13
Fe K	30.22	11.80

Table 5.4 EDX of acid treated laterite after adsorbtion

Element	Weight%	Atomic%
C K	16.97	24.77
O K	51.66	56.60
F K	2.33	2.15
Al K	6.09	3.96
Si K	16.73	10.44
Mn K	3.60	1.15
Fe K	1.50	0.47

5.2 BATCH EXPERIMENTAL STUDY

The effect of various parameters such as pH, concentration , fluoride dose, adsorbent dose , time and temperature were studied.

5.2.1Effect of pH

The pH of the solution affects the surface charge of the adsorbent. It also affects the degree of ionisation**.** The hydrogen ion and hydroxyl ion formation affects the adsorption of other ions. It also affects the dissociation of the functional groups, shift in reaction kinetics and equilibrium characteristics of the adsorption process. The figure 5.12 below shows that pH value of 6 is most suitable for acid base treated soil for fluoride removal. The maximum percentage removal was observed at this pH because of the surface charge. It was observed that fluoride adsorption decreased at very low pH and at very high pH , because at high pH the hydroxyl ion hinders the adsorption of fluoride ion. However from the figure below it was observed that pH value of 2 is most suitable for acid treated laterite soil it as at lower pH the surface of the laterite soil gets covered with H^+ ions and the as the pH value is increased further the percentage removal decreases as H^+ ion concentration decreases.

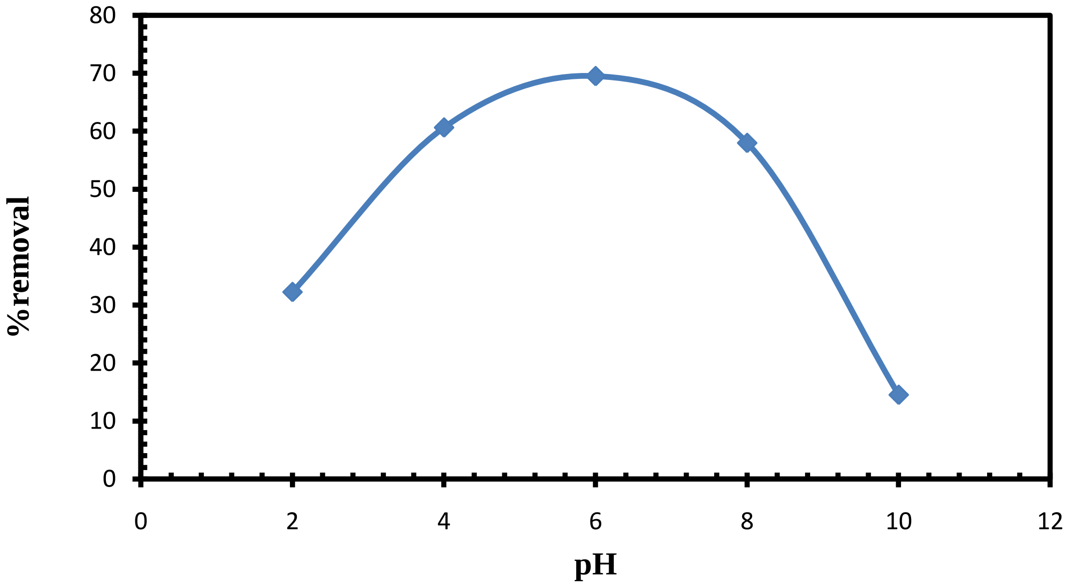


Figure 5.12 Effect of initial pH on adsorption of fluoride by acid base treated laterite (C_0=45 ppm, T=303 K, m =1 g/l).

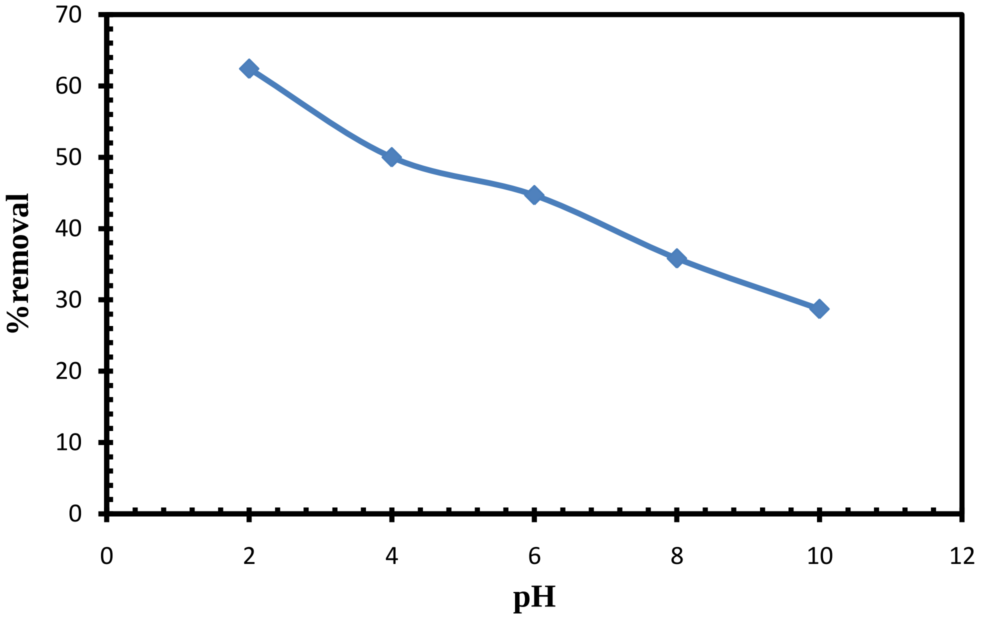


Figure 5.13 Effect of initial pH on adsorption of fluoride by acid base treated laterite (C_0=22.5, ppm, T=303 K, m =1 g/l).

5.2.2 Effect of adsorbent dosage (m)

The effect of m on the removal of fluoride ion by acid base treated laterite soil was studied by varying the adsorbent dose from .0125 g to .125 g in 100 ml of fluoride solution of 45 ppm concentration at a pH value of 6 and time 3 hrs. The figures 5.14 and 5.15 given below , for acid base treated laterite soil and acid treated laterite , show that as the adsorbent dose was increased from .0125 g to .125 g the percentage removal increased as more sorption sites were available for adsorption of fluoride on laterite. It was observed that percentage removal is more for acid base treated laterite in comparison to acid treated at same adsorbent dose of 1g/l .

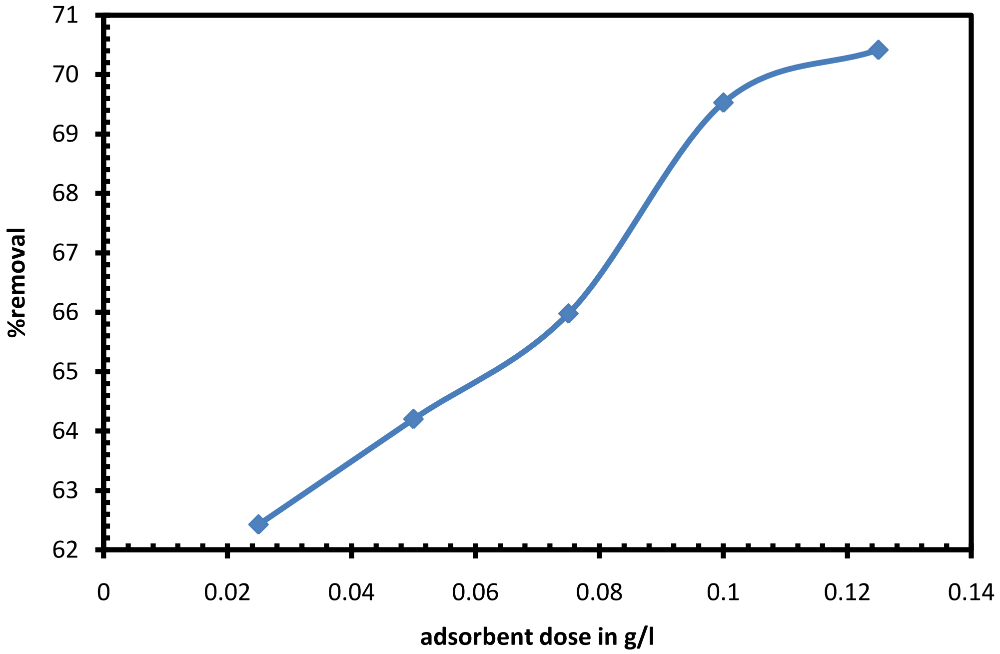


Figure 5.14 Effect of adsorbent dose on adsorption of fluoride by acid base treated laterite (C_0=45 ppm, T=303 K, pH=6).

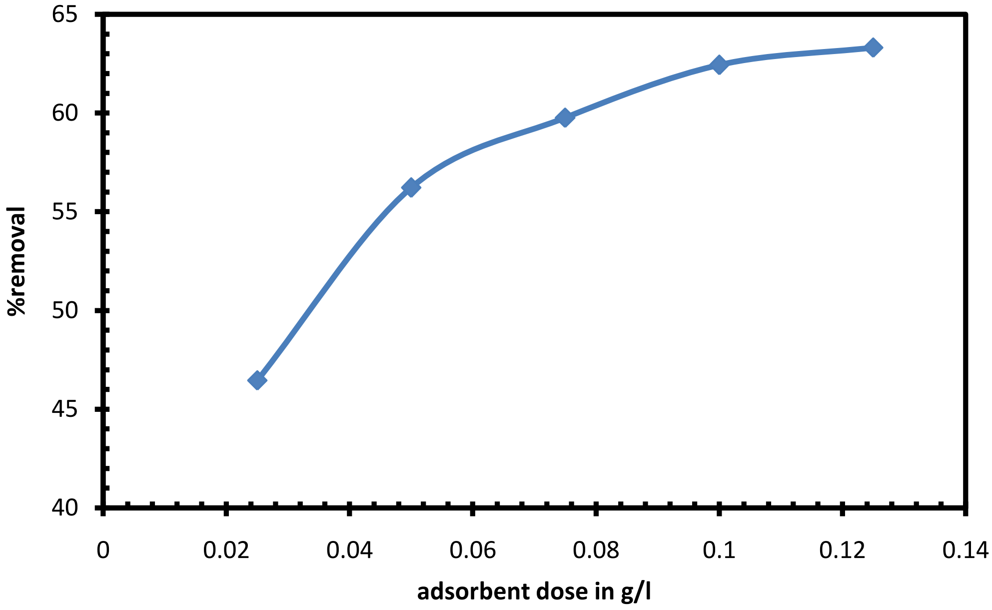


Figure 5.15 Effect of adsorbent dose on adsorption of fluoride by acid treated laterite (C_0=22.5 ppm, T=303 K, pH=2).

5.2.3 Effect of initial fluoride concentration C_o

The effect of initial fluoride dose C_o was analysed by varying the fluoride dose from 5.625 ppm to 45 ppm at pH value of 6 for 22.5 ppm concentration and adsorbent dose of .1 g for 100 ml of fluoride solution. The figures 5.16 and 5.17 given below , for acid base treated laterite soil and acid treated laterite , show that the rate of adsorption increases with an increase in C_o due to an increased driving force. However as the fluoride dose was increased the percentage removal decreased as lesser sorption sites were available for adsorption of fluoride on laterite and the already adsorbed fluoride ions hindered the adsorbtion of new fluoride ions on the adsorbtion surface. It was observed that percentage removal is more for acid base treated laterite in comparison to acid treated at same fluoride dose.

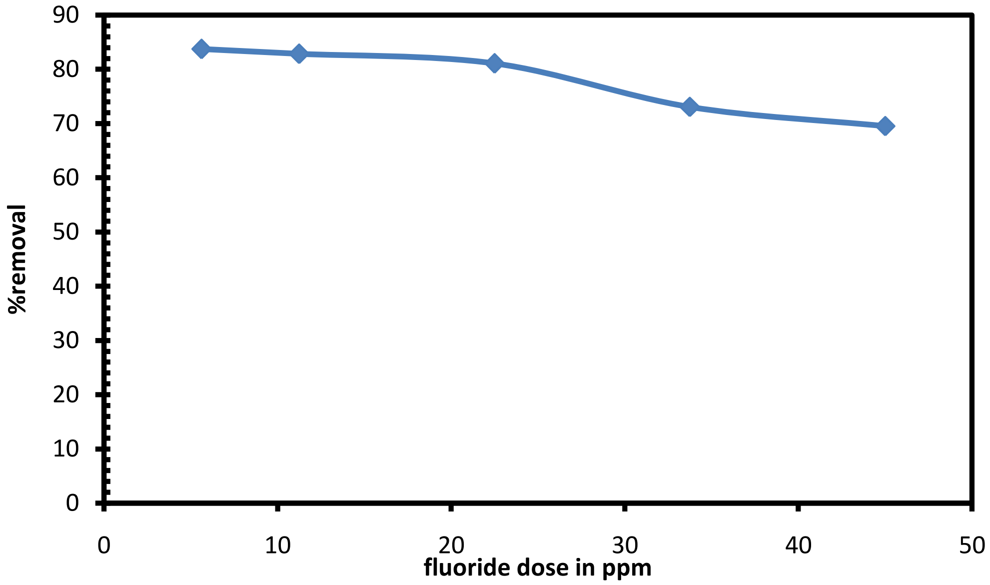


Figure 5.16 Effect of fluoride dose on adsorption of fluoride by acid base treated laterite (,m=1 g/l, pH=6,T=303 K).

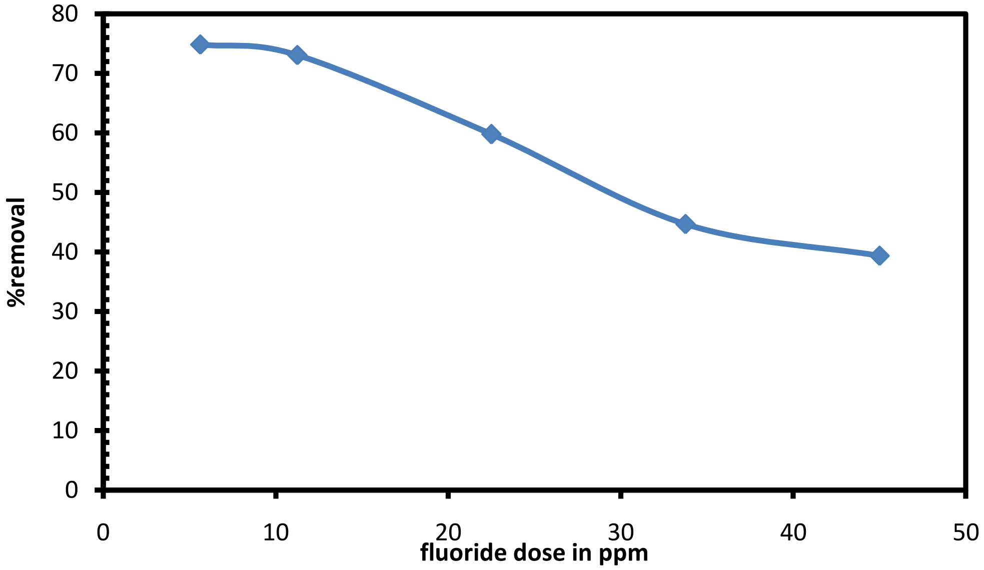


Figure 5.17 Effect of fluoride dose on adsorption of fluoride by acid treated laterite (m=1 g/l, pH=2,T=303 K).

5.2.4 Effect of contact time (t)

The effect of contact time was studied by varying the contact time from 15 min to 360 min for an adsorbent dose of .1 g in 100 ml of 50 ppm fluoride solution. The figures 5.18 and 5.19 given below , for acid base treated laterite soil and acid treated laterite , show that initially rapid defluoridation occurs due to large number of sorption sites available but as the time increases the rate of adsorption decreases as the remaining vacant sites for adsorption are difficult to be occupied due to repulsive force between the solute molecules on solid surface and bulk phase. It was observed that initially rapid defluoridation occurs because of physical adsorption but more time is required for the occurrence of reaction and equilibrium attainment for chemical adsorption. It was observed acid base treated laterite attains equilibrium after 3 hrs while acid treated laterite attains equilibrium after 1 hour.

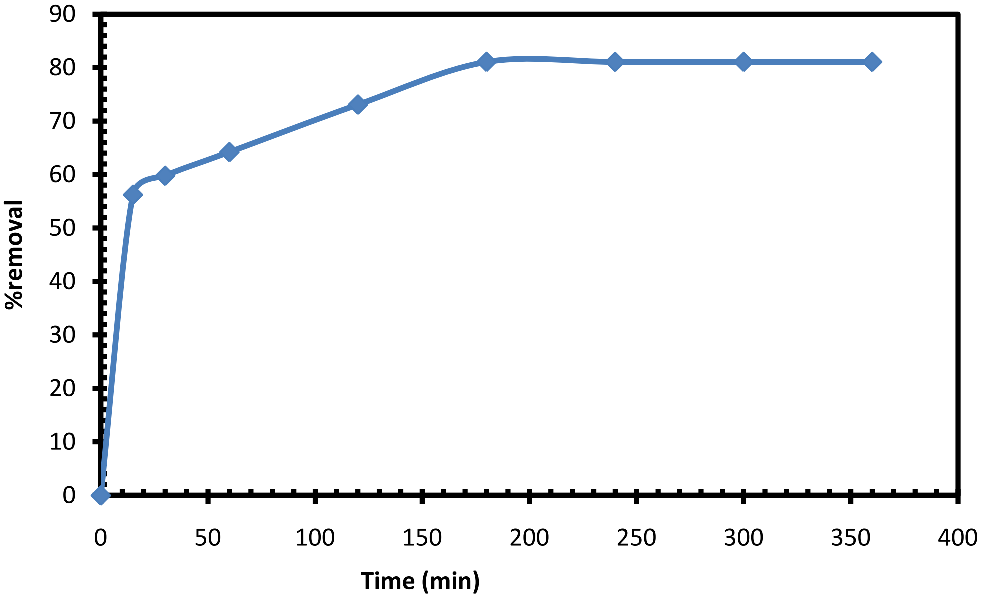


Figure 5.18 Effect of contact time on adsorption of fluoride by Acid base treated laterite (pH_0=6, C_0= 22.5 ppm, m=1 g/l, T=303 K).

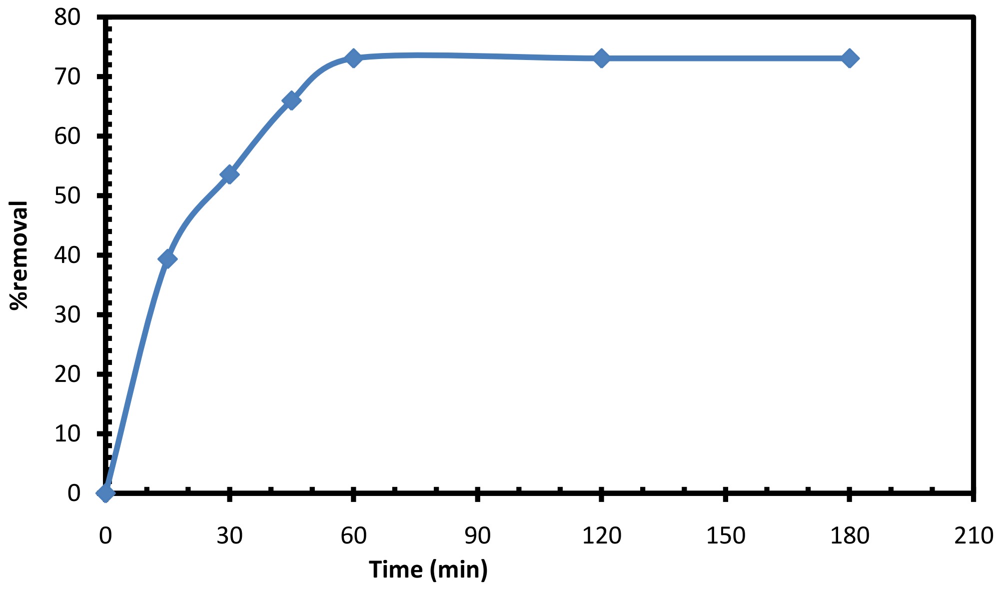


Figure 5.19 Effect of contact time on adsorption of fluoride by Acid treated laterite (pH_0=2, C_0= 22.5 ppm, m=1 g/l,pH=2, T=303 K).

5.2.5Effect of temperature

The effect of temperature was studied by varying the temperature from 15 ^{o}C min to 50 ^{o}C min for an adsorbent dose of .1 g in 100 ml of 22.5 ppm fluoride solution. The figures 5.20 and 5.21 given below , for acid base treated laterite soil and acid treated laterite , show that It was observed percentage removal increases with the increase in temperature as the mobility of the medium increases. The variation of percentage removal with temperature for acid base treated laterite and acid treated laterite are almost similar although percentage removal for acid base treated laterite is higher.

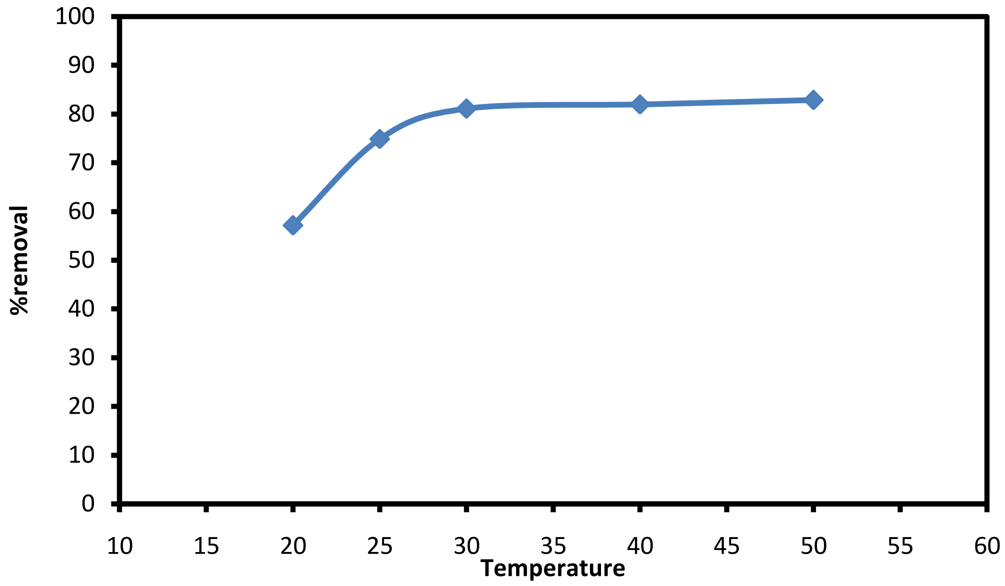


Figure 5.20 Effect of contact time on adsorption of fluoride by Acid treated laterite (pH_0=6, C_0= 22.5 ppm, m=1 g/l, T=303 K).

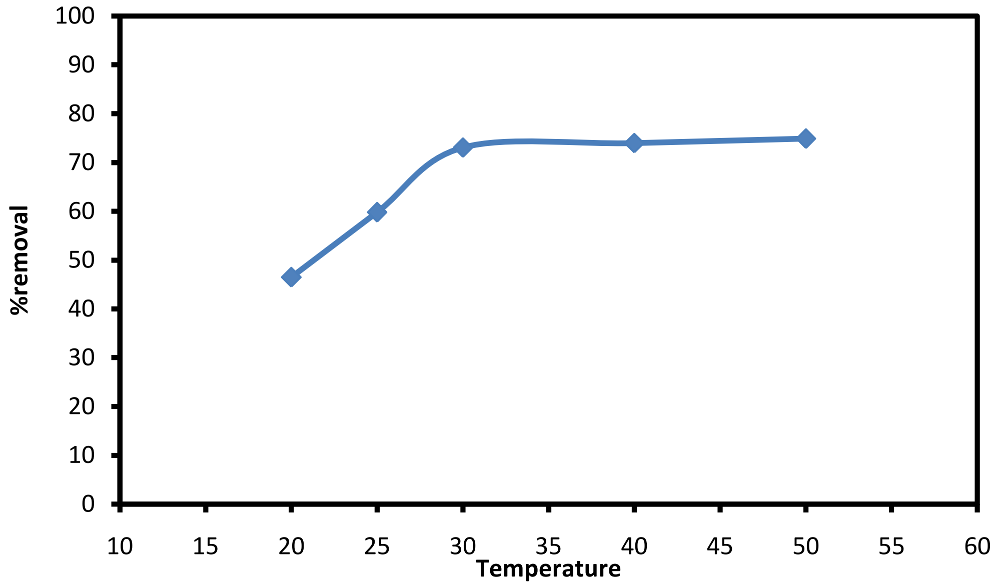


Figure 5.21 Effect of temperature on adsorption of fluoride by acid treated laterite(pH_0=2, C_0= 22.5 ppm, m=1 g/l, t=60 min).

5.3 Experimental Procedure

The effect of various parameters such as flow rate, fluoride dose, volume, bed height of laterite soil and time were studied. The effect of various parameters like flow rate , fluoride dose and bed height were studied for the column reactor.

5.3.1 EFFECT OF FLOURIDE CONCENTRATION

In order to study the effect of fluoride concentration on the removal by column the fluoride dose was varied from 11.25 ppm to 33.75 ppm .The flow rate was kept constant at 21.74 ml/min. The value of fluoride in the effluent was determined at different time intervals. The figure 5.22 below shows the variation of equilibrium concentration Ce at different concentrations at different time intervals. It was observed that at 33.75 pp the value of Ce became constant at earlier point of time while for lesser Ce value became constant at a higher time.

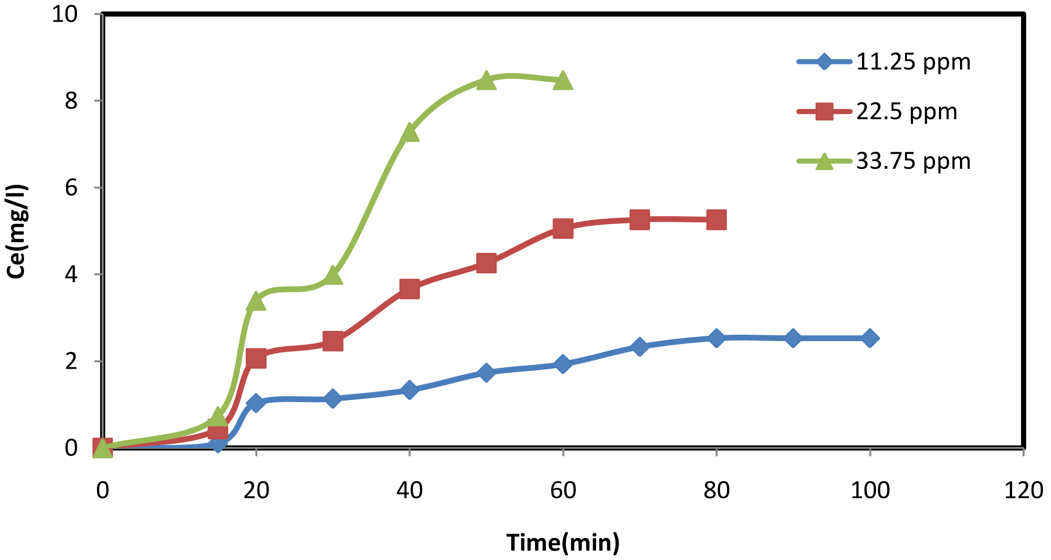


Figure 5.22 The variation of fluoride Ce at different concentrations at different time intervals and flow rate 21.74 ml/min.

5.3.2 EFFECT OF FLOW RATE

In order to study the effect of flow rate on the removal by column the the flow rate was varied from 21.74 to 108.6 ml/min by varying the rpm and the value of fluoride in the effluent was determined. The figure 5.23 below shows the variation of fluoride Ce and flow rate. It was observed that lower percentage removal occurs at higher flow rate as retention time decreases with flow rate.

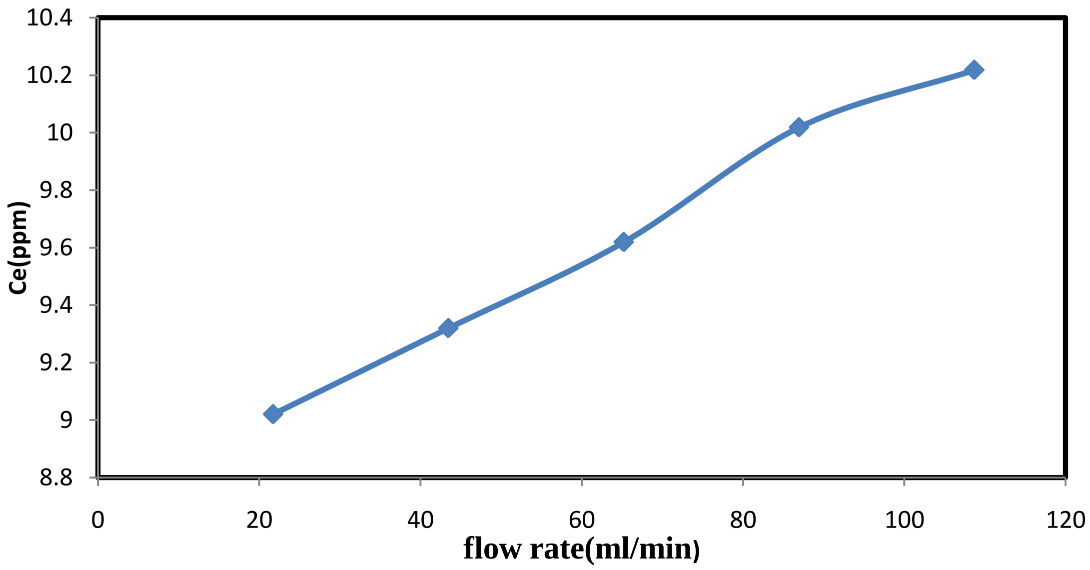


Figure 5.23 The variation of fluoride Ce and flow rate at 22.5 ppm concentration.

5.3.3 EFFECT OF BED HEIGHT

In order to study the effect of bed height on the removal by varying the bed height from 15 cm to 45 cm and the value of fluoride in the effluent was determined. The figure below shows the variation of fluoride Ce and flow rate. It was observed that higher percentage removal occure at higher bed height as retention time increases with bed height.

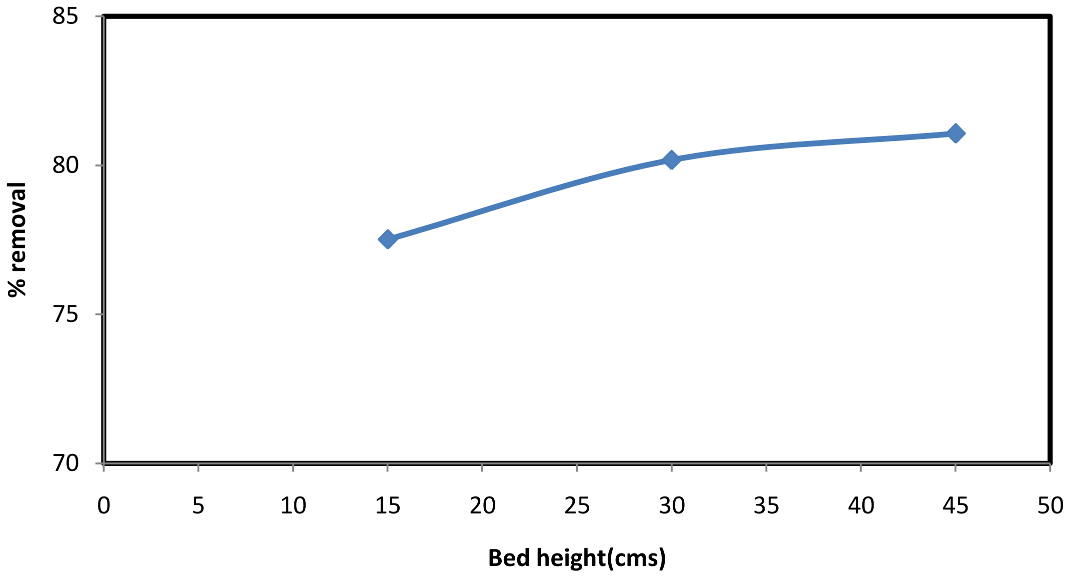


Figure 5.24 The variation of percentage removal with bed height at flow rate 21.74 ml/min and 22.5 ppm conc.

5.4 Adsorption isotherm study

The various equilibrium isotherms such as Freundlich , Langmuir and Tempkin are fitted using Microsoft Office Excel. Various values of theoretical q_e were obtained by various isotherm models. Values of qm , Kf and 1/n were determined. Higher the value of 1/n higher is the affinity and more heterogeneous the system becomes i.e closer the value of 1/n to unity more is the heterogeneity of the system and closer the value of 1/n to 0 the lesser is the heterogeneity of the system in the present 1/n is close to 1 hence system is heterogeneous.. Tempkin isotherm fits better to the experimental data as the value of R^2 is near unity in this case.

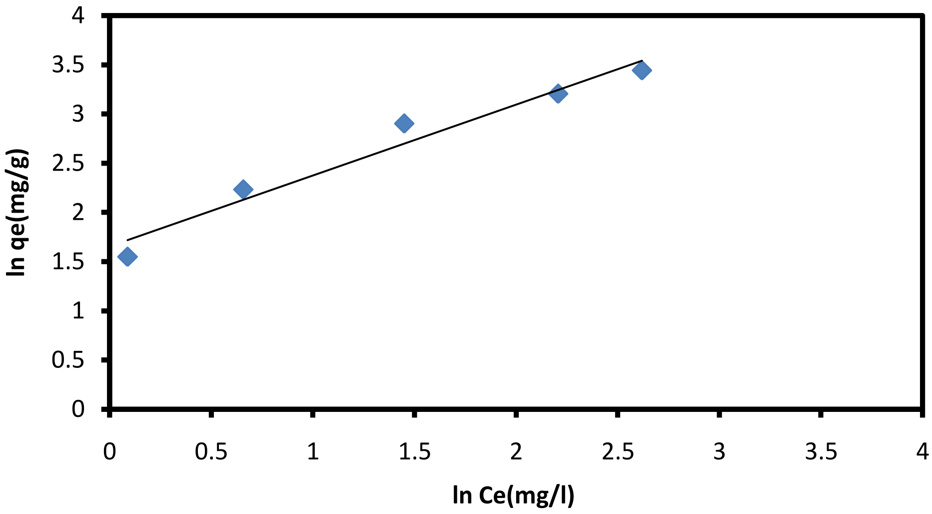


Figure 5.25 Freundlich isotherm for adsorption of fluoride by Acid base treated laterite(pH=6, T=303 K, m=1 g/l, t=180 min,Co 22.5 ppm).

Table 5.5:Freundlich parameters

Freundlich isotherm			
Adsorbent	Kf((mg g-^{1})(mgl-1)$^{-1/n}$)	1/n	R^{2}
Acid base treated laterite	5.22	0.721	0.96

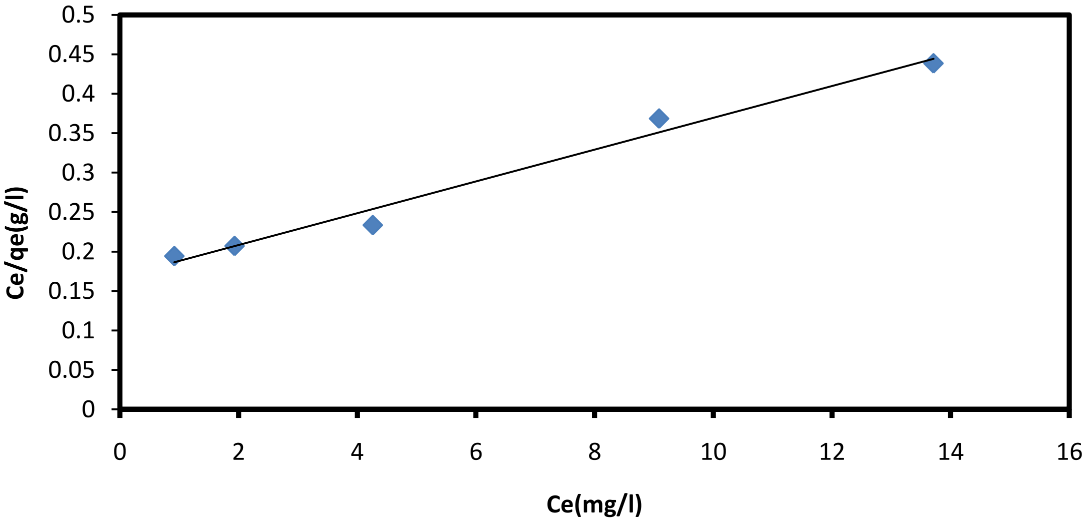


Figure 5.26 Langmuir isotherm for adsorption of fluoride by acid base treated laterite (pH=6, T=303 K, m=1 g/l, time=180min).

Table 5.6: Langmuir parameters

Langmuir isotherm			
Adsorbent	K_L(l mg^{-1})	q_m(mg $g-^1$)	R^2
Acid base treated laterite	0 .140	42.60	0.982

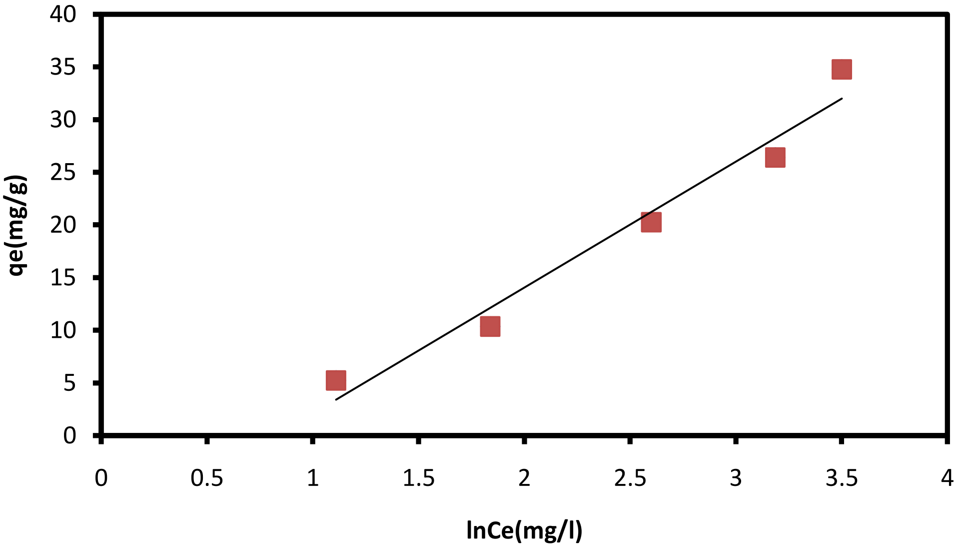


Figure 5.27 Tempkin isotherm for adsorption of fluoride by acid base treated laterite(pH=6, T=303 K, m=1 g/l, time=180 min)

Table 5.7.Tempkin Parameters

Tempkin isotherm			
Adsorbent	K_T(l mg^{-1})	B1	R^2
Acid base treated laterite	1.55	9.746	0.985

5.5 ADSORPTION KINETIC STUDY

Experiments are conducted and the value of Ce are obtained at different time intervals .The equilibrium data is fitted using Microsoft Office Excel .It was observed that the adsorption process for acid base treated laterite follows the pseudo second order kinetics better than pseudo first order kinetics as the calculated value of correlation coefficient R^2 was closer to unity for pseudo second order model. From the figure 5.28 it is clear that pore diffusion and intra particle diffusion plays a major on adsorption of fluoride on acid base treated laterite.

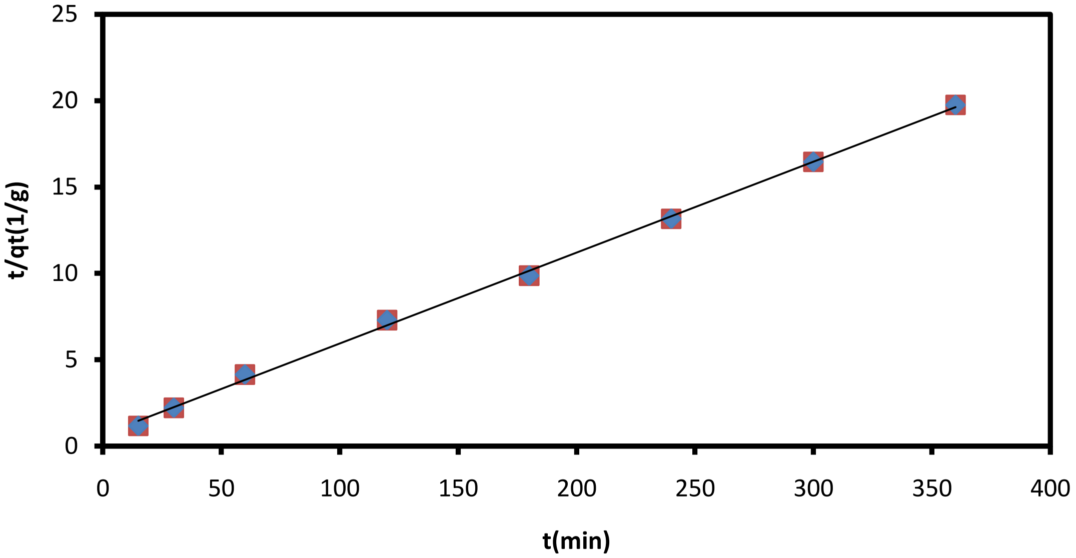


Figure 5.28:Pseudo-second order kinetics for fluoride by acid base treated laterite (pH_0=6, T=303 K, m=1 g/l, C_0=22.5 ppm, contact time =180 min).

Table 5.8.Pseudo second order parameters

pseudo second order				
Adsorbent	q_e(mg g^{-1})	h (mg g^{-1} min^{-1})	Ks(g mg^{-1} min^{-1})	R^2
Acid base treated laterite	19.25	1.49	0.004	0.998

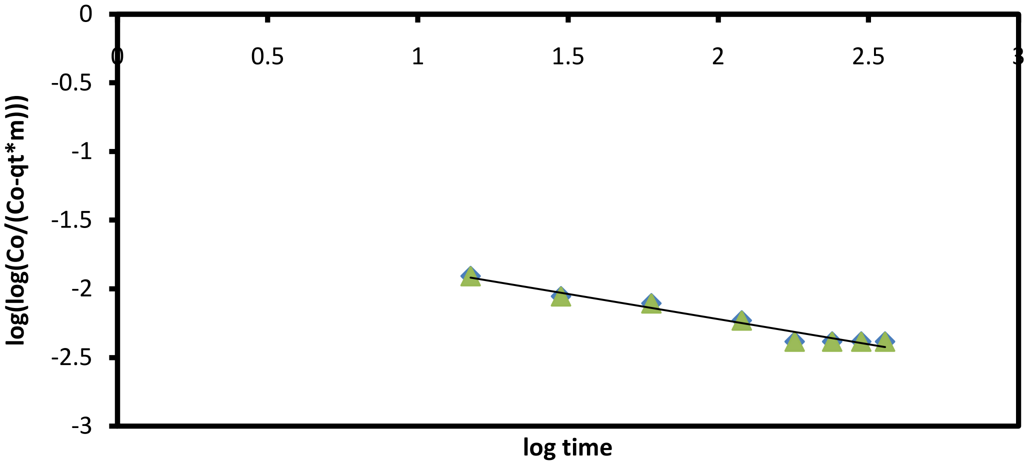


Figure 5.29: Bangham equation for fluoride by acid base treated laterite (pH=6, T=303K, m=1 g/l, C_0=22.5 ppm, contact time =180 min).

Table 5.9 : Bangham Parameters

bangham equation			
Adsorbent	K_0(g)	α	R^2
Acid base treated laterite	0.521	0.367	0.961

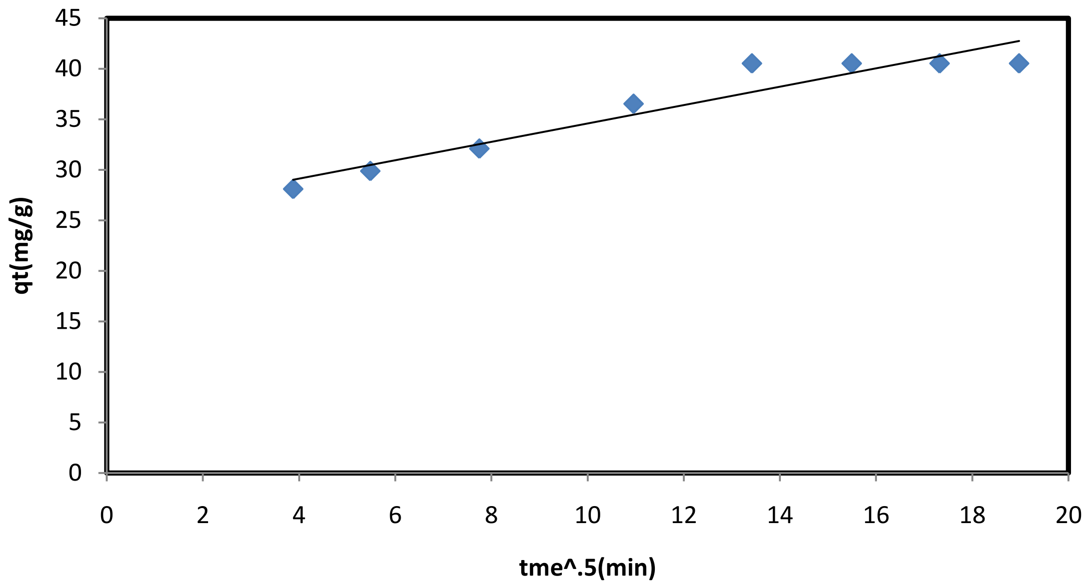


Figure 5.30: Weber morris for fluoride by acid base treated laterite (pH_0=6, T=303 K, m=1 g/l, C_0=22.5 ppm, contact time =180 min).

Table 5.10 : Intra Particle diffusion parameters

intra-particle diffusion			
Adsorbent	K_{id} (mg g^{-1} $min^{-1/2}$)	I	R^2
Acid base treated laterite	25.49	25.49	.914

CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

6.1 CONCLUSIONS:

In general the present studies shows that surface modified laterite serves as an inexpensive , abundantly available and highly efficient adsorbent for fluoride removal. Specifically following conclusions can be drawn from the results of the study.

Fluoride adsorbtion on surface modified laterite soil is highly dependent on pH of the solution. The most suitable pH for acid base treated laterite and acid treated laterite are 2 and 6 respectively.

Maximum removal fluoride occurs at adsorbent dose for 1g/l . Thus 1g/l is optimum dosage for fluoride removal under at pH 6, fluoride dose 22.5 ppm and temperature 313 K for acid base treated laterite and pH 2, fluoride dose 22.5 ppm and temperature 313 K for acid treated laterite.

The adsorption capacity for acid base treated laterite was found to be 18.24 mg/g at pH 6, fluoride dose 22.5 ppm and temperature 313 K and the percentage removal was 81 %.

It was found that initially rapid defluoridation occurs but as the time increased further sorption sites get saturated with fluoride and no further removal occurs. The equilibrium time for acid base treated and acid treated laterite was found to be 3 hours and 1 hour respectively

Pseudo second order model explains the kinetics of adsorption better than intra particle diffusion models and pseudo first order model.

Tempkin model fits the adsorption data better than the Langmuir isotherm and Freundlich isotherm.

The percentage removal for acid base treated laterite on impregnation with $FeCl_3$ increases from 81.4 % to 85.4 % and the adsorption capacity increases from 18.24 to 19.23 mg/g.

When defluoridation was carried out in column reactor it was observed that as the concentration was increased from 22.5 ppm to 37.5 ppm the retention time decreased.

It was found that optimum flow rate for fluoride removal is 21.74 ml/min.

It was also found that maximum percentage removal occurs at a bed height of 45 cm.with flow rate of 21.74 ml/min was most suitable for fluoride removal.

6.2 RECOMMENDATIONS

Based on the results of the present study, the following recommendations are suggested for further investigations.

The effect of temperature can be studied.

The spent adsorbent could be used for useful purposes like brick manufacturing.

The efficiency of column after regeneration by treatment with NaOH can be studied.

The variation of column capacity with time can be studied.

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