ADSORPTION STUDIES OF FLUORIDE REMOVAL FROM GROUNDWATER USING LOCALLY AVAILABLE LATERITE SOIL IN BANKURA AND PURULIA DISTRICTS OF WEST BENGAL

A thesis submitted towards partial fulfilment of the
requirements for the degree of

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Submitted by

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CERTIFICATE OF RECOMMENDATION

This is to certify that the thesis entitled **"*ADSORPTION STUDIES OF FLUORIDE REMOVAL FROM GROUND WATER USING LOCALLY AVAILABLE LATERITE SOIL IN BANKURA AND PURULIA DISTRICTS OF WEST BENGAL*"** is bonafide work carried out by **PRATIK MAITI** under our supervision and guidance for partial fulfilment of the requirement for Post Graduate Degree of Master of Engineering in Water Resources & Hydraulic Engineering during the academic session 2020-2022.

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This foregoing thesis is hereby approved as a credible study of an engineering subject carried out and presented in a manner satisfactorily to warranty its acceptance as a pre-requisite to the degree for which it has been submitted. It is understood that by this approval the undersigned do not endorse or approve any statement made or opinion expressed or conclusion drawn therein but approve the thesis only for purpose for which it has been submitted.

Committee of final examination
For the evaluation of the thesis

**** Only in case the thesis is approved.**

Declaration of Originality and Compliance of Academic Ethics

I hereby declare that this thesis contains literature survey and original research work by the undersigned candidate, as a part of my Master of Water Resources & Hydraulic Engineering degree during academic session 2020-2022.

All information in this document has been obtained and presented in accordance with academic rules and ethical conduct.

I also declare that, as required by this rules and conduct, I have fully cited and referred all material and results that are not original to this work.

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ABSTRACT

The groundwater has undergone a change to such an extent that it could be very risky and hazardous due to the contamination of fluoride. The presence of excess fluoride (>1mg L^{-1}) in groundwater is area-specific and sources of contamination are mostly natural and geogenic. Excess fluoride contaminated groundwater consumption for a long time galvanizes the risk of dental fluorosis, skeletal and non-skeletal fluorosis etc. Fluoride-free safe drinking water can be supplied in affected areas by applying the appropriate fluoride removal technologies to groundwater. Fluoride removal from groundwater is commonly accomplished through the adsorption process. The efficacy of laterite soil (collected from fluoride contaminated zone) for removal of fluoride was investigated using the batch methods under various laterite dosages, initial fluoride concentrations, agitation times, and solute pH to understand adsorption behavior. The effect on other several other parameters (pH, TDS, iron) of water quality was also noticed after the removal of fluoride. The fluoride adsorption behavior of two types of laterites (red and white laterite) was studied under the same condition. Red laterite was found better fluoride removal efficiency (up to 98.02%, at 28℃, initial fluoride condition 5mg L^{-1},20 gm dosage,5 hours agitation time) than white laterite (91.11%, at same experimental conditions). The Langmuir, Freundlich and Temkin models were found to be best to describe equilibrium isotherm data. The kinetic study indicated that adsorption of fluoride using laterite is best fit with pseudo second order reaction in case of both red and white laterite soil. In fixed-bed column study 26.28 liters of water was filtered with fluoride concentration below the permissible limit. The capacity of red laterite soil was found 111.826 mg/kg and having average removal efficiency 82.411% in column study. The use of laterite as an adsorbent for fluoride removal is found to be cost effective and hence can be considered as an alternative for defluoridation.

CHAPTER 1

2.1 INTRODUCTION

Water is one of the most precious natural resources that is needed for survival. Mother earth is known as the “Blue Planet” as 71 percent of the Earth's surface is covered with water. 97 percent of the earth's water is found in the ocean as ocean water which contains a high percentage of chloride and salinity which make the water undrinkable. Out of the rest 3 percent fresh water, 2 percent of water is accessible due to the presence of glaciers and polar ice caps. The remaining 1 percent is found in Groundwater (0.62 percent), freshwater lakes (0.009 percent), inland seas (0.008 percent), atmosphere (0.001 percent), and rivers (0.0001 percent).Groundwater is the most available fresh water source. Groundwater is the water that presents underground in saturated zones beneath the earth's surface in rock and soil pore spaces and fractures of rock formations. Groundwater is more convenient and less vulnerable to pollution than surface water. In the 21st century around the globe fluoride contamination in groundwater is a major issue where Ethiopia, China, and India are among the most affected [1]. Prolonged consumption of fluoride contaminated water (excess of the permissible limit of 1.5 mg/L) caused skeletal, dental fluorosis, and non-skeletal fluorosis [2]. Fluorosis is estimated to affect more than 260 million people worldwide [3].During the last twenty years, with support from various Governments have taken up action for mitigation of excess fluoride problems as well as awareness programs. WHO and UNICEF have also stretched their hands to assist Governments' efforts.

2.1.1 Fluoride

Fluoride (F^-) is a monoatomic anion of fluorine, which comes under the halogen group of gases. Being highly electronegative in nature (having electronegativity -4.0), Fexists only in combination with other elements to form compounds and minerals such as fluorspar, cryolite and fluorapatite[4]. Fluorine ranks 13th in earthly abundance as fluoride, comprising 0.09% of the surface of the earth. Fluoride has been recommended as a therapy for osteoporosis since the 1960s, but despite producing denser bone, fracture risk is not reduced. Indeed, there is some evidence that nonvertebral fractures may be increased [5]. Fluoride in drinking water can be used as two folded-edged blades, because of its use when ideal limits and hazard when excess or maximum exceeds. The permissible limit of fluoride in drinking water is described in the Table-1

Table 1: Permissible Limits of Fluoride

Contaminants	***Indian Standard*** ***DRINKING WATER-SPECIFICATION*** ***IS 10500:2012***	***GUIDELINES FOR DRINKING-WATER QUALITY*** **WHO (2017)**	***European Union (EU)***
Fluoride (F^-)	Acceptable limit :1.0 mg/l **Permissible limit in the absence of Alternate Source**: 1.5mg/l	1.5 mg/l	1.5 mg/l

2.1.2 Sources of Fluoride

A. *Natural Source : Geogenic*

Fluorine occurs in the form of fluoride in various minerals like cryolite [Na_3AlF_6], fluorspar, fluorite (CaF_2) and fluorapatite [$Ca_5(PO4)_3F$], among which fluorite and fluorapatite are usually considered to be the minerals responsible for fluoride contamination [4]. These mineral rocks were naturally weathered and leached out by rainwater thereby allowing them to contaminate the ground.

B. Anthropogenic sources

- ***Domestic and food***

The food which contains fluoride depends upon the fluoride contents of the soil and water used for irrigation. So, the fluoride contamination the food items may vary from place to place [6]. All vegetables contain some fluoride, which is absorbed from soil and water. The fluorine content of plants, mostly cultivated plants, is generally low, apart from tea, which contains up to 440 mg/L fluorides. Seafood contains significantly higher amounts of fluorine compared to freshwater food [7].

- ***Industry***

The use of fluorides in the industry leads to occupational exposure such as inorganic fluoride compounds used in the production of aluminium from cryolite. It is found that fluoride reaches drinking water mainly through industrial (such as processing of semiconductors, glass and ceramics, power plants of coal-fired, beryllium extraction plants, bricks and iron works) discharges as wastewater [8].

2.1.3 Effects of varying concentrations of fluoride on human health

- ***Fluoride toxicity on Human health***

Fluoride is a highly electronegative (electronegativity -4) element that has a tendency to get attracted by positively charged ions like Ca^{2+}. The effect of fluoride on mineralized tissues like bone and teeth leading to development alternations is of clinical significance as they have the highest amount of Ca^{2+} and attract the most quantity of fluoride that gets deposited as calcium–fluorapatite crystals [9]. It is observed that in adults exposed to high fluoride ingestion in tropical and subtropical countries the defence mechanism inside the body fix excess fluorides into hydroxyl-apatite material of the bone by replacement of OH^- by fluorides.

Table 2 Effects of varying concentrations of fluoride on human health

Concentration of fluoride	***Effects***
Nil	Limited growth and fertility
0.8-1.2 mg/L	Prevention of tooth decay, strengthening of skeleton
Above 1.5 mg/L	Fluorosis: pitting of tooth enamel and deposits in bones

- ***Effects on bones:***

Fluoride caused the weakening of bones that leads to an increase in hip and wrist. The lower bound of fluoride levels is reported in the literature as causing a higher risk of bone fracture fractures [10]. Fluoride readily accumulates in the lattice of bone [11]. Characteristic structural changes in fluorosed bones are:

- Increased bone mass and density.
- Exostosis (bony outgrowth) at bone surfaces.

- Increased osteoid seam and re-sorption surfaces.
- Increased trabecular bone volume, critical porosity, and periosteocyclic lacunar surfaces.
- Formation of un-mineralized cartilaginous loci within the trabeculae of the bone but not in the cortical bone.
- Accumulation of glycosaminoglycans especially the isomer Dermatan sulphate in the cartilaginous.

Skeletal Fluorosis:

Skeletal fluorosis is defined as excessive deposition of fluorine in bone. With prolonged consumption of high fluoride drinking water (>8 mg/L) during adolescence, severe forms of skeletal deformities may occur. It has been found that crippling skeletal fluorosis and osteoporosis develop when drinking water contains over 10 mg/L of fluoride [12]. Significantly much higher incidence of skeletal abnormalities (wavy ribs, 14th rib, less than six sternal dumbbell-shaped second and fifth sternebrae, incomplete ossification of skull and thickening of tibia) were observed in NaF^- treated dams than in controls. Skeletal fluorosis is not easily diagnosable until the disease has developed to an advanced stage. Based on their microscopic structure, bones can be classified into two types: cancellous and cortical. When excessive quantities of fluoride are deposited in the skeleton, there is more in cancellous bone compared to cortical bone. With increased severity of skeletal fluorosis, pain is associated with rigidity and restricted movement of the cervical and lumbar spine, knee and pelvic joints and shoulder joints [13].

***Non-skeletal fluorosis*:**

The pre-skeletal stage of fluoride intoxication poses problems for diagnosis. The symptoms that are shown are so varied that they may be identifiable with those of various other diseases. The complaints of the patients in this regard are so commonplace that those resulting from other ailments, such as muscle and neurological involvement, in children may be mistaken for poliomyelitis [13].

Dental fluorosis:

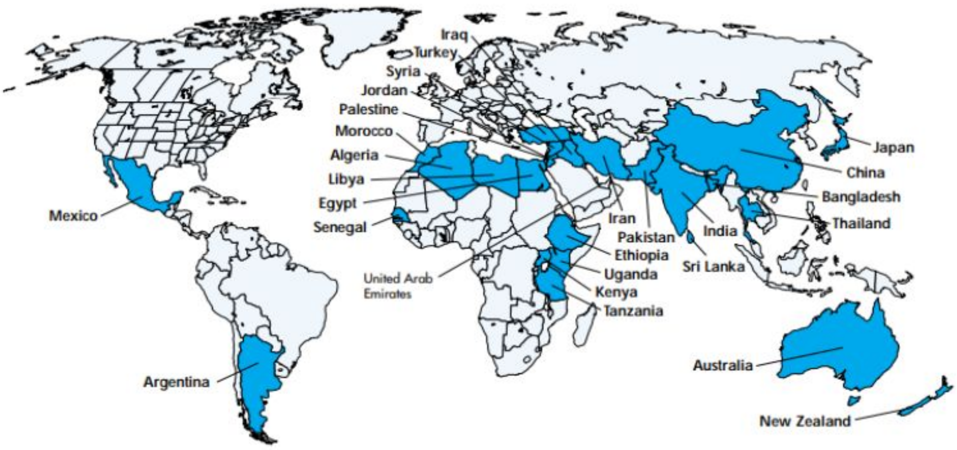
It has been found that the greatest non-dietary fluoride source is toothpaste and other dental products, which often contain concentrations around 0.25–1.5 mg F/g. Dental products for children contain a little less fluoride than dental products for grown-ups, due to the fact that children are more likely to swallow the products [14-15]. Dental fluorosis is one of the aesthetic and social problems besides being a health problem. The discoloration of teeth may change the colour from white or yellow-brown to black. This discoloration may be in spots or streaks invariably horizontal in orientation, as during development new layers of the matrix are added horizontally.

Apart from these, heavy intake of fluoride may cause adverse effects on the kidney and hamper the mental growth of the children. [4]

2.1.4 Magnitude of excess Fluoride contamination Problem

A. *Magnitude Fluoride contamination problem in the World*:

The occurrence of high fluoride content in groundwater has one of the most important health-related geo-environmental issues in the world. The latest report is shown that fluorosis is endemic in at least 25 countries across the globe. The country like Mexico, Argentina, Turkey, Morocco, Algeria, Iraq, Syria, Libya, Egypt, Iran, Ethiopia, Uganda, Kenya, Tanzania, India, Pakistan, Srilanka, Bangladesh, Thailand, Australia, and New Zealand are affected (Fig.-1) . The total number of people affected is a conservative estimate would number in the tens of millions. In Mexico, 5 million people (about 6% of the population) are affected by fluoride in groundwater. Fluorosis is prevalent in some parts of central and western China and is caused not only by drinking fluoride in groundwater but also by breathing airborne fluoride released from the burning of fluoride-laden coal. It has been found that worldwide, such instances of industrial fluorosis are on the rise [16].



Countries with endemic fluorosis due to excess fluoride in drinking water

Fig. 1: Endemicity of Fluorosis around the globe [16]

B. *Magnitude of Fluoride contamination problem in India*:

In India, fluoride contamination is found in almost every state. It has been found that the first footstep of fluorosis was the reported in Prakasam district of Andhra Pradesh [17,18]. Out of a total 29 states in India, groundwater of 20 states is fluoride affected. Total population of fluoride endemic 201 districts of India is 411 million (40% of Indian population) and more than 66 million people are estimated to be suffering from fluorosis including 6 million children below 14 years of age. The fluoride affected districts in India is shown below in Table-3 [19].

Table 3: State-wise details of the distribution of Flouride in Ground Water above the permissible limit [19]

Sl. No.	***State***	***Fluoride***	
		No.of districts affected	***Districts (in parts)***
1.	Andhra Pradesh	19	Adilabad, Anantpur, Chitoor, Guntur, Hyderabad, Karimnagar, Khammam, Krishna, Kurnool, Mehboobnagar, Medak, Nalgonda, Nellore, Prakasham, Rangareddy, Vishakhapatnam, Viziangaram, Warangal, West Godawari
2.	Assam	4	Goalpara, Kamrup, Karbi Anglong, Naugaon
3	Bihar	9	Aurangabad, Banka, Buxar, Jamui, Kaimur, Munger, Nawada, Rohtas, Supaul
4.	Chhattisgarh	12	Bastar, Bilaspur, Dantewara, Janjgir-Champa, Jashpur, Kanker, Korba, Koriya, Mahasamund, Raipur, Rajnandgaon, Suguja
5.	Delhi	6	East Delhi, New Delhi, Northwest Delhi, South Delhi, Southwest Delhi, West Delhi
6.	Gujarat	18	Ahmedabad, Amreli, Anand, Banaskantha, Bharuch, Bhavnagar, Dahod, Junagarh, Kachchh, Mahesana, Narmada, Panchmahals, Patan, Rajkot, Sabarkantha, Surat, Surendranagar, Vadodara
7.	Haryana	14	Bhiwani, Faridabad, Gurgaon, Hissar, Jhajjar, Jind, Kaithal, Kurkshetra, Mahendragarh, Panipat, Rewari, Rohtak, Sirsa, Sonepat
8.	Jammu & Kashmir	2	Rajauri, Udhampur
9.	Jharkhand	6	Bokaro, Giridih, Godda, Gumla, Palamau, Ranchi

10..	Karnataka	20	Bagalkot, Bangalore, Bellary, Belgaum, Bidar, Bijapur, Chamarajnagar, Chikmagalur, Chitradurga, Devangere, Dharwar, Gadag, Gulbarga, Haveri, Kolar, Koppala, Mandya, Mysore, Raichur, Tumkur.
11.	Kerala	1	Palakkad
12.	Madhya Pradesh	19	Bhind, Chhatarpur, Chhindwara, Datia, Dewas, Dhar, Guna, Gwalior, Harda, Jabalpur, Jhabua, Khargone, Mandsaur, Rajgarh, Satna, Seoni, Shajapur, Sheopur, Sidhi.
13.	Maharashtra	8	Amrawati, Chandrapur, Dhule, Gadchiroli, Gondia, Jalna, Nagpur, Nanded,
14.	Orissa	11	Angul, Balasore, Bargarh, Bhadrak, Boudh, Cuttack, Deogarh, Dhenkanal, Jajpur, Keonjhar, Suvarnapur
15.	Punjab	11	Amritsar, Bhatinda, Faridkot, Fatehgarh-Saheb, Firozpur, Gurdaspur, Mansa, Moga, Muktsar, Patiala, Sangrur,
16.	Rajasthan	30	Ajmer, Alwar, Banswara, Barmer, Bharatpur, Bhilwara, Bikaner, Bundi, Chhittorgarh, Churu, Dausa, Dholpur, Dungarpur, Ganganagar, Hanumangarh, Jaipur, Jaisalmer, Jalore, Jhunjhunu, Jodhpur, Karauli, Kota, Nagaur, Pali, Rajasamand, SawaiMadhopur, Sikar, Sirohi, Tonk, Udaipur
17.	Tamil Nadu	16	Coimbatore, Dharmapuri, Dindigul, Erode, Karur, Krishnagiri, Namakkal, Perambalur, Puddukotai, Ramnathpuram, Salem, Shivaganga, Theni, Thiruvannamalai, Vellore, Virudunagar
18.	Uttar Pradesh	10	Agra, Aligarh, Etah, Firozabad, Jaunpur, Kannauj, Mahamayanagar, Mainpuri, Mathura, Maunathbhanjan,
19.	West Bengal	8	Bankura, Bardhhman, Birbhum, Dakhin Dinajpur, Malda, Nadia, Purulia, Uttar Dinajpur

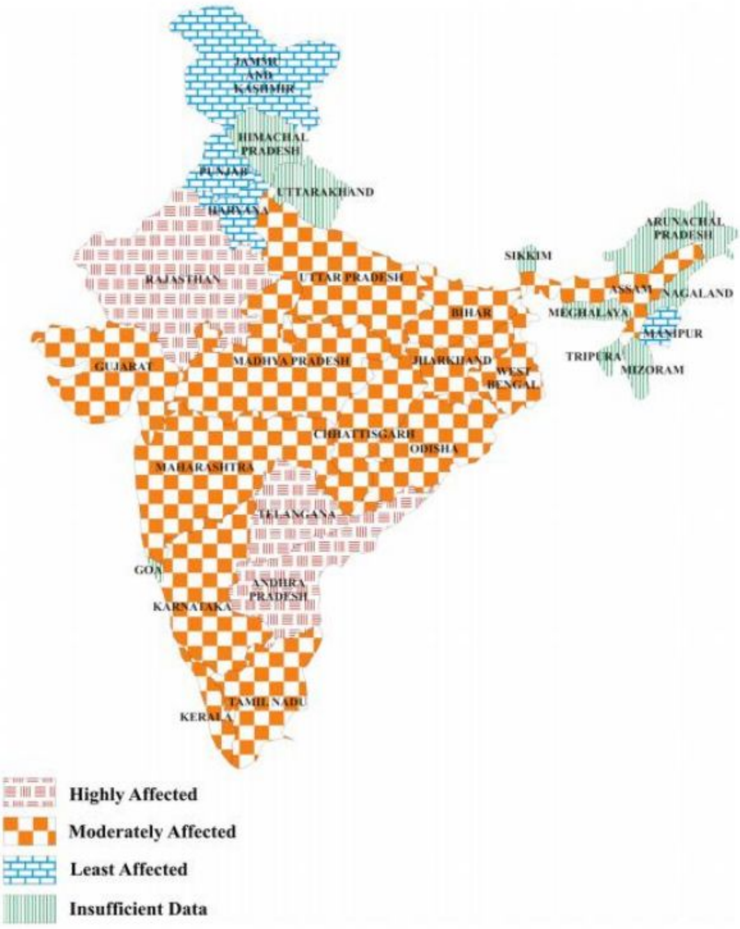


Fig. 2 State-wise details of the distribution of Fluoride in Ground Water above the permissible limit [18]

C. Magnitude of Fluoride contamination problem in West Bengal:

Fluoride-contaminated groundwater was first identified in West Bengal in 1997. The Govt. had taken fast action to produce an alternate facility-supported river-bed tube well from river Tripita when exceedances were noted within the Nasipur space of Nalhati-I block within the district of Birbhum. The Geological Survey of India (GSI) undertook an investigation during 1999–2000 [20] covering an area of some 600 sq. km of West Bengal to determine the scale and cause of contamination. Fluoride problems were spotted to be generally associated with tube wells abstracting from basaltic rocks of the Rajmahal Traps. Shear zones in Precambrian rocks were also found to be correlated with high-fluoride groundwater in parts of the Purulia and Bankura districts. All dug wells, ponds, and shallow tube wells tapping alluvium had low fluoride concentrations. WBPHED constituted a committee for fluoride with the involvement of several organizations and instigated a rapid assessment of fluoride in groundwater sources across West Bengal in the year 2003. The survey was done in 107 blocks in 12 districts and spotted fluoride concentrations exceeding 1.5 mg/L in groundwater from 43 blocks in seven districts (Fig.-3). After doing subsequent testing of all hand-pumped tube wells in the 43 blocks noticed that 3.88% exceeded the acceptable government standard. Fluoride affected blocks are shown in the table 4 below:

Table 4: Blocks in West Bengal Affected by Fluoride at Concentrations >1.5 mg/L

District	***Fluoride-affected blocks***	***No. blocks***
Bankura	Bankura-II,Barjora,Chhatna,Gangajalghati, Hirbandh,Indpur,Raipur,Saltora,Simlapal,Taldangra	10
Birbhum	Khoyrasol, Mayureswar-I, Nalhati-I, Rajnagar, Rampurhat-I, Sainthia, Suri-II	7
Dakshin Dinajpur	Bansihari, Gangarampur, Kumarganj, Kushmundi, Tapan	5
Purulia	Arsha, Bagmundi, Balarampur, Barabazar, Hura, Jaipur, Jhalda-I, Kashipur, Manbazar-I, Neturia, Para, Puncha, Purulia-I, Purulia-II, Raghunathpur-I, Raghunathpur-II, Santuri	17
South 24 Parganas	Baruipur	1
Uttar Dinajpur	Itahar	1
	Total	**43**

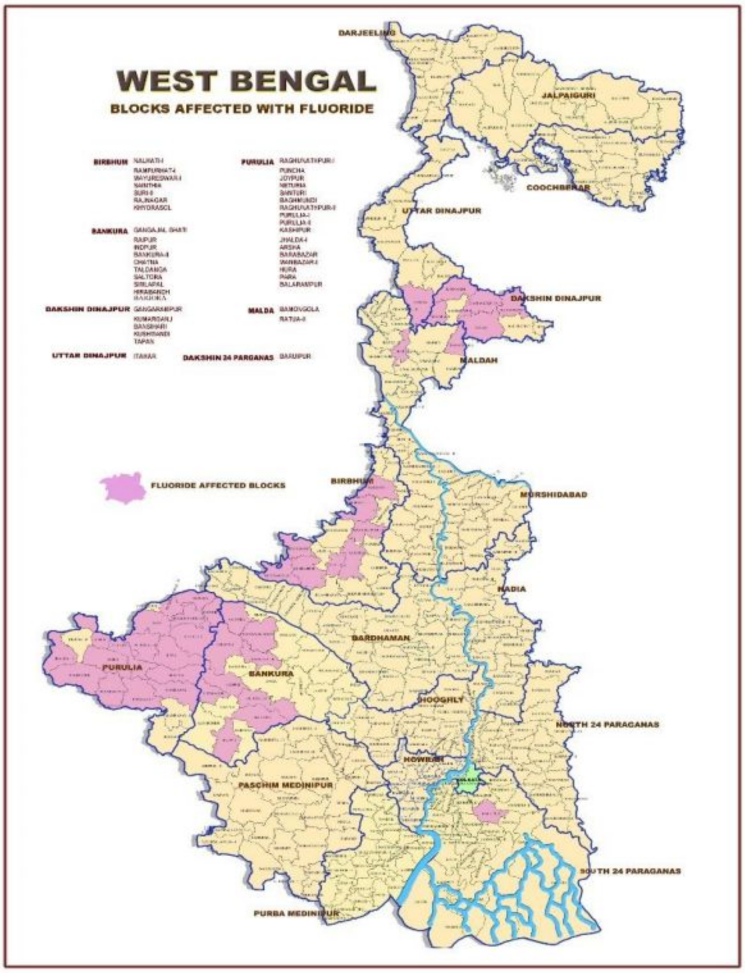


Fig. 3: District-wise details of the distribution of Fluoride in Ground Water above the permissible limit [20]

2.1.5 Fluoride Mitigation strategy:

Defluoridation involves removal of fluoride ions present in drinking water. Defluoridating methods may mainly be classified in two categories namely Additive methods and Adsorptive methods. In additive methods, certain reagents are added and optimum conditions for the defluoridation are sustained. The present Fluoride ion in water reacts with the reagents added and forms an insoluble complex and was removed as ad flocs. In adsorptive methods, a bed of greater surface activity is picked and water is passed through the bed. Due to surface activity, fluoride ions get preferentially adsorbed on the bed surface thereby causing a of fluoride declination ion in the exit stream. The different methods are generally used for the removal of excess fluoride from water can be mainly classified into four basic types [21]:

a) Precipitation technique
b) Adsorption technique
c) Ion-Exchange technique
d) Miscellaneous methods.

a) Precipitation technique:

- ***Nalgonda technique:***

The Nalagonda technique was developed by the National Environment Engineering Research Institute (NEERI), Nagpur [21]. In Nalgonda Technique aluminium salts, lime, and bleaching powder is used followed by rapid mixing, flocculation, sedimentation, filtration, and disinfection. Aluminium salts are added as aluminium sulphate (alum) or aluminium chloride or combination of these two which is responsible for removal of fluoride from water. With the increase in the fluoride and alkalinity levels of the raw water the dosage of aluminium salt increases. Lime is used to facilitate forming dense flocks for rapid settling of insoluble fluoride salts. The dosage of lime is generally 1/20th of that of the dosage of aluminium salt. Bleaching powder is added for disinfection in the amount of 3 mg/l.

- ***Use of Polymeric aluminium hydroxide:***

The combination of polymeric aluminium hydroxide and calcium salts, for the treatment of fluoridated waste water. In this treatment, polymeric aluminium hydroxide acts as a coagulant and the calcium ion acts as a precipitant. The use of calcium fluoride seeds (approximate 20 mg/l) results in the acceleration of the precipitation process and the residual fluoride concentrations were closed to the theoretical levels. Under the above conditions fine CaF_2 precipitate with poor ability to settle was formed. The addition of a small amount of polymeric aluminium hydroxide greatly facilities the ability to settle of the precipitate. The advantage of using polymeric hydroxide over the use of alum for the removal of fluoride is that less concentration of the former is required and the results are fine.

- ***Efficient defluoridation process*:**

In this process an efficient defluoridation process in which aluminium bipolar electrodes was used. In the first step, certain parameters such as inter-electrode distance fluoride concentration, temperature and the pH of the solution were looked over and optimized with synthetic water in batch mode. The electro-congratulation process with aluminium bipolar electrodes permitted the defluoridation of water without adding soluble salts to the treated water. The aluminium fluoride weight ratio took part in as 7. The technique is highly versatile and has applications for large communities and fill and draw technique for small communities as well as for rural water supply, for domestic defluoridation.

- ***Advantages:***

i. Precipitation technique can be used at both domestic and community level
ii. This technique is adopted because of its simplicity in design, construction, operation and maintenance
iii. Technology is Low, adaptable at point of use and point of source level
iv. Apart from fluoride, turbidity, colour, odour, pesticides and organic substances are also removed in this method.

- ***Disadvantages:***

i. Disadvantages of this Precipitation technique is operations require a trained operator daily.
ii. This technique, there is a possibility of excess aluminium contaminating the water. The maximum concentration of aluminium permitted is 0.03 mg to 0.2 mg/litre of water according to IS 10500:2012, as an excess aluminium is suspected to cause Alzheimer's disease
iii. Biggest problem is discarding the sludge from the Nalgonda process is a serious environmental health problem. The sludge is toxic because it contains the removed fluoride in a concentrated form, so sludge disposal is a problem
iv. Periodic analysis of feed as well as treated water is required to calculate the correct dosage of chemicals to be added [22].

b) Adsorption technique:

In the adsorption technique, many adsorbent materials have been used in the past to find out an efficient and economical defluoridating agent. Activated alumina, activated carbon, calcite, activated sawdust, activated alumina coated silica gel, activated coconut shell carbon, and activated fly ash, groundnut shell, coffee husk, rice husk, magnesia, serpentine, tricalcium phosphate, bone charcoal, activated soil sorbent, carbion, defluoron-1, defluoron-2, etc., are different adsorbent materials. The most commonly used adsorbents are activated alumina and activated carbon [23].

➢ *Activated alumina:*

Activated alumina technology is one of the widely used adsorption methods for the defloridation of water**.** The fluoride removing efficiency of activated alumina is affected by hardness and surface loading. The process is pH specific, so the pH of the solution should be between 5.0-6.0 because at pH greater than 7, silicate and hydroxide become a stronger competitor of the fluoride ions for exchange sites on activated alumina and at pH less than 5 the activated alumina gets dissolved in the acidic environment leading to loss of adsorbing media. The process is highly selective but it has low adsorption capacity and poor physical integrity. It requires acidification and pre-treatment. The effectiveness of activated alumina for fluoride removal reduces after each regeneration.

➢ *Activated Carbon:*

The use of powdered activated carbon for fluoride removal achieved good results [23]. The process is pH dependent with good results only at pH 3.0 or less. So, the use of this material is expensive due to the need for pH adjustment.

- ***Advantages:***

i. Adsorption technique process can remove fluoride up more than 90%
ii. This technique is effective and economical
iii. In this process requires minimum contact time for maximum defluoridation
iv. It is indigenously available and cheap
v. Adsorption technique percentage of regeneration is considerably high.

- ***Disadvantages:***

i. The adsorption technique process is highly pH dependent and works only in a pH range of 5-6
ii. In this process high concentration of total dissolved salts (TDS) can result in fouling of the alumina bed
iii. Presence of sulphate, phosphate or carbonate results in ionic competition
iv. The regeneration is required after every 4-5 months
v. In this technique disposal of fluoride laden sludge is also a problem
vi. Skilled personnel are required for plant operation
vii. Biggest disadvantage is suitable grades may not be indigenously available in less developed countries
viii. This treatment is not effective if TDS exceeds 1500 mg/L
ix. This process requires time to time regeneration as after some time activated alumina is exhausted.

c) ***Ion exchange technique:***

Ion Exchange technique synthetic chemicals named as anion and cation exchange resins have been used for fluoride removal. Some of these are Tul-sion A-27, Deacedite FF (IP), Lewatit MIH-59, Amberllte IRA 400, and Amberlite XE-75, Polyanion (NCL). The fluoride exchange capacity of these resins depends upon the ratio of fluoride to total anions present in water. The resins increased the concentration of chloride in treated water, which can cause corrosion of the water storage tanks or utensils. The treated water also had a very high pH.

- ***Advantages***

i. Ion exchange technique the removes fluoride up to 90-95%
ii. It helps in the retention of taste and colour of water intact.

- ***Disadvantages***

i. Ion exchange process, efficiency is reduced in presence of other ions like sulphate, carbonate, phosphate and alkalinity

ii. In this process the regeneration of resin is the most problematic because it leads to fluoride-rich waste, which has to be treated separately before final disposal
iii. The process is expensive because of the cost of resin
iv. The biggest problem is the treated water has a very low pH and high levels of chloride [23].

d) Miscellaneous methods:

- **Reverse osmosis:**

  In the reverse osmosis technique, the hydraulic pressure is exerted on one side of the semi-permeable membrane which forces the water across the membrane leaving the salts behind. The relative size of the pollutants left behind depends on the pressure exerted on the membrane. The removal of fluoride in the reverse osmosis process has been reported to differ from 45-90% as the water is raised from 5.5-7. The membranes are very sensitive to temperature and pH. The economics of the approach also deserves evaluation under specific circumstances. The R.O units are also subject to chemical attacks, plugging, fouling by particulate matter, and concentrated and large quantities of waste. The volume of the wastes is even larger than the ion exchange process. Sometimes, the pre-treatment requirements are extensive.

- **Electro dialysis:**

  In electro dialysis, the membranes allow the ions to pass but not the water. In this process, the driving force is an electric current which carries the ions through the membranes. Electro dialysis technique is highly energy-intensive and expensive [21].

- **Advantages**

i. Ion exchange technique the removes fluoride up to 90-95%
ii. It helps in the retention of taste and colour of water intact.

- **Disadvantages**

i. Ion exchange process, efficiency is reduced in presence of other ions like sulphate, carbonate, phosphate and alkalinity

ii. In this process the regeneration of resin is the most problematic because it leads to fluoride-rich waste, which has to be treated separately before final disposal

iii. The process is expensive because of the cost of resin. The biggest problem is the treated water has a very low pH and high levels of chloride [23].

iv. Biggest problem is lots of water gets wasted as brine and disposal of brine is also a problem [23].

CHAPTER-2

3.1 LITERATURE REVIEW:

3.1.1 Literature Review

Singh *et al.* (2004) presented high fluoride groundwater especially in the hard rock areas south of the Ganges valley and in the arid north-western part of the country. The phenomenon is related to groundwater with residual alkalinity $Ca^{2+} < HCO_3$. Fluoride concentrations are governed by adsorption equilibria and by fluorite solubility. Evapotranspiration leads to precipitation of calcite, a lowering of Ca activity and an increase in Na/Ca ratios, and this allows an increase in F^- levels. In southern India, Mg seems to be controlled by dolomite, while sepiolite and palygorskite are Mg sinks in Rajasthan but may then release F^- under alkaline conditions. The latter two minerals are probably also important sources and sink for F^- in the hydroxy-positions. The increase in the extent of sodic soils as a result of irrigation is a contributing factor to the increasing incidence of fluorosis. [**25**]

Deng *et. al.* (2012) described the lithological features of the aquifer sediments and fluoride in rocks to determine the distribution and genesis of high fluoride groundwater (>1.5 mg/L) in Hangjinhouqi, which is an endemic fluorosis areas. Groundwater with high fluoride (>1.5 mg/L) is mainly of HCO_3-Na or HCO_3-Cl-Na type for both fresh and brackish water. Different from other halide ions of Cl^-, Br^- , I^-, and F^- in groundwater decreased with the TDS. [26]

Belkhalfa *et. al.* (2021):This study aimed to work out the fluoride concentrations in drinking water consumed by the Ouarthegla population (south-east of Algeria) in 2021, assess non-carcinogenic health risks via daily human intake, and calculate the upper acceptable fluoride concentration in drinking water by Galgan and Vermillion formula. During the spring season, forty-two water samples were collected and the fluoride was measured with the help of a validated spectrophotometric method. Hazard quotient of fluoride (HQ) and estimated daily intake (EDI) were calculated. It was found that the fluoride concentrations in water were much higher in rural areas than in the central city ($p = 0.05$). Hazard quotient (HQ) values were less than one for adults but greater than 1 for infants and children, suggesting health risks associated with water consumption for these vulnerable groups ($p = 0.007$). The main outcome of this study is the establishment of a database concerning fluoride levels and hazard quotient in the south of Algeria. Keeping an eye on drinking water and controlling fluorosis is essential to avoid potential health risks. [27]

Dutta *et.al.*(2016) described the geochemistry and the genesis of fluoride (F^-) in an alluvial aquifer with an emphasis on the prevalence of dental and skeletal fluorosis among the endemic population Hydro-geochemical outcomes reveal that chemical weathering and ion-exchange phenomena are the two dominant processes that make study area groundwater into $NaeHCO_3$ water type. The presence of intercalated zeolite-rich sediments having higher ion-exchange capacity within the aquifer is the source and mobilizing factor of F^- in groundwater respectively. A health survey reveals done and it was found that in 235 studied populations more than 60% suffer from dental fluorosis while females above 30 years of age became exposed early to osteoporosis disease. [28]

D.Karunanidhi *et.al*.(2020) represented the human health hazard based on the intake and dermal contact of fluoride enriched potable groundwater used for rural water supply in a semi-arid region (Shanmuganadhi River basin) of south India. A variance decomposition based Sobol sensitivity method was used to assess the relative contribution as well as interaction of input variables for both oral and dermal models. Three different scores were evaluated: FOE (first order effect), SOE (second order effect) and TE (total effect) for different age groups of population including gender (kids, women and men). The spatio-temporal mapping indicates that about 26% of water supply wells exceeded the recommended limit (WHO) of fluoride ($>1.5\ \mathrm{mg\ l^{-1}}$) for safe intake. These wells spread over $104.03\ \mathrm{km}^2$ area consisting 16 villages in the basin. [29]

Choubisa SL. *et al.* (2016) represented waterborne hydrofluorosis in both man and domestic animals and has been widely studied almost in every state in India. Patterns of dental mottling or dental fluorosis and Osteal deformities or skeletal fluorosis cases are also studied. It is found that in contrast, reports on industrial fluoride pollution or contamination along with industrial and neighbourhood fluorosis in residents and animals living in the vicinity of fluoride discharging industries are very limited. [30]

Cai H. *et al.* (2016) described a low-cost and highly efficient bio sorbent for fluoride removal. It was prepared by loading zirconium (IV) onto ball-milled, ultrafine tea powder (UTP-Zr). To evaluate the fluoride adsorption capacity of UTP-Zr over a wide range of conditions, the biosorbent dosage, contact time, initial pH, initial fluoride concentration and presence of other ions were varied. UTP-Zr performed well over the considerably wide pH range of 3-10. The residual concentration of Zr in the treated water was below the limit of detection (0.01 mg/L). Fluoride adsorption by the UTP-Zr biosorbent followed the Langmuir model, with a maximum adsorption capacity of 12.43 mgF^-/g at room temperature. The fluoride adsorption kinetics fit the pseudo-second-order kinetic model. Results from this study demonstrated that UTP-based biosorbents will be useful and safe for the removal of fluoride from drinking water. [31]

Zhang K. *et al.*(2016) discussed about the development of a nanosphere adsorbent for the removal of fluoride from water. A new uniform-sized $CeCO_3OH$ nanosphere adsorbent was developed, and tested to establish its efficiency, using kinetic and thermodynamic studies, for fluoride removal. The results demonstrated that the $CeCO_3OH$ nanospheres exhibited much high adsorption capacities for fluoride anions due to electrostatic interactions and exchange of the carbonate and hydroxyl groups on the adsorbent surface with fluoride anions. Adsorption kinetics was fitted well by the pseudo-second-order model as compared to a pseudo-first-order rate expression, and adsorption isotherm data were well described by Langmuir model with max adsorption capacity of 45 mg/g at pH 7.0. Thermodynamic examination demonstrated that fluoride adsorption on the $CeCO_3OH$ nanospheres was reasonably endothermic and spontaneous. Moreover, the $CeCO_3OH$ nanospheres have less influence on adsorption of fluoride by pH and co-exiting ions, such as SO_4^{2-} ,Cl^-, HCO_3^- CO_3^{2-} and PO_4^{3-}, and the adsorption efficiency is very high at the low initial fluoride concentrations in the basis of the equilibrium adsorption capacities. This study indicated that the $CeCO_3OH$ nanospheres could be developed into a very viable technology for highly effective removal of fluoride from drinking water. [32]

Wu S. *et al.*(2016) stated a novel adsorbent, hydroxyl aluminum oxalate (HAO), for the high efficient removal of fluoride from aqueous solution was successfully synthesized. The adsorbent was characterized and its performance in fluoride (F^-) removal was evaluated for the first time. Kinetic data reveal that the F^- adsorption is rapid in the beginning followed by a slower adsorption process; 75.9% adsorption can be achieved within 1 min and only 16%

additional removal occurred in the following 239 min. The F^- adsorption kinetics was well described by the pseudo second-order kinetic model. The calculated adsorption capacity of this adsorbent for F^- by Langmuir model was 400 mg/g at pH 6.5, which is one of the highest capabilities of today's materials. The thermodynamic parameters calculated from the temperature-dependent isotherms indicate that the adsorption reaction of F^- on the HAO is a spontaneous process. [33]

Bhattacharyya *et.al.* (2015) represented neem leaf powder (NLP), which was developed from the mature leaves of Neem (*Azadirachta indica*) trees has been shown to be an active biosorbent for the removal of fluoride from water. The effects of solution pH, contact time, adsorbent amount and solution temperature on fluoride sorption have been investigated. The biosorbent was effective at the pH range of 5.0–7.0 and its fluoride removal capacity was found to be above 80%. [34]

Sarkar *et.al.* (2006) discussed the effects of different operational variables on the mechanistic function of laterite in the removal of fluoride have been investigated. Thermodynamic parameters such as free energy change, enthalpy, and entropy of the process, as well as the sorption isotherm, were evaluated. The extent of solute removal is determined by initial solute concentration, operational conditions, laterite dosage, and solution pH. The effect of dependent and extraneous variables on the removal characteristics is also evaluated. In order to evaluate the efficiency of the process, feasibility criteria are also determined. [35]

3.1.2 Research Gap:

From the literature review, some papers are found on the adsorption studies of fluoride using laterite soil [35]. From there following research gaps are found:

- ✓ It is found that the dosages of the laterite are restricted up to 1-2 gm, so the fluoride removal capacity of laterite soil is not attractive.
- ✓ Research papers are only focused on the fluoride removal capacity of laterite, not other parameters of water quality like pH, Total Dissolved Solid (TDS), iron etc.
- ✓ None of the papers is discussed on the isotherm study for the column using laterite.
- ✓ Not a single paper is focused on fluoride removal capacity of weathered laterite soil (White laterite)

CHAPTER-3

4.1 OBJECTIVE & SCOPE OF WORK

4.1.1 Objective of the study:

The objective of the present study are:

1. To study the stretch and degree of high fluoride concentration in the groundwater in some western districts which are connected with the Chotonagpur Plateau.

2. To study the fluoride adsorption capacity of laterite at different conditions.

3. Design and fabrication of fluoride removal filtration system to provide a sustainable water system in rural West Bengal.

4.1.2 Scope of the study:

The scope of the present studies are:

1. To identify the fluoride-affected zone.

2. To observe the fluoride concentration in groundwater in affected areas.

3. Fluoride removal capacity of the locally available laterite soil.

4. Comparative study of fluoride removal efficiency of red laterite soil and weathered laterite soil (white laterite).

5. Cost analysis of the filter developed as a mitigation strategy.

CHAPTER-4

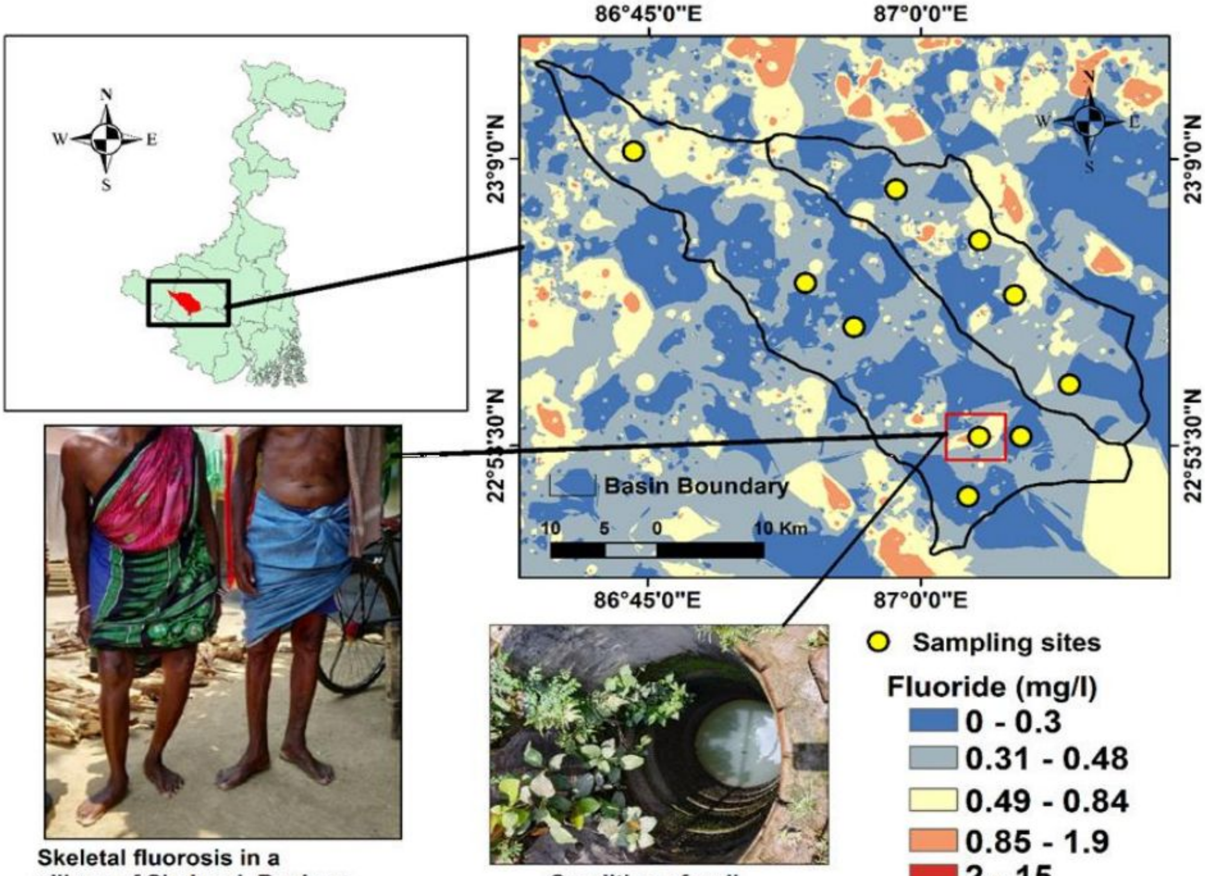
5.1 STUDY AREA

5.1.1 Location of the study area

Shilabati river basin is an important river basin located at the eastern part of West Bengal, India, extending between 23°14′18.03″ N and 22°26′ 25.12″ N latitude and 86°38′ 46.08″ E and 87°46′ 36.65″ E longitude. The river originates from the dissected upland of Chotonagpur Plateau of Puncha block of Purulia district, West Bengal and flows in the south-easterly direction through Simlapal, Taldangra, Indpur, Khatra and Hirabandh block of Bankura district, West Bengal and then enter West Medinapore district where it joins with Rupnarayan River. Shilabati-Joypanda is the tributary of the Shilabati river basin. Both the basin are location at the upstream section comprising hard rock terrain and rolling lands. The minerals composition of the basin have a massive influence on the groundwater quality. The Shilabati-Joypanda basin is affected with high fluoride concentration of more than 1.5 mg/l.

5.1.2 Fluoride-affected Zone:

The fluoride-affected areas were identified from the official website of the Public Health Engineering Department Government of West Bengal (WBPHED) for the present study. Fluoride-contaminated groundwater is found in Puncha block of Purulia district, Simlapal, Taldangra, Indpur and Hirabandh block of Bankura district of West Bengal according to the levels. In fact, fluoride level is reported as high as 15 mg L^{-1} present in groundwater. The water samples has been collected from the few affected zone within the basin for laboratory analysis, experiment and column study for fluoride removal.



Skeletal fluorosis in a village of Simlapal, Bankura

Condition of well

Fig. 4: Fluoride-contaminated groundwater zone in the study area

CHAPTER- 5

6.1 MATERIAL & METHODS

6.1.1 Laterite Soil collection:

The laterite soil was primarily collected from Simlapal block of Bankura. Two types of soil are collected: red laterite soil and weathered laterite soil (white laterite). Soil samples were collected from one meter below the surface because the surface run-off in most cases interacts with top surface (upto 15 cm).

(a) (b)

Fig. 5: Laterite Soil sample collection (a) Red Laterite (b) White Laterite

6.1.2 Preparation of Soil:

The soil samples collected from the field were dried for ten days under the sun for moisture absorption. Then the dart particles, root of the plants, plastic present in the soil were removed. After that, soil sample was sieved. Only the soil particles which were between 1-2 mm were used for batch experiment as well as column study because finer particles provide more surface area , the solute finds more accessible sites for adsorption. Particle size below 1 mm not selected for the study because it dissolved with water and increase the TDS of the water also chances of choking the laterite bed during column operation.

(a) (b)

Fig. 6: Sun drying of Laterite Soil, (a) White Laterite (b) Red Laterite

6.1.3 Water sample collection:

Water samples were collected from the fluoride-contaminated zone. Samples were collected using 1 liter clean plastic bottle. Samples were collected from tube well. The water samples were collected after 10 minutes of pumping of tube well (Fig.-7). For the iron test 50 ml samples were acid fixed in different platic containers. The pH and TDS results were taken just after collection of the samples. The water samples collected details given below (Table-5):

Table 5: Water sample collection details

Sl .No.	Location	Latitude & Longitude	pH & Temp	TDS (mg L^{-1})
1	Gharpathar	N23° 06' 34.49" E86° 59' 07.32"	6.51 (30.5℃)	150
2	Kharjuria	N22° 56' 09.11" E86° 58' 58.63"	6.59 (26℃)	197
3	Niasa	N23° 12' 11.34"	6.68 (27.8℃)	244

		E86° 41’ 34.60”		
4	Pachaparar	22° 93’ 05” 87° 01’ 66”	**5.65** (27.8℃)	6
5	Poradi	N23° 07’ 07.11” E86° 39’ 52.35”	**6.31** (28.1℃)	121
6	Manipur	N23° 53’ 05” E86° 39’ 69”	6.50 (29.1℃)	149
7	Lakshisagar(Market)	N22° 55' 58" E87° 00' 40"	7.23 (29℃)	83
8	Lakshisagar (Bus Stand)	N22° 55' 38" E87° 00' 39"	7.21 (36℃)	127
9	Lakshisagar (Village)	N22° 55' 48" E87° 00' 52"	7.40 (36℃)	**610**
10	Lakshisagar (Primary Health Centre)	N22° 55' 07" E87° 01' 42"	7.56 (36℃)	102
11	Lakshisagar (Village)	N22° 55' 28" E87° 00' 27"	7.20 (37℃)	351

Fig. 7: Water sample collection from fluoride contaminated zone

6.1.4 Stock solution preparation:

For the preparation of a fluoride stock solution of 100 mg L^{-1}, Sodium fluoride (NaF) and double distilled water is used.

The molar mass of NaF is 41.99 gm mol^{-1} and the molar mass of F is 18.99 gm mol^{-1}

So, 18.99 gm F^- present in 41.99 gm NaF

1 gm F^- present in = $(41.99/18.99\times1)$ gm = 2.211 gm

100mg (0.1 gm) F^- present in = $(2.211/0.1)$ gm = 0.2211 gm =221.1 mg NaF

To prepare 100 mg L^{-1} (100 ppm) fluoride stock, in 1000 ml distilled water, 0.2211 gm or 221.1 mg NaF has to be mixed. After the preparation of the stock solution, the concentration of fluoride must need to be checked for confirmation.

6.1.5 Preparation of Synthetic Solution:

2 mg L^{-1} Fluoride stock:

For preparation of 50ml 2mg/L conc. F^- synthetic solution

Initial volume (V_1) × initial conc.(S_1) = Final volume(V_2) × Final conc.(S_2)

or, $V_1 \times 100 = 50 \times 2$ [here Final conc.(V_2)=50 ml and final conc. (S_2) = 2 mg L^{-1}]

or, $V_1 = 1$

So, 1 ml fluoride stock has to mix with (50-1)ml=49 ml distilled water

5 mg L^{-1} Fluoride stock:

For preparation of 50ml 5mg/L conc. F^- synthetic solution

Initial volume (V_1) × initial conc.(S_1) = Final volume(V_2) × Final conc.(S_2)

or, $V_1 \times 100 = 50 \times 5$ [here Final conc.(V_2)=50 ml and final conc. (S_2) = 5 mg L^{-1}]

or, $V_1 = 2.5$

So, 2.5 ml fluoride stock has to mix with (50-2.5)ml=47.5 ml distilled water

10 mg L^{-1} Fluoride stock:

For preparation of 50ml 10mg/L conc. F^- synthetic solution

Initial volume (V_1) × initial conc. (S_1) = Final volume(V_2) × Final conc.(S_2)

or, $V_1 \times 100 = 50 \times 10$ [here Final conc.(V_2)=50 ml and final conc. (S_2) = 10 mg L^{-1}]

or, $V_1 = 5$

So, 5 ml fluoride stock has to mix with (50-5) ml=45 ml distilled water.

20 mg L^{-1} Fluoride stock:

For preparation of 50ml 20mg/L conc. F^- synthetic solution

Initial volume (V_1) × initial conc. (S_1) = Final volume(V_2) × Final conc.(S_2)

or, $V_1 \times 100 = 50 \times 20$ [here Final conc.(V_2)=50 ml and final conc. (S_2) = 20 mg L^{-1}]

or, $V_1 = 10$

So, 10 ml fluoride stock has to mix with (50-10) ml=40 ml distilled water.

Table 6: Fluoride Synthetic Stock preparation

Fluoride Conc. (mg L^{-1})	**Stock Solution used (ml)**	**Distilled water used (ml)**
2	1.0	49.0
5	2.5	47.5
10	5.0	45.0
20	10.0	40.0

6.1.6 Method for measuring Fluoride concentration in water:

The ion-selective method is adopted for the analysis of fluoride in water. Hach Intellical ISEF121 combination fluoride ISE is used as a probe and HQ40d portable is used as a multimeter for measuring fluoride contamination in water. The following steps are followed in this method:

1. 50 mL of sample is added to a clean plastic beaker.
2. Then 1 pillow of TISAB (Total Ionic Strength Adjustment Buffer) is added to the sample.
3. After that Stir bar is added and the beaker is put on a magnetic stirrer and is stirred at a moderate rate.
4. The probe is put in the solution in such a way that probe did not touch the stir bar, bottom or sides of the container. Have to remove the air bubbles from under the probe tip.
5. The 'read' button is pushed when the measurement is stable, and the lock icon is shown. Then the reading is noted down.
6. After completion of every test the probe is washed using deionized distilled water and the probe is dried using tissue paper.

Fig. 8: Ion Selective Electrode Method

6.1.7 Point of Zero Charge

The point of zero charge (PZC) is actually the pH at which the net surface charge of the adsorbent is equal to zero. At that pH, the charges of all positive sites become equal to negative ions.

$$pH = PZC$$

- ***Importance of PZC***

The PZC gives us information regarding ionization of the functional groups and contact of metal ions with the adsorbent in the aqueous system.

- ***Procedure***

The salt addition method is taken into account for the point of zero charge test. The following steps are followed for this experiment:

1. An aliquot of 40 mL of $NaNo_3$ (0.1M) is collected in ten different plastic conical flasks
2. Set the different pH values (3-12) of the solution with either HNO_3 (0.1 M) or NaOH (0.1 M) solution using a pH probe.
3. Then in each flask 1 gm of laterite is added.
4. Then the flasks are inserted inside the shaker at 28℃ and at a speed of 150 rpm for 24 hours.
5. After the equilibrium, the sample is filtered in plastic beakers.
6. At last, the pH of the filtered water is noted down.

6.1.8 Batch Study

Batch experiments were performed to determine the equilibrium time, kinetics and the selection of an isotherm. The batch experiment was performed following way:

1. ***Variation in Dosage***

   Fixed conc. of F^- was taken in different plastic conical flasks and different dosage of laterite (2gm,4gm,6gm,8gm,10gm,12gm,14gm,16gm,18 gm,20 gm) were taken and flasks were shaken at a speed of 150 rpm for 5 hours to identify the removal efficiency of fluoride at a fixed temperature (28℃) and the experiment was repeated for fluoride concentration of 10 mg L^{-1}, 5 mg L^{-1}, 2 mg L^{-1}. The experiment was performed for both red and white laterite.

2. ***Variation in fluoride Concentration***

   Different concentrations of fluoride (2 mg L^{-1}, 4 mg L^{-1}, 6 mg L^{-1}, 8 mg L^{-1}, 10 mg L^{-1}, 12 mg L^{-1}, 14 mg L^{-1}, 16 mg L^{-1}, 18mg L^{-1}, 20 mg L^{-1}) were taken in different plastic conical flasks and fixed 10 gm of laterite is added inside every flask and were shaken at a speed of 150 rpm at a fixed temperature (28℃) for 5 hours. The main purpose of the experiment was to check the efficiency of laterite at different fluoride concentration levels. The experiment was repeated for both white and red laterite. This experiment was an important role in the isotherm study.

3. ***Variation in Agitation time***

   Fixed conc. (20 mg L^{-1}) of fluoride was taken in different plastic conical flasks and a fixed amount of laterite (20 gm) was added to every conical flask. Then inside the incubator, the flasks were shaken at a speed of 150 rpm at a fixed temperature (28℃). Every 50 min time interval one flask was taken out from the incubator and the final concentration was checked. The experiment was conducted for 300 minutes. The experiment was done for both red and white laterite. This experiment had an important role in the kinetic analysis of adsorption.

4. ***Variation in pH***

   Fixed concentration (10 mg L^{-1}) fluoride was taken in different plastic conical flasks. The each conical flask was fixed at different pH level with help of 0.1N NaOH and 0.1N HNo_3. pH levels are fixed from 4 to 10 and a fixed amount of laterite (10 gm) was added in every conical flasks. After 5 hours of agitation with a speed of 150 rpm .The efficiency of removal of fluoride was observed at different pH level. The test was conducted for both laterite soil at 32℃.

6.2 ADSORPTION ISOTHERM FOR BATCH EXPERIMENT

Adsorption isotherm is the representation of the relationship between the adsorbate in the liquid phase and the adsorbate adsorbed on the surface of the adsorbent at equilibrium at an equilibrium state.

The amount of fluoride (adsorbate) adsorbed onto the adsorbents was determined from the following equation:

$$q_e = \frac{(Ci - Ce)}{m} \times V$$

Where q_e is the fluoride adsorbed (mg g^{-1}); C_i is the initial concentration of fluoride (mg L^{-1}); Ce is the concentration of fluoride in solution at equilibrium time; V, solution volume (L); m, adsorbent dosage (gm)

The equilibrium adsorption isotherm is the most important to design the adsorption systems. For solid-liquid systems, several isotherms adsorption. The most important adsorption models are Langmuir, Freundlich, and Temkin adsorption isotherm models.

6.2.1 Langmuir Isotherm

The Langmuir adsorption model is based on the assumption that maximum sorption corresponds to a saturated monolayer of solute on the sorbent surface. This model also supposes that all the sorption sites are assumed to be identical, each site retains one molecule of the given compound and all sites are energetically and sterically independent of the sorbed quantity.

The Langmuir isotherm model equation is:

$$q = q_m \left(K_L \frac{Ce}{1 + KL\, Ce}\right)$$

The linear form of the Langmuir the equation can be described by:

$$\frac{\text{Ce}}{\text{qe}} = \frac{\text{Ce}}{\text{qm}} + \frac{1}{\text{KL} \;\; \times \text{qm}}$$

where C_e (mg L^{-1}) is the equilibrium concentration of the sorbate, q_e (mg g^{-1}) is the amount of adsorbate per unit mass of adsorbent, q_m (mg g^{-1}) is the maximum adsorption capacity (theoretical monolayer saturation capacity) and K_L (L mg^{-1}) is the Langmuir constant related to sorption capacity and rate of sorption.

The main characteristics of the Langmuir equation, constants K_L and qm, can be determined by plotting the $1/C_e$ versus $1/q_e$ curve for linearized form and the C_e versus q_e curve for non-linearized form.

The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless equilibrium parameter (R_L) defined by

$$R_L = \frac{1}{(1+KL\times Ci)}$$

The value of R_L indicates the type of the isotherm to be either favourable ($0<R_L<1$), unfavourable ($R_L>1$), linear ($R_L= 1$), or irreversible ($R_L=0$) [40].

6.2.2 Freundlich Model

The Freundlich isotherm model was originally an empirical nature but was later interpreted as sorption to heterogeneous surfaces or surface supporting sites of varied affinities. It is assumed that the stronger binding sites are occupied first and that binding strength decreases with increasing degree of site occupation. The Freundlich isotherm model can describe the adsorption of organic as well as inorganic compound on a wide variety of adsorbents [41].

The empirical form of the Freundlich isotherm model [42]:

$$q_e = K_F.C_e^{1/n}$$

where q_e is the adsorption (mg g^{-1}); C_e is the concentration of adsorbate in the solution (mg/L); K_F and n were empirical constants that are characteristics of the system, indicating the adsorption capacity and the adsorption intensity, respectively. The above equation can be linearized as the following form, also used to confirm the applicability of the model

$$\ln q_e = \ln K_F + \frac{1}{n \ln Ce}$$

K_F is the measure of sorption capacity and 1/n is the sorption intensity. The value of *n* of this model fell in the range of 1–10, indicating favorable sorption. The numerical value of $1/n < 1$ indicated that adsorption capacity was only slightly suppressed at lower equilibrium concentration [41].

The equilibrium data have further been analysed by using the linearized form of Freundlich isotherm, by plotting ln q_e versus ln C_e.

6.2.3 Temkin Isotherm

Temkin isotherm, which considers the effects of the heat of adsorption, decreases linearly with coverage of the adsorbate and adsorbent interactions. The Temkin isotherm has been used in the form as follows:

$$q_e = \frac{RT}{bt\times \ln(Kt)}$$

Where b_t is the Temkin constant related to the heat of sorption (J mol^{-1}), K_t is the Temkin isotherm constant (L mg^{-1}), R is the gas constant (8.314 J mol^{-1} K^{-1}) and T is the absolute temperature (in K). The parameters of Temkin model are determined by plotting the q_e versus $\ln C_e$.

6.3 KINETICS STUDY FOR BATCH EXPERIMENT

For the determination of the adsorption rate constant, equilibrium adsorption capacity and adsorption mechanism of the experiment, a kinetic study was performed [43]. The kinetics of fluoride adsorption on both the laterite soils have been determined by using three different kinetic models, which are pseudo-first-order, pseudo-second-order and intra-particle diffusion models.

6.3.1 Pseudo-first-order model

This is the first equation for the sorption of liquid/solid system based on solid capacity.[44] The following equation was considered for pseudo-first-order kinetic which was introduced by Lagergren [45,46]:

$$\frac{d(qt)}{dt} = k_1 (q_e - q_t)$$

The above equation can be integrated for following boundary conditions to obtain Equation

$t = 0$, $q_t = 0$, $t = t$, $q_t = q_t$

$$\ln (q_e - q_t) = \ln q_e - k_1 . t$$

Where, q_e is the amount of solute on the surface of the sorbent at equilibrium, (mg g^{-1}), q_t is the amount of solute on the surface of the sorbent at time t, (mg g^{-1}), k_1 is the equilibrium rate constant of pseudo-first sorption, (L min^{-1}).

The pseudo-first-order rate constant (k_1) and theoretical equilibrium adsorption capacities (q_e) were calculated from a linear plot of $\ln (q_e - q_t)$ versus t.

6.3.2 Pseudo-second-order model

The pseudo-second-order model predicts the behavior over the whole adsorption time and is in agreement with the adsorption mechanism being the rate-controlling step. The pseudo-second-order rate equation is expressed as [47]:

$$dq_t / dt = k_2 (q_e - q_t)^2$$

Where k_2 is the pseudo-second-order rate constant. After integration and applying boundary conditions, $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$; the integrated form of above Eq. becomes:

$$t/q_t = 1/k_2.q_e^2 + t/q_e$$

The second-order rate constant k_2 and maximum adsorption capacity q_e have been calculated by plotting the graph of t/qt versus t for the linear pseudo-second-order model from the intercept and slope of this graph, respectively.

6.3.3 Intra-particle diffusion Model

Intra-particle diffusion model suggested by Weber and Morris [48], the initial rate of intra-particle diffusion can be calculated by plotting the q_t versus $t^{0.5}$ graph

$$q_t = k_{diff} \,.\, t^{1/2} + c$$

Where, q_t is amount of solute on the surface of the sorbent at time t, (mg gm^{-1}), k_{diff} is the intra-particle rate constant (mg gm^{-1} $min^{1/2}$), t is the time (min) and c (mg gm^{-1}) is a constant that gives an idea about the thickness of the boundary layer. If the Weber–Morris plot of q_t versus $t^{1/2}$ gives a straight line, then the adsorption process is controlled by intra-particle diffusion only.

6.4 COLUMN STUDY

6.4.1 Calculation of Filtration Rate

The filtration rate for the slow sand fix bed column filter is 100 to 200 lit./m^2/hour [as per clause no 5.2 of **IS 11401 (Part 2):1990** and clause 7.6.2.4 (c) of **Manual on water supply and Treatment (CPHEEO), 1999**]

When taking the Filtration Rate as 200 lit/m^2/hr for calculation of discharge:

The diameter of the designed filter is 4 cm

Plan area (A) = $[\frac{\pi}{4} \times (4)^2]\ cm^2 = 12.566\ cm^2$

$$\text{Plan area (A)} = \frac{\text{Discharge (Q)}}{\text{Rate of Filtration}}$$

$\therefore 12.566 \times 10^{-4} = \frac{Q}{200}$ [Rate of Filtration 200 lit/m^2/hr]

- ⇨ Q = 0.25132 lit/hr
- ⇨ $Q = 0.25132 \times 10^3$ ml/hr
- ⇨ = 4.1886 ml/ min

But in our filter, we maintain discharge (Q) as 6 ml/min

∴Q = 360 ml/hr =0.36 lit/hr

So, In our case, the Rate of filtration = $\frac{\text{Discharge (Q)}}{\text{Plan Area (A)}}$ = $[0.36/ (12.566 \times 10^{-4})]$ lit/m^2/hr

≈300 lit/m^2/hr

6.4.2 Manufacturing of Fix Bed Column Filter

A PVC pipe of 4.5 cm diameter and 80 cm length is taken for making the filter. Then the adapter UPVC adaptor (reducer) is attached to the bottom of the pipe. After that, a PVC flexible pipe is attached with the help of a threaded PVC cup. At the bottom of the PVC pipe, a plastic tap is connected for collecting water. The design of the filter is shown in the Fig. 9 below:

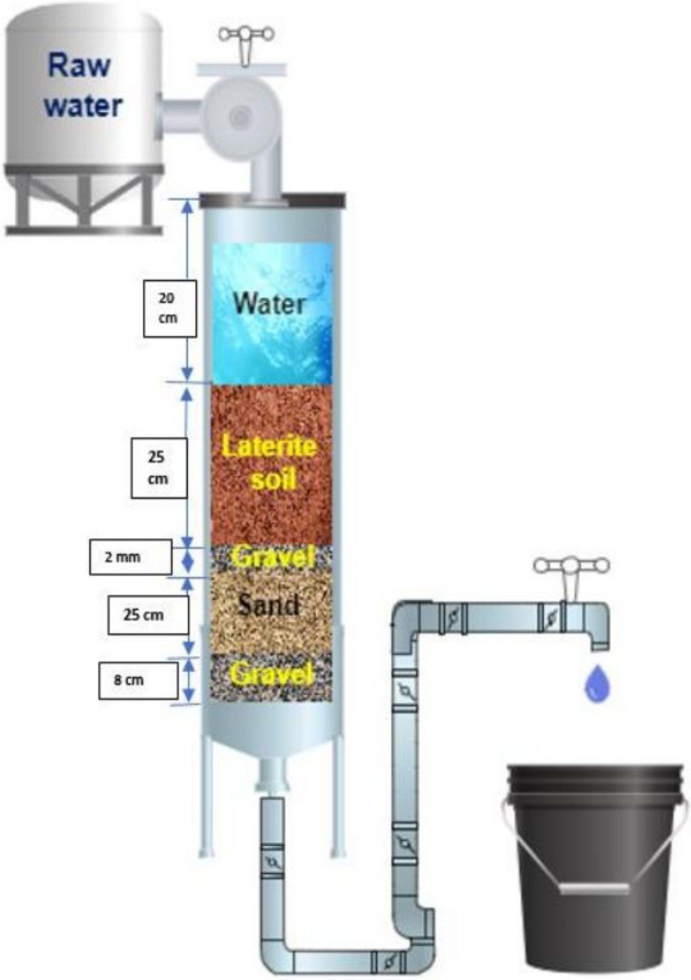


Fig. 9: Schematic Diagram of the adsorption Fixed bed Column Filter

6.4.3 Development of the De-fluoridation Unit

De-fluoridation unit actually refers to the fixed bed column filter where the operation of adsorption as well as filtration is taking place. The development of the unit involves nothing but the sequential laying of all the media. But before packing the media within the column, it must have to be ascertained that the gravel and sand are washed in water, cleaned properly and dried in air.

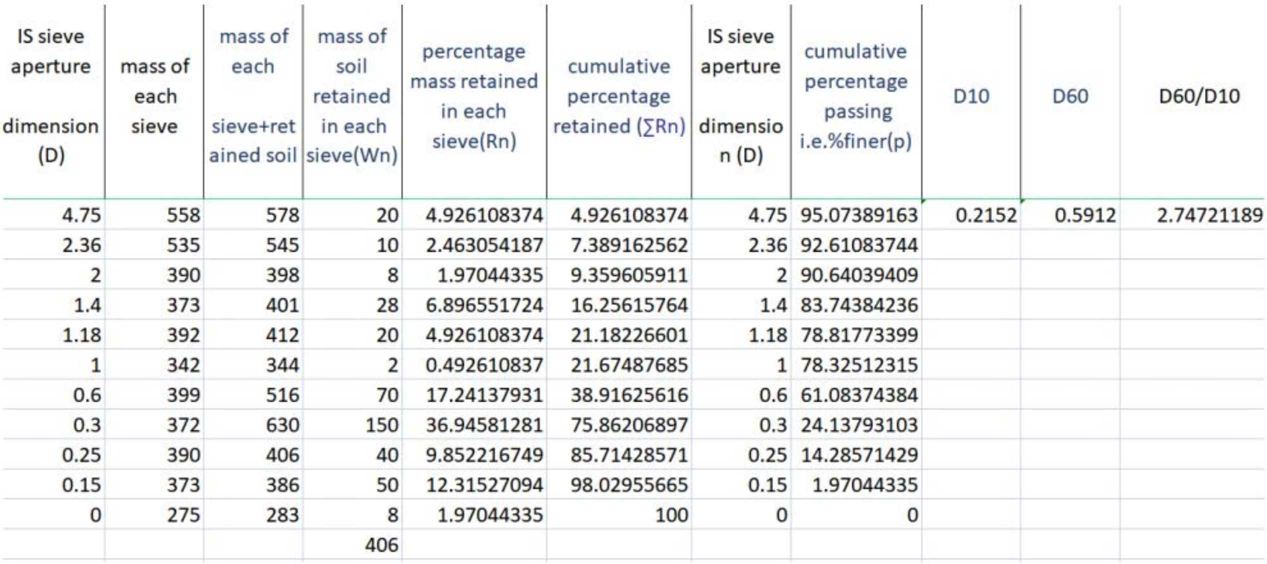
The first 8 cm length is allotted for the three different sizes of gravel. Gravel of size 8 mm to 10 mm is first poured into the column for a length or depth of 3 cm. The next depth of 5 cm is filled with gravel of size 4.75 mm to 8 mm.

The next 25 cm length of the column is then filled up with well-graded sand which has an effective size (D_{10}) of 0.215 mm and uniformity coefficient (D_{60}/D_{10}) of 2.74

[D_{10}=0.15-0.30 mm and D_{60}/D_{10} = preferably below 3, as per clause no 5.1(table-1) of **IS 11401 (Part 2):1990]**

In this filter, 501 grams of sand is used just over the gravel layer.

Table 7 : Particle size distribution for used sand in Filter



IS sieve aperture dimension (D)	mass of each sieve	mass of each sieve+retained soil	mass of soil retained in each sieve(Wn)	percentage mass retained in each sieve(Rn)	cumulative percentage retained (∑Rn)	IS sieve aperture dimension (D)	cumulative percentage passing i.e.%finer(p)	D10	D60	D60/D10
4.75	558	578	20	4.926108374	4.926108374	4.75	95.07389163	0.2152	0.5912	2.74721189
2.36	535	545	10	2.463054187	7.389162562	2.36	92.61083744			
2	390	398	8	1.97044335	9.359605911	2	90.64039409			
1.4	373	401	28	6.896551724	16.25615764	1.4	83.74384236			
1.18	392	412	20	4.926108374	21.18226601	1.18	78.81773399			
1	342	344	2	0.492610837	21.67487685	1	78.32512315			
0.6	399	516	70	17.24137931	38.91625616	0.6	61.08374384			
0.3	372	630	150	36.94581281	75.86206897	0.3	24.13793103			
0.25	390	406	40	9.852216749	85.71428571	0.25	14.28571429			
0.15	373	386	50	12.31527094	98.02955665	0.15	1.97044335			
0	275	283	8	1.97044335	100	0	0			
			406							

After the sand layer, a 2 cm mixed gravel layer is provided to restrict the red laterite particle (used over this layer) to insert inside the sand layer. Basically, a mixed gravel layer is provided to keep the laterite away from the sand layer.

Then a red laterite soil of 25 cm in length (diameter more than 1 mm and less than 2 mm) is provided above the mixed gravel layer. The total amount of laterite is used 459 grams. In this filter, a 20 cm head is provided for uniform flow.

The De-fluoridation unit is now developed to get attached to the other parts of the experimental setup.

6.4.4 Experimental Set-up

The overall experimental set-up consists of a plastic bucket fitted with a plastic tap that acts as the inlet tank which stored the fluoride-contaminated groundwater. An outlet tap of the inlet tank is connected with the de-fluoridation unit with a rubber pipe. At the outlet tap of the de-fluoridation unit, a bucket is placed to store filtered water. One of the most important points that have to be kept in mind during setting up all the parts is that the height of the outlet plastic tap of the inlet tank has to be adjusted carefully. It must be kept at an elevation higher than the elevation of the top level of the adsorbent in the filter column fitted by its side. Otherwise, the water level in the column may go down below the top level of the laterite soil which may result from unsatisfactory efficiency of the adsorbent by forming cracks due to drying.

6.4.5 Procedure

- The inlet bucket is first filled with fluoride-contaminated groundwater collected at Lakshmisagar (2.38 mg/l), in Bankura district of West Bengal, India.
- The water is allowed to enter the filter column through the inlet pipe connected to the outlet tap of the inlet tank.
- The flow rate is adjusted to 6 ml/min initially by adjusting the tap at the inlet bucket and the plastic tap attached to the outlet rubber pipe.
- After filtration the water is coming out of the outlet tap which is stored in another plastic bucket.
- Sample is collected from the outlet in a plastic beaker every 30 min interval which is tested in the Water Quality Lab for determination of Fluoride content, pH, TDS, Turbidity, and Iron quantity.

Fig. 10: Experimental setup of the fixed bed column filter

6.5 ADSORPTION MODELS FOR COLUMN STUDY

Various practical features such as sorbent capacity, operating life span, regeneration time, and prediction of the time necessary play a vital role during the operation of the column using adsorption dynamics acquaintance and modeling. The column model study provides detailed conclusions about the mechanism of the process. The adsorption column is subjected to axial dispersion, external film resistance, and intra-particle diffusion resistance. To determine the adsorption mechanism of fluoride using laterite soil and to design the adsorption process in a dynamic regime, it is necessary to know the evolution of the residual concentration of the effluent in time. In this case, three models can be used, namely the Adams–Bohart, Yoon–Nelson, and Thomas models to analyze the breakthrough curves and for the prediction of the dynamic nature of the column [49].

6.5.1 Bohart–Adams Model

The Bohart–Adams Model is used to describe the first part of the column breakpoint curve. The Bohart–Adams equation is linearly expressed as [50]:

$$\ln(C_t/C_o) = k_{BA}.Co.t - k_{BA}.N_0.(Z/F)$$

where: C_o is the effluent concentration, (mg L^{-1}); C_t is the effluent concentration,(mg L^{-1}); t is time, (min); k_{BA} is the kinetic constant of the Bohart-Adam model, (L mg^{-1} min^{-1}); F-is the linear velocity calculated by dividing the flow rate by the column section area,(cm min^{-1}); Z is the bed height of the column, (cm); N_0 is the saturation concentration, (mg L^{-1}). Bohart–Adams Model model $\ln(C_t/C_o)$ is plotted against time (t).

6.5.2 Yoon–Nelson Model

The Yoon-Nelson Model is most commonly adopted to describe the breakpoint curve [51]. It is a model used especially for the single-component system and does not require information about the adsorbent, such as type, physical properties, or other characteristics. Yoon-Nelson equation is linearly expressed as:

$$\ln [C_t/(C_0-C_t)] = k_{YN.}t - \tau.k_{YN}$$

Where: C_t is the solution concentration at time t, (mg L^{-1}); C_0 is the initial solution concentration, (mg L^{-1}); k_{YN} is the rate constant, (min^{-1}); τ is the time required for 50%

adsorbate breakthrough, (min). The parameters τ and k_{YN} can be obtained from the plot of the function $\ln[C_t/(C_0 - C_t)]$ against time (t).

6.5.3 Thomas Model

The Thomas model is the generally used model to describe the adsorption column performance and to establish breakthrough curves [52]. It is frequently used to determine the adsorption capacity of the material. The Thomas equation is linearly expressed as:

$$\ln [(C_0/C_t)^{-1}] = (k_{TH.}.q_{TH}.m/Q) - k_{Th.}C_0 .t$$

where: C_0 is the solution concentration in the effluent, (mg L^{-1}); C_t is the solution concentration at time t in the effluent, (mg L^{-1}); k_{TH} is the Thomas rate constant, (L min^{-1} mg^{-1}); q_{TH} is the equilibrium compounds uptake per gm, (mg gm^{-1}); m—is the mass of adsorbent, (gm); Q is the flow rate, (mL min^{-1}). k_{TH} and q_{TH} are determined by plotting the ln $[(C_0/C_t)^{-1}]$ against the time (t) graph.

CHAPTER-6

7.1 RESULT & DISCUSSION

7.1.1 Water Quality Analysis

The water collected from the field were analysed in the water quality laboratory. The outcome of the test results are given table (8).From the results, the fluoride contaminated groundwater was found three locations of Lakshmisagar (market, village, primary health centre-PH). Apart from that one village, the water of the tube-well the total dissolved solid (TDS) level was found very high (610 mg L^{-1}), more than acceptable limit of 500 mg L^{-1}. Iron quantity in groundwater is less than permissible all locations apart from Gharpathar where iron quantity is found 1.22 mg L^{-1}. pH level in groundwater was obtained more than requirement at Pachaparar and Poradi.

Table 8: Water Quality Test Results

Location	**Latitude & Longitude**	**pH**	**TDS (mg L^{-1})**	**Fluoride (mg L^{-1})**	**Iron (mg L^{-1})**
Gharpathar	N23° 06’ 34.49” E86° 59’ 07.32”	6.51 (30.5°C)	150	0.134	1.22
Kharjuria	N22° 56’ 09.11” E86° 58’ 58.63”	6.59 (26.0°C)	197	0.304	5.00
Niasa	N23° 12’ 11.34” E86° 41’ 34.60”	6.68 (27.8°C)	244	0.297	0.36
Pachaparar	N22° 93’ 05” E87° 01’ 66”	5.65 (27.8°C)	6	0.0235	0.16
Poradi	N23° 07’ 07.11” E86° 39’ 52.35”	6.31 (28.1°C)	121	0.675	0.49
Manipur	N23° 53’ 05” E86° 39’ 69”	6.50 (29.1°C)	149	0.194	0.35
Lakshisagar (Market)	N22° 55' 58" E87° 00' 40"	7.23 (29°C)	83	2.38	0.43
Lakshisagar (Bus Stand)	N22° 55' 38" E87° 00' 39"	7.21 (36°C)	127	0.778	0.41
Lakshisagar (Village)	N22° 55' 48" E87° 00' 52"	7.40 (36°C)	610	2.40	0.18
Lakshisagar (Primary Health Centre)	N22° 55' 07" E87° 01' 42"	7.56 (36°C)	102	1.130	0.05
Lakshisagar (Village)	N22° 55' 28" E87° 00' 27"	7.20 (37°C)	351	0.193	0.32

7.1.2 Point of Zero charge

For point of zero charge test salt addition method is adopted. From the graph (Fig.10), at 5.67 pH (Fig.11), the charges of all positive sites become equal to negative ions. The experimental point of zero charge value is very close to the theoretical point of zero charge value of 4.81 [39]. The difference may be because of the presence of other oxides along with silica and alumina in laterite.

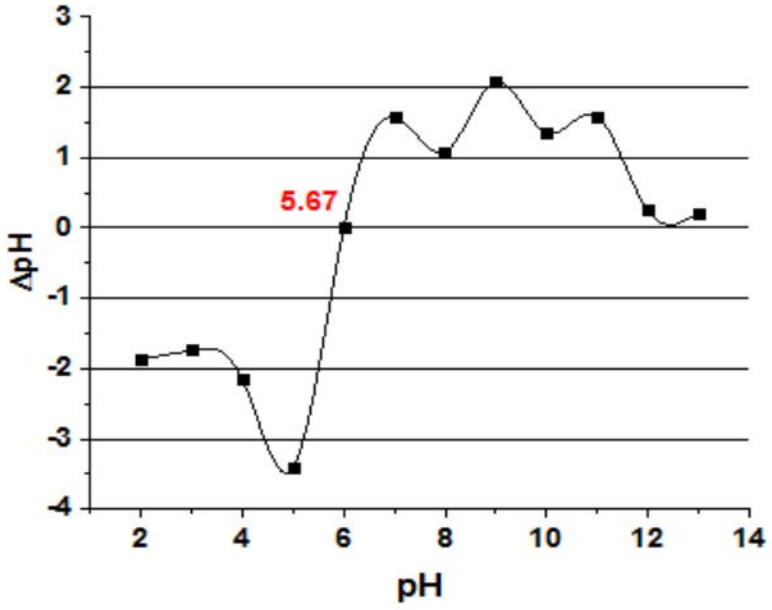


Fig. 11: Determination of pH at point-of-zero charge of laterite soil

7.1.3 Effect of absorbent dose

The batch experiments were conducted on the basis of variation of laterite dose, variation of initial fluoride concentration, variation of agitation time and variation of initial pH conditions. The laterite dose was varied from 4 gm to 20 gm for the selected agitation time (150 rpm) and fixed initial solute concentration. It is observed that as the dose of laterite increases the extent of fluoride adsorbed increases. It is seen that for all concentrations the adsorption corresponding to a laterite dose of 4 gm is poor; it increases afterward with increased laterite dose and reaches a maximum value corresponding to a dose of 20 gm of laterite. The obtained experimental test results are represented below for both white and red laterite samples in separate graphs (Fig.12):

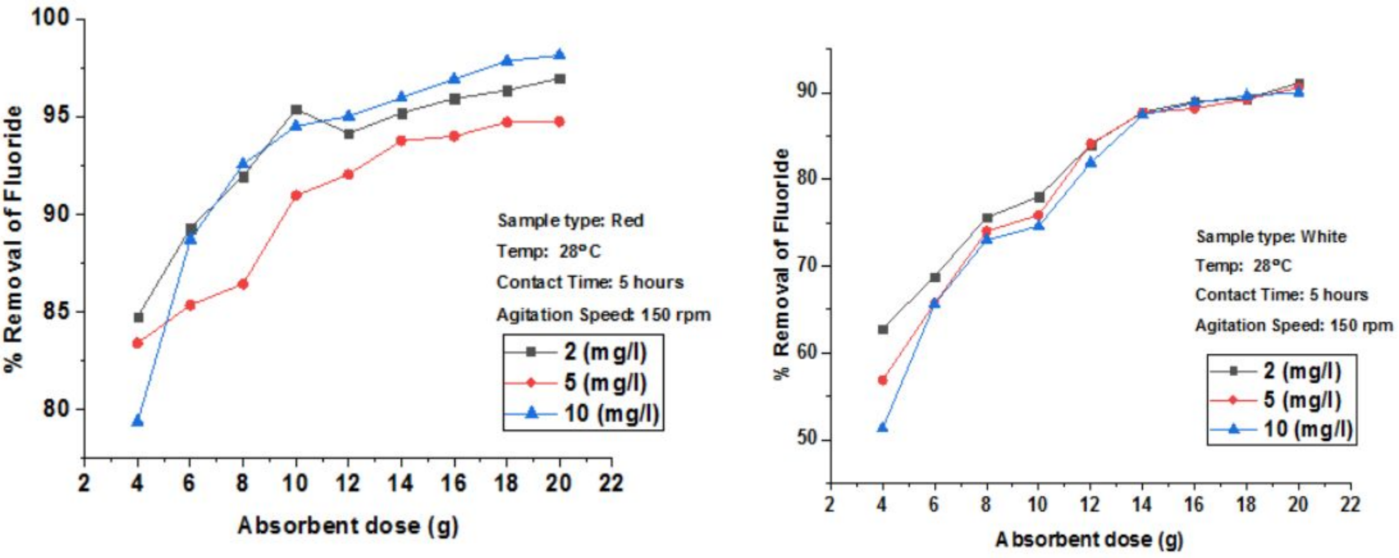


Fig. 12: Variation of adsorbent dose on the percentage removal of Fluoride by the laterite soil. Sample type: Red laterite and weathered (white) laterite soil

7.1.4 Effect of variation in concentrations

The fluoride concentrations were varied from 2 mg L^{-1} to 20 mg L^{-1} and 10 gm of laterite is used at a fixed agitation speed of 150 rpm and fixed time (5 hours). It was observed that the removal efficiency was the maximum at a fluoride concentration of 2 mg L^{-1}. With the increment of fluoride concentrations, the removal efficiency of laterite declined. The removal efficiency was the worst at 20 mg L^{-1}. The same result was shown for both red and white laterite soils. This experiment has a very important role in adsorption isotherm study. The removal efficiency of both red and white laterite soil are represented by the graph shown below (Fig. 13).

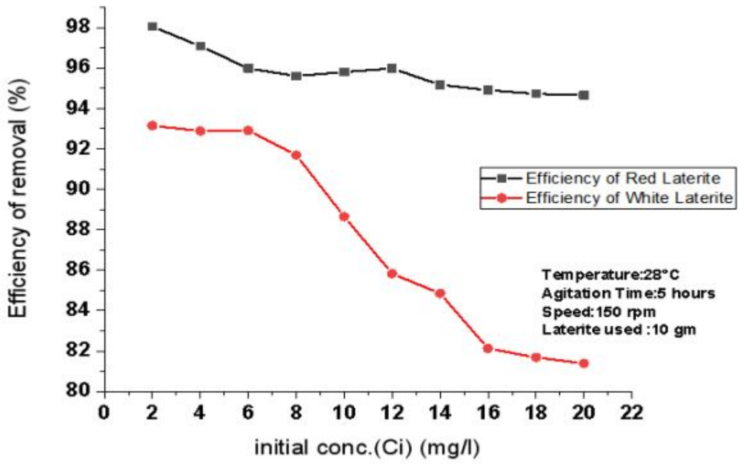


Fig. 13: Variation of fluoride concentration on the percentage removal efficiency of Fluoride by the laterite soil. Sample type: Red and White Laterite Soil

7.1.5 Effect of variation in Agitation time

At fixed fluoride concentration (20 mg L^{-1}), fixed adsorbent dose (20gm), and fixed agitation speed (20 gm) the fluoride removal efficiency of the laterite is increased with the increase of agitation time. It is observed that at a fixed concentration, there is an increase in the amount adsorbed with increasing agitation time due to the availability of large vacant adsorbent sites and a high concentration gradient between the solution and solid laterite phase. The fluoride removal efficiency gradually slows down when a certain agitation time arrives. The experiment was conducted for both red and laterite soil at 28°C. This experiment has an important role in kinetic study analysis. The removal efficiency of both red and white laterite soil is represented by the graph shown on Fig. 14.

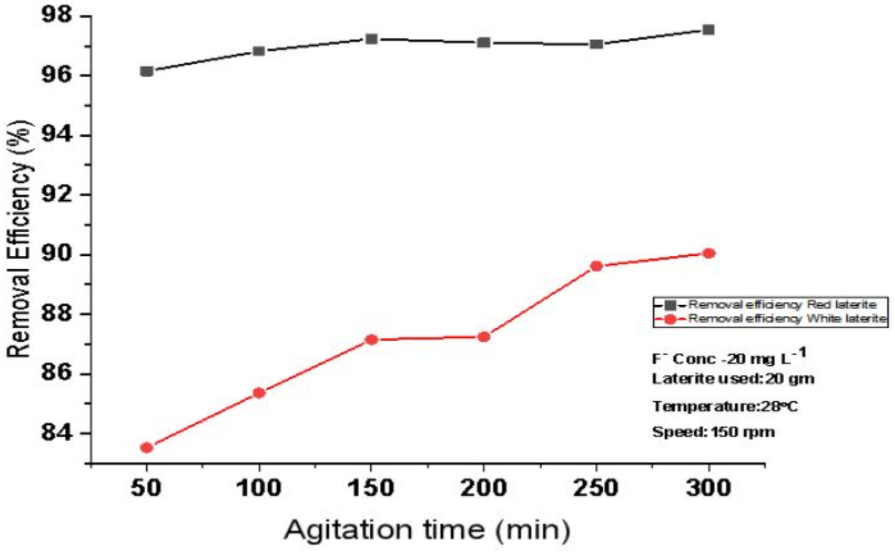


Fig. 14: Variation of agitation time on the percentage removal efficiency of Fluoride by the laterite soil. Sample type: Red and White Laterite Soil

7.1.6 Effect of pH on Removal

The adsorption process of fluoride on laterite in the pH range from 4 to 10 is presented in Fig. 6.6 for red laterite soil and Fig. 6.7 for white laterite soil. The adsorption is found to be influenced by solution pH, as the surface charge of laterite is determined by pH. At pH 8 and pH 9 the fluoride removal efficiency was found to be maximum for red laterite for fluoride concentrations of 5 mg/L and 10mg/L respectively. Before and after that pH the efficiency of removal of fluoride declined. For white laterite soil, at pH 7 and pH 8, the fluoride removal efficiency was found to be maximum for fluoride concentrations of 10 mg/L and 5mg/L respectively. The effect of pH on fluoride removal is shown in Fig.-15

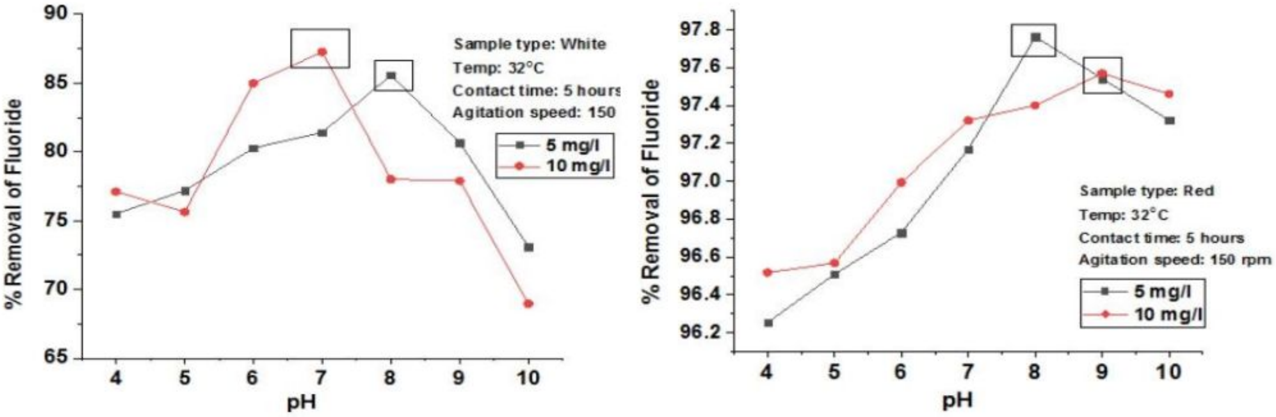


Fig. 15: Effect of pH on the removal of fluoride using laterite soil. Experimental conditions: Sample type: White and Red Laterite, dose: 10g

7.1.7 Adsorption isotherm for Batch Experiment

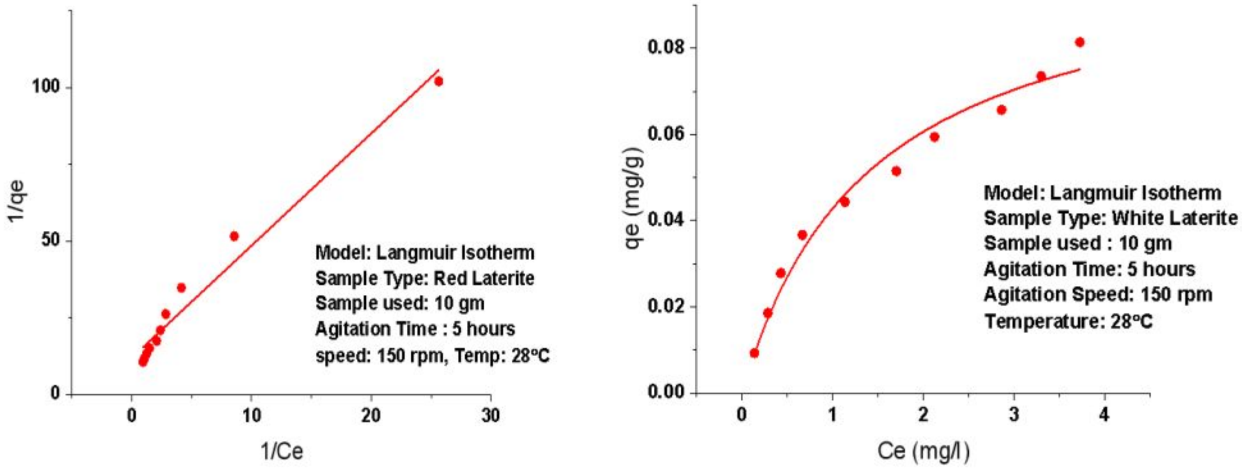
The equilibrium adsorption isotherm is the most important to design the adsorption systems. The Langmuir, Freundlich, and Temkin adsorption isotherm models are adopted for adsorption isotherm analysis for the batch experiment.

- ***Langmuir Isotherm***

  Fig. 16(a) represents the experimental data for red laterite that are fitted by the linear form of Langmiur model, ($1/q_e$) versus ($1/C_e$) at temperature 28°C. The value of q_m and K_L are evaluated from the slope and intercept, respectively. The sorption capacity, q_m, which is a measure of the maximum adsorption capacity corresponding to complete monolayer coverage found to be 0.084 mg g^{-1} for the experiments carried out at 28°C for red laterite soil. The adsorption coefficient, K_L, value which is related to the apparent energy of adsorption is obtained as 3.26 L mg^{-1}. Dimensionless equilibrium parameter, R_L, value is found out 0.133, so the R_L values lying between 0 and 1 indicate the favorable conditions for adsorption at 28°C [40]. The correlation coefficient (R^2) of Langmuir isotherm is 0.966 for red laterite soil.

  Fig. 16(b) represents the experimental data for white laterite that are fitted by the non-linear form of Langmiur model, (q_e) versus (C_e) at temperature 28°C. The sorption capacity (q_m) and adsorption coefficient (K_L) are obtained 0.104 mg g^{-1} and

0.706 L mg^{-1} respectively. The dimensionless equilibrium parameter, R_L, value is found out 0.415. So favorable conditions for adsorption at 28°C [40]. The correlation coefficient of Langmuir isotherm (R^2) is 0.974 for white laterite soil.



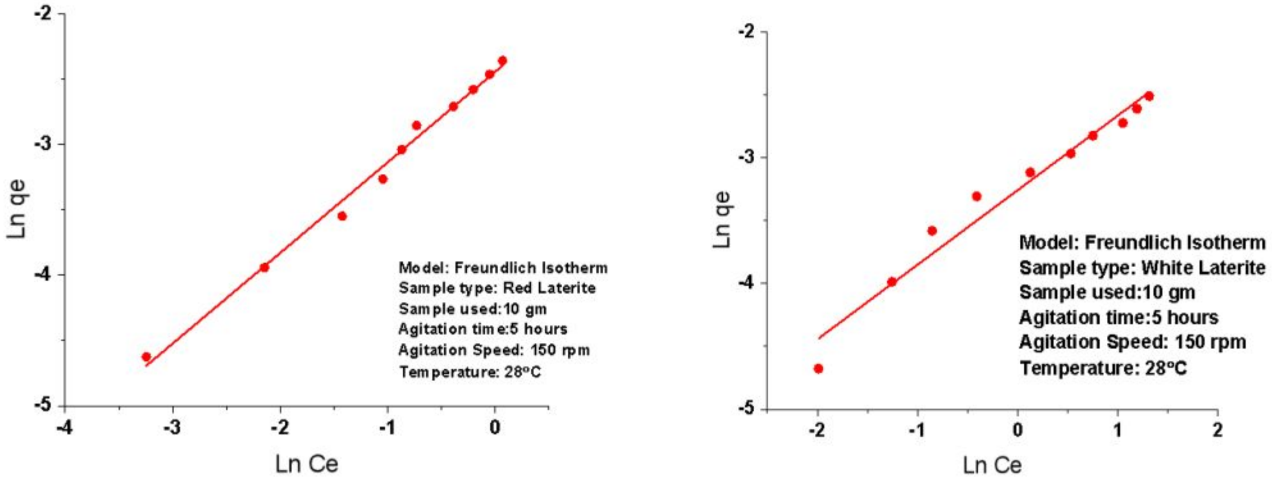
(a) (b)

Fig. 16: Langmuir Isotherm Model, Sample Type: Red (a) and White Laterite Soil (b)

- **Freundlich Model**

In the present study, Freundlich isotherm parameters sorption capacity (K_F) and sorption intensity (n) are calculated 0.087 ($mg^{1-(1/n)}L^{(1/n)}$ gm^{-1}) and 1.441 for red laterite soil (Fig. 17a). So, value of n is lying between 1 and 10 indicates the favorable conditions for adsorption at 28°C [41]. The correlation coefficient (R^2) of Freundlich isotherm (R^2) is 0.990 for red laterite soil.

For white laterite sample, Freundlich isotherm parameters sorption capacity (K_F) and sorption intensity (n) are calculated 0.0385 ($mg^{1-(1/n)}L^{(1/n)}$ gm^{-1}) and 1.685 for white laterite soil at 28°C. Value of n is suggested that indicates the favorable conditions for adsorption at 28°C [41]. The correlation coefficient (R^2) of Freundlich isotherm (R^2) is 0.961 for white laterite soil (Fig.17b).



(a) (b)

Fig. 17: Freundlich Isotherm Model, Sample Type: Red Laterite (a) and White Laterite Soil (b)

- ***Temkin Isotherm***

In the present study of Temkin isotherm for red laterite soil, the Temkin constant related to the heat of sorption (b_t) is obtained 0.026 J mol^{-1} and the Temkin isotherm constant K_t is found 20.964 L mg^{-1} at 28°C (or 301 K). The correlation coefficient (R^2) of Temkin isotherm (R^2) is 0.856 for red laterite soil (Fig. 18).

For White laterite soil, the Temkin constant related to the heat of sorption (b_t) and the Temkin isotherm constant K_t is obtained 0.0208 J mol^{-1} and 9.133 L mg^{-1} respectively at 28°C (or 301 K) .The correlation coefficient (R^2) of Temkin isotherm (R^2) is 0.968 for white laterite soil. (Fig. 18)

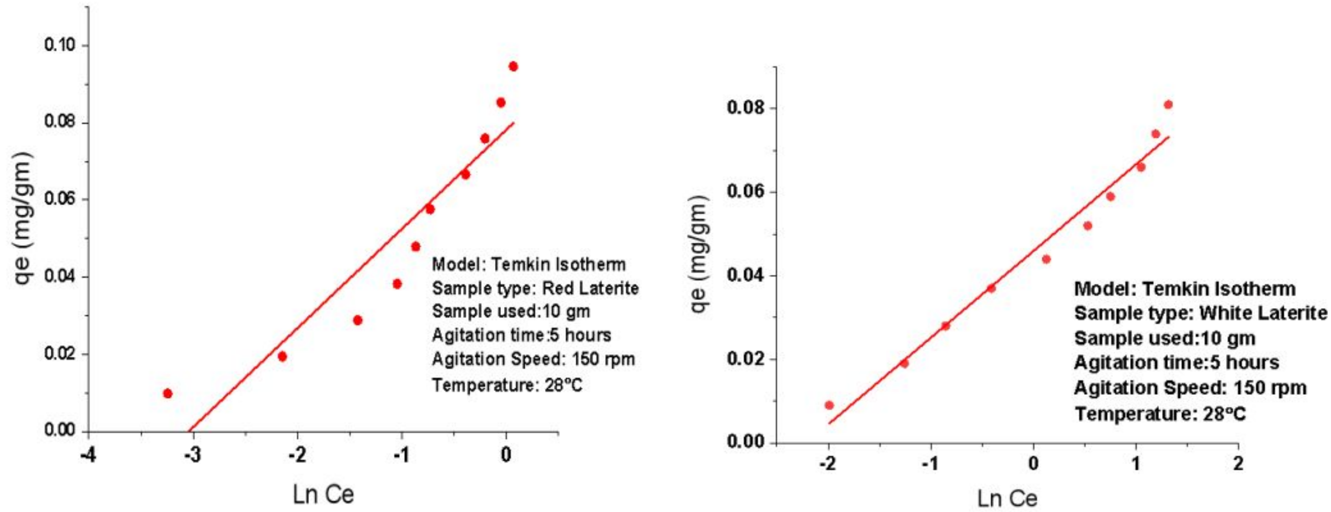


Fig. 18: Temkin Isotherm Model, Sample Type: Red Laterite (left) & White Laterite Soil (right)

Table 9: Parameters for each isotherm model in the studies

Isotherm Model	Isotherm Constants	Red Laterite	White Laterite
Langmuir	K_L (L mg^{-1})	3.257	0.706
	q_m (mg gm^{-1})	0.084	0.104
	R^2	0.966	0.974
Freundlich	K_F (gm^{-1})	0.087	0.039
	n	1.441	1.685
	R^2	0.990	0.961
Temkin	b_t (J mol^{-1})	0.026	0.021
	K_t (L mg^{-1})	20.964	9.133
	R^2	0.856	0.968

*at 28°C temperature

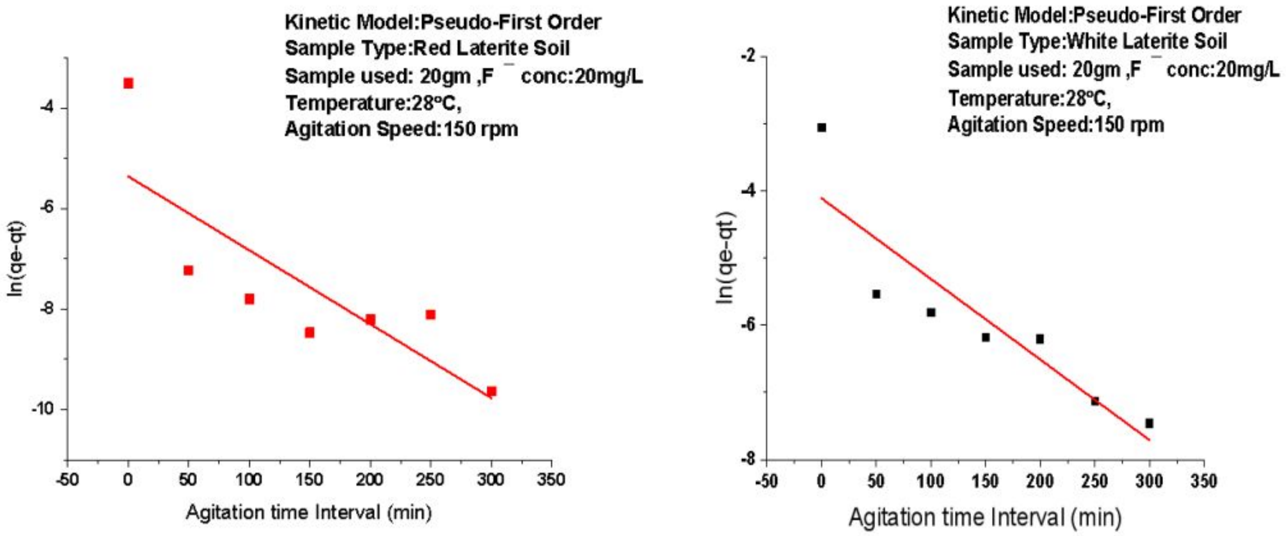
7.1.8 Kinetics Study:

For the determination of adsorption rate constant, equilibrium adsorption capacity and adsorption mechanism of the experiment, a kinetic study was carried out.

- ***Pseudo-first-order model***

  Fig.19 (a) represents the experimental data for red laterite that are fitted by the linear form of the Pseudo-first-order model, ln (q_e - q_t) versus agitation time (t) at temperature 28°C. $q_{e,calculated}$ and pseudo-first-order rate constant (k_1) are calculated from intercept and slope respectively. The calculated value of $q_{e,calculated}$ is obtained 0.005 mg gm^{-1} but $q_{e,experimental}$ is 0.0464 mg gm^{-1}. The pseudo-first-order rate constant (k_1) is obtained at 8.2×10^{-7} sec^{-1} and the correlation coefficient (R^2) for Pseudo-first-order is 0.607.

  Fig. 19 (b) represents the experimental data for white laterite, $q_{e,calculated}$ and pseudo-first-order rate constant (k_1) are 0.016 mg gm^{-1} and 6.672×10^{-7} sec^{-1} respectively at 28°C . The $q_{e,experimental}$ is 0.0472 mg gm^{-1}. The correlation coefficient (R^2) for Pseudo-first-order is 0.779.



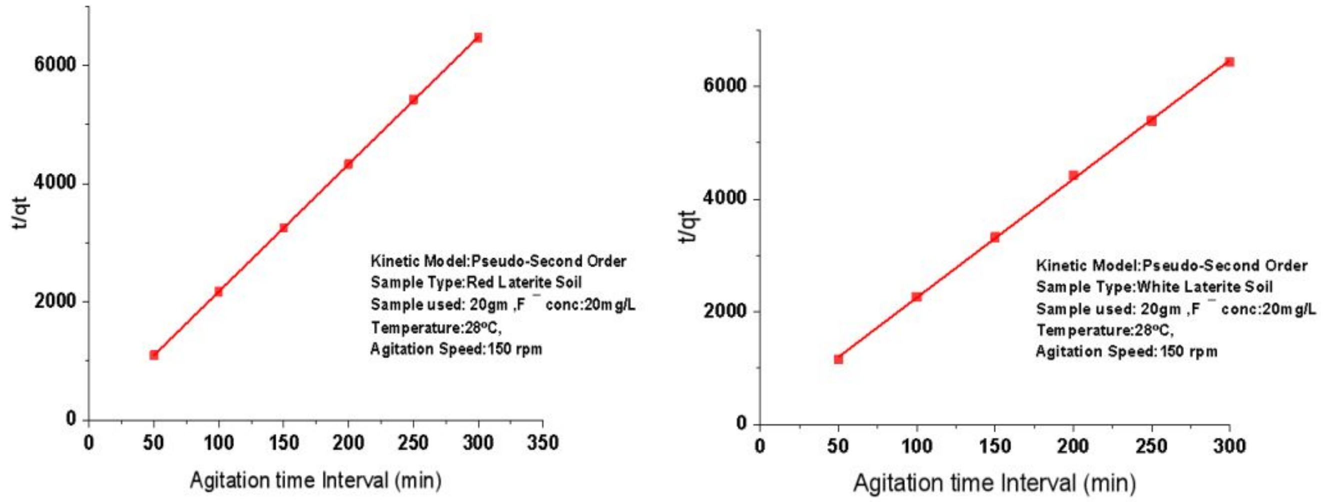
(a) (b)

Fig. 19: Pseudo-First-Order Reaction, Sample Type: Red Laterite Soil (a) & White Laterite soil (b)

- ***Pseudo-Second-order***

Fig. 20(a) represents the experimental data for red laterite that are fitted by the linear form of the Pseudo-second-order model, t/q_t versus agitation time (t) at temperature 28°C. $q_{e,calculated}$ and pseudo-second-order rate constant (k_2) are calculated from intercept and slope respectively. From graph, k_2 is calculated as 0.424 sec^{-1}. $q_{e,calculated}$ is obtained 0.0463 mg gm^{-1} and $q_{e,experimental}$ is 0.0464 mg gm^{-1}. So, $q_{e,calculated}$ and $q_{e,experimental}$ are nearly same. The correlation coefficient (R^2) value is magnificent 0.9999.

Fig. 20 (b) represents the experimental data for white laterite, $q_{e,calculated}$ and pseudo--second-order rate constant (k_2) are 0.0474 mg gm^{-1} and 0.051 sec^{-1} respectively at 28°C. The $q_{e,experimental}$ is 0.0472 mg gm^{-1}. So, $q_{e,calculated}$ and $q_{e,experimental}$ are nearly same. The correlation coefficient (R^2) value is also great 0.9995.



(a) (b)

Fig. 20: Pseudo-Second Order Reaction, Sample Type: Red Laterite (a) & White Laterite Soil (b)

- ***Intra-particle diffusion Model***

Fig. 21 (a) represents the experimental data for red laterite that are fitted by the non-linear form of intra-particle diffusion model. From the graph calculated intra-particle rate constant (k_{diff}) 5.24 $\times 10^{-5}$ mg gm^{-1} $min^{1/2}$ and c value is obtained 0.045 mg gm^{-1} at 28°C. The correlation coefficient (R^2) value is 0.737.

Fig.21 (b) represents the experimental data for white laterite that are fitted by the non-linear form of intra-particle diffusion model. From the graph calculated intra-particle rate constant (k_{diff}) 3.32 $\times 10^{-4}$ mg gm^{-1} $min^{1/2}$ and c value is obtained 0.041 mg gm^{-1} at 28°C. The correlation coefficient (R^2) value is 0.960.

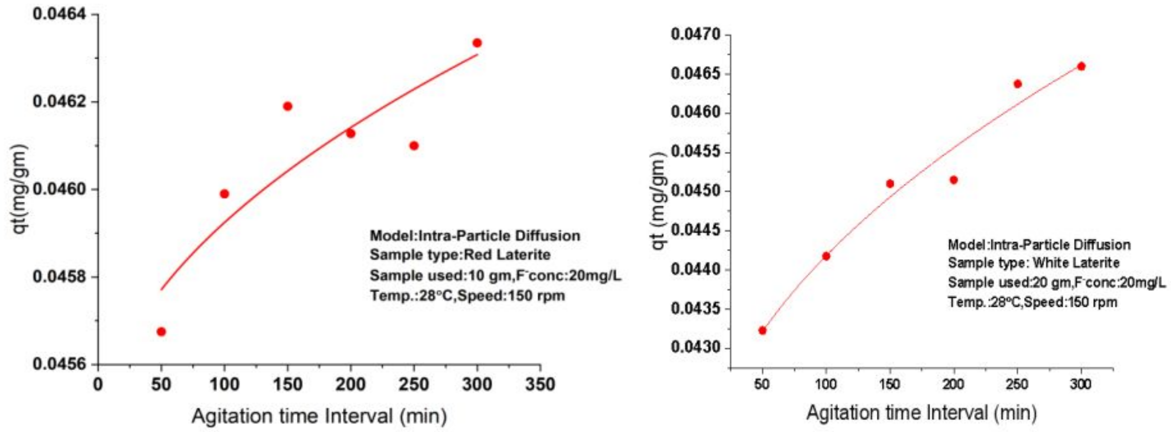


Fig. 21: Intra-Particle diffusion model. Sample type: Red Laterite (left) & White Laterite Soil

Table 10: The Kinetic parameters obtained for Fluoride Adsorption using Laterite Soil

Kinetic equations	Parameters	Red Laterite	White Laterite
Pseudo-First Order	K_1 (sec^{-1})	8.2×10^{-7}	6.7×10^{-7}
	$q_{e,calculated}$ ($mg\ gm^{-1}$)	0.0047	0.016
	$q_{e,experimental}$ ($mg\ gm^{-1}$)	0.607	0.779
	R^2	0.607	0.779
Pseudo-Second Order	K_2 (sec^{-1})	0.424	0.051
	$q_{e,calculated}$ ($mg\ gm^{-1}$)	0.0463	0.0474
	$q_{e,experimental}$ ($mg\ gm^{-1}$)	0.0464	0.0472
	R^2	0.9999	0.9995
Intra-Particle diffusion	K_{diff} ($gm\ mg^{-1} min^{0.5}$)	5.24×10^{-5}	3.32×10^{-7}
	C ($mg\ gm^{-1}$)	0.045	0.041
	R^2	0.737	0.960

*at 28°C temperature

As a result, it can be concluded that the pseudo-second-order kinetic model suggested a better correlation for the adsorption of fluoride with using the laterite soil than the pseudo-first-order model and intra-particle diffusion model, so the pseudo-second-order model is suitable for modeling the adsorption of fluoride using laterite soil at 28°C.

7.1.9 Optimal Conditions for Fluoride removal from Batch Experiment:

For Red Laterite Soil

Table 11: Optimal condition for fluoride adsorption using Red Laterite Soil

Sl. No.	Optimal Condition	Removal Efficiency (%)
1.	pH:7.12, Initial F^- concentration: 10 mg/L , Contact Time:5 hours, Weight of sample used: 20gm, Temperature: 28°C	97.978
2.	pH: 7.22, Initial F^- concentration: 5 mg/L , Contact Time:5 hours, Weight of Laterite used: 20gm, Temperature: 28°C	98.020
3.	pH: 7.20, Initial F^- concentration: 1.99 mg/L ,Contact Time:5 hours, Weight of Laterite used 20gm,Temperature: 28°C	97.945

4.	pH 7.08, Initial F^- concentration:20 mg/L, Contact Time:300 min, Weight of Laterite used 20gm,Temperature: 28°C	97.547
5.	pH 9, Initial F^- concentration: 10.0 mg/L, Contact Time:5 hours, Weight of Laterite used 10gm, Temperature: 32°C	97.569
6.	pH 7.16, Initial F^- concentration: 2 mg/L, Contact Time:300 min, Weight of Laterite used 10gm, Temperature: 28°C	98.05

For White Laterite Soil

Table 12: Optimal condition for fluoride adsorption using White Laterite Soil

Sl. No.	**Optimal Condition**	**Removal Efficiency (%)**
1.	pH:7.26, Initial F^- concentration: 10 mg/L , Contact Time:5 hours, Weight of sample used: 20gm, Temperature: 28°C	90.01
2.	pH: 7.24, Initial F^- concentration: 5 mg/L , Contact Time:5 hours, Weight of Laterite used: 20gm, Temperature: 28°C	91.11
3.	pH: 7.21, Initial F^- concentration: 2 mg/L , Contact Time:5 hours, Weight of Laterite used 20gm,Temperature: 28°C	91.89
4.	pH 7.08,Initial F^- concentration: 20 mg/L, Contact Time:300 min, Weight of Laterite used 20gm, Temperature: 28°C	90.048
5.	pH 6.71, Initial F^- concentration: 10.0 mg/L, Contact Time:5 hours, Weight of Laterite used 10gm, Temperature: 32°C	87.264
6.	pH 7.16, Initial F^- concentration: 2 mg/L, Contact Time:5 hours, Weight of Laterite used 10gm, Temperature: 28°C	93.15

7.2 COLUMN STUDY

The water used for the column study is the groundwater collected from Lakshmisagar, Bankura district of West Bengal having water quality parameters: Fluoride conc.:2.38 mg L^{-1}, pH:7.60, T.D.S. :358 mg L^{-1}, Iron :0.18 mg L^{-1}, Turbidity: 0.4 NTU at 35°C. The amount of water collected from the site is 40 liters.

Table 13: Data obtained in adsorption of fluoride using Red Laterite Soil

Sl.	Time Interval (min)	The cumulative amount of water passed through the filter (ml)	Initial conc. of Fluoride in used Ground Water (mg L^{-1})	Final conc. of Fluoride in Filtered water (mg L^{-1})	Percentage removal of the Fluoride (%)	pH	TDS (mg L^{-1})	Iron (mg L^{-1})
1	30	180	2.38	0.683	71.30	7.83	347	0.12
2	60	360	2.38	0.265	88.87	7.64	346	0.03
3	90	540	2.38	0.0745	96.87	7.54	345	0.06
4	120	720	2.38	0.0706	97.03	7.58	344	0.03
5	150	900	2.38	0.0665	97.21	7.59	343	0.05
6	180	1080	2.38	0.0682	97.13	7.62	342	0.06
7	210	1260	2.38	0.0646	97.29	7.65	341	0.13
8	240	1440	2.38	0.0809	96.60	7.67	340	0.17
9	270	1620	2.38	0.0989	95.84	7.70	338	0.19
10	300	1800	2.38	0.1080	95.46	7.72	336	0.20
11	330	1980	2.38	0.1240	94.79	7.75	337	0.10
12	360	2160	2.38	0.1190	95.00	7.77	338	0.12
13	390	2340	2.38	0.127	94.66	7.80	340	0.13
14	420	2520	2.38	0.138	94.20	7.82	343	0.22
15	450	2700	2.38	0.139	94.16	7.85	349	0.14
16	480	2880	2.38	0.137	94.24	7.87	334	0.07
17	510	3060	2.38	0.141	94.08	7.90	349	0.08
18	540	3240	2.38	0.149	93.74	7.92	350	0.10
19	570	3420	2.38	0.166	93.03	7.95	355	0.11
20	600	3600	2.38	0.143	93.99	7.97	333	0.14
21	630	3780	2.38	0.185	92.23	8.00	350	0.12
22	660	3960	2.38	0.216	90.92	8.02	345	0.11
23	690	4140	2.38	0.238	90.00	8.05	346	0.17
24	720	4320	2.38	0.226	90.50	8.07	347	0.19
25	750	4500	2.38	0.227	90.46	8.10	348	0.22
26	780	4680	2.38	0.230	90.34	8.12	350	0.20
27	810	4860	2.38	0.232	90.25	8.15	348	0.17
28	840	5040	2.38	0.235	90.13	8.17	349	0.17
29	870	5220	2.38	0.234	90.17	8.20	348	0.16
30	900	5400	2.38	0.235	90.13	8.22	348	0.16
31	930	5580	2.38	0.238	89.96	8.25	347	0.17
32	960	5760	2.38	0.240	89.87	8.27	347	0.20
33	990	5940	2.38	0.24	89.87	8.30	347	0.19
34	1020	6120	2.38	0.241	89.83	8.32	346	0.22
35	1050	6300	2.38	0.24	89.87	8.35	346	0.18
36	1080	6480	2.38	0.26	89.03	8.31	345	0.22
37	1110	6660	2.38	0.265	88.82	8.31	345	0.21

38	1140	6840	2.38	0.262	88.95	8.32	345	0.23
39	1170	7020	2.38	0.263	88.90	8.32	344	0.22
40	1200	7200	2.38	0.268	88.69	8.33	344	0.23
41	1230	7380	2.37	0.27	88.61	8.33	343	0.22
42	1260	7560	2.37	0.271	88.57	8.34	343	0.25
43	1290	7740	2.37	0.269	88.65	8.34	343	0.20
44	1320	7920	2.37	0.27	88.61	8.35	342	0.22
45	1350	8100	2.37	0.272	88.52	8.35	342	0.21
46	1380	8280	2.37	0.275	88.40	8.36	341	0.20
47	1410	8460	2.37	0.278	88.27	8.37	341	0.23
48	1440	8640	2.37	0.277	88.31	8.37	341	0.22
49	1470	8820	2.37	0.275	88.40	8.38	340	0.24
50	1500	9000	2.37	0.279	88.23	8.38	340	0.25
51	1530	9180	2.37	0.281	88.14	8.39	341	0.22
52	1560	9360	2.37	0.289	87.81	8.38	346	0.20
53	1590	9540	2.37	0.29	87.76	8.38	341	0.19
54	1620	9720	2.37	0.291	87.72	8.40	345	0.18
55	1650	9900	2.37	0.293	87.64	8.37	344	0.21
56	1680	10080	2.37	0.301	87.30	8.35	346	0.20
57	1710	10260	2.37	0.277	88.31	8.36	346	0.20
58	1740	10440	2.37	0.298	87.43	8.35	347	0.20
59	1770	10620	2.37	0.311	86.88	8.34	348	0.21
60	1800	10800	2.37	0.343	85.53	8.33	349	0.21
61	1830	10980	2.37	0.401	83.08	8.33	349	0.21
62	1860	11160	2.37	0.421	82.24	8.32	350	0.21
63	1890	11340	2.37	0.419	82.32	8.40	351	0.21
64	1920	11520	2.37	0.423	82.15	8.44	352	0.22
65	1950	11700	2.37	0.425	82.07	8.37	353	0.22
66	1980	11880	2.37	0.428	81.94	8.41	353	0.22
67	2010	12060	2.37	0.429	81.90	8.46	354	0.22
68	2040	12240	2.37	0.432	81.77	8.43	355	0.22
69	2070	12420	2.37	0.433	81.73	8.45	356	0.23
70	2100	12600	2.37	0.435	81.63	8.46	356	0.23
71	2130	12780	2.37	0.437	81.55	8.38	357	0.23
72	2160	12960	2.37	0.439	81.46	8.42	358	0.23
73	2190	13140	2.37	0.441	81.38	8.38	354	0.23
74	2220	13320	2.37	0.443	81.31	8.36	355	0.19
75	2250	13500	2.37	0.444	81.27	8.38	353	0.24
76	2280	13680	2.37	0.447	81.14	8.38	351	0.26
77	2310	13860	2.37	0.445	81.22	8.40	350	0.22
78	2340	14040	2.37	0.446	81.18	8.47	361	0.08
79	2370	14220	2.37	0.449	81.05	8.19	364	0.17
80	2400	14400	2.37	0.451	80.97	8.35	365	0.25
81	2430	14580	2.37	0.455	80.80	8.50	367	0.25

82	2460	14760	2.37	0.456	80.76	8.47	369	0.21
83	2490	14940	2.37	0.456	80.76	8.45	371	0.25
84	2520	15120	2.37	0.457	80.72	8.26	373	0.19
85	2550	15300	2.37	0.459	80.63	8.27	375	0.26
86	2580	15480	2.37	0.464	80.42	8.28	377	0.27
87	2610	15660	2.37	0.466	80.34	8.29	379	0.22
88	2640	15840	2.37	0.468	80.25	8.3	380	0.26
89	2670	16020	2.37	0.472	80.08	8.31	382	0.27
90	2700	16200	2.37	0.481	79.70	8.32	384	0.26
91	2730	16380	2.37	0.482	79.66	8.33	386	0.27
92	2760	16560	2.37	0.478	79.83	8.34	388	0.14
93	2790	16740	2.37	0.486	79.49	8.35	390	0.27
94	2820	16920	2.37	0.487	79.45	8.36	392	0.28
95	2850	17100	2.37	0.490	79.32	8.37	394	0.28
96	2880	17280	2.37	0.492	79.24	8.38	396	0.28
97	2910	17460	2.37	0.494	79.16	8.39	398	0.28
98	2940	17640	2.37	0.495	79.11	8.4	399	0.28
99	2970	17820	2.37	0.496	79.07	8.41	401	0.29
100	3000	18000	2.37	0.498	78.99	8.43	403	0.29
101	3030	18180	2.37	0.502	78.82	8.41	405	0.29
102	3060	18360	2.37	0.503	78.78	8.43	407	0.29
103	3090	18540	2.37	0.504	78.73	8.37	409	0.28
104	3120	18720	2.37	0.508	78.57	8.45	411	0.25
105	3150	18900	2.37	0.506	78.65	8.43	413	0.24
106	3180	19080	2.37	0.506	78.65	8.44	415	0.21
107	3210	19260	2.37	0.507	78.61	8.44	417	0.19
108	3240	19440	2.37	0.510	78.48	8.45	418	0.15
109	3270	19620	2.37	0.512	78.40	8.45	420	0.26
110	3300	19800	2.37	0.515	78.27	8.46	422	0.11
111	3330	19980	2.37	0.517	78.19	8.47	424	0.13
112	3360	20160	2.37	0.519	78.10	8.49	426	0.18
113	3390	20340	2.37	0.520	78.06	8.47	428	0.22
114	3420	20520	2.37	0.517	78.19	8.48	430	0.21
115	3450	20700	2.37	0.520	78.06	8.40	432	0.20
116	3480	20880	2.37	0.522	77.97	8.41	434	0.17
117	3510	21060	2.37	0.524	77.89	8.42	436	0.14
118	3540	21240	2.37	0.527	77.76	8.41	437	0.11
119	3570	21420	2.37	0.547	76.92	8.43	439	0.13
120	3600	21600	2.37	0.560	76.37	8.43	441	0.13
121	3630	21780	2.37	0.562	76.29	8.44	443	0.15
122	3660	21960	2.37	0.565	76.16	8.42	445	0.15
123	3690	22140	2.35	0.567	75.86	8.45	447	0.14
124	3720	22320	2.35	0.570	75.75	8.45	449	0.21
125	3750	22500	2.35	0.572	75.65	8.46	451	0.25

126	3780	22680	2.35	0.575	75.54	8.46	453	0.27
127	3810	22860	2.35	0.577	75.43	8.47	455	0.22
128	3840	23040	2.35	0.580	75.33	8.47	456	0.19
129	3870	23220	2.35	0.582	75.22	8.48	458	0.17
130	3900	23400	2.35	0.585	75.11	8.35	460	0.20
131	3930	23580	2.35	0.601	74.43	8.37	469	0.19
132	3960	23760	2.35	0.600	74.47	8.39	473	0.21
133	3990	23940	2.35	0.610	74.04	8.41	478	0.22
134	4020	24120	2.35	0.615	73.83	8.43	475	0.20
135	4050	24300	2.35	0.624	73.45	8.45	489	0.23
136	4080	24480	2.35	0.630	73.19	8.45	498	0.19
137	4110	24660	2.35	0.654	72.17	8.46	511	0.25
138	4140	24840	2.35	0.670	71.49	8.47	500	0.28
139	4170	25020	2.35	0.713	69.66	8.45	502	0.24
140	4200	25200	2.35	0.841	64.21	8.46	507	0.28
141	4230	25380	2.35	0.869	63.02	8.44	512	0.27
142	4260	25560	2.35	0.903	61.57	8.47	522	0.30
143	4290	25740	2.35	0.963	59.02	8.48	528	0.29
144	4320	25920	2.35	0.988	57.96	8.50	530	0.30
145	4350	26100	2.35	1.300	44.68	8.49	535	0.31
146	4380	26280	2.35	1.351	42.51	**8.52**	549	0.32

- The average fluoride conc. was 2.368 mg L^{-1}
- The amount of water passed through the adsorbent was 26.28 liters
- Taking uniform average initial concentration of fluoride as 2.37 mg/L
- The fluoride present in the total amount of the influent water (26.28×2.37) mg

  = 62.284 mg
- The total amount of fluoride adsorbed in the media was 51.328 mg
- The amount of red laterite was used in the filter 459 gm
- It means 459 gm red laterite was adsorbed 51.328 mg
- The capacity of red laterite soil was (51.328× 1000/459) mg/kg =111.826 mg/kg
- The average efficiency of the media =(51.328/62.284) ×100=82.411 %

7.2.1 Adsorption Models for Column Study

In the column study, three models are used, namely the Adams–Bohart, Yoon–Nelson, and Thomas models to analyze the breakthrough curves and for the prediction of the dynamic nature of the column.

- **Bohart–Adams Model:**

Bohart–Adams Model model $\ln(C_t/C_o)$ is plotted against time (t). k_{BA} is the kinetic constant of the Bohart-Adam model is found from the graph is 0.000189 L mg^{-1} min^{-1} ; N_0 is the saturation concentration, is obtained 91.773 mg L^{-1}. The correlation coefficient (R^2) value is 0.854 (Fig.22)

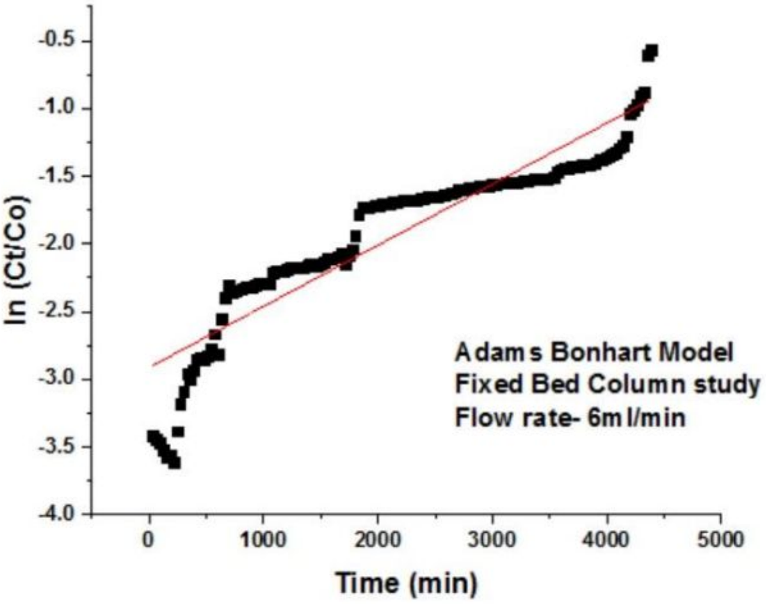


Fig. 22: Bohart–Adams Model model plots for the adsorption of F^- in the fixed-bed column, adsorbent material: Red Laterite

- **Yoon–Nelson Model:**

The parameters of the time required for 50% adsorbate breakthrough (τ) and the rate constant (k_{YN}) can be obtained from the plot of the function $\ln[C_t/(C_0 - C_t)]$ versus t (time). The obtained value of τ and k_{YN} are 5795.8 min and 0.00052 min^{-1}. The correlation coefficient (R^2) value is 0.868 (Fig. 23).

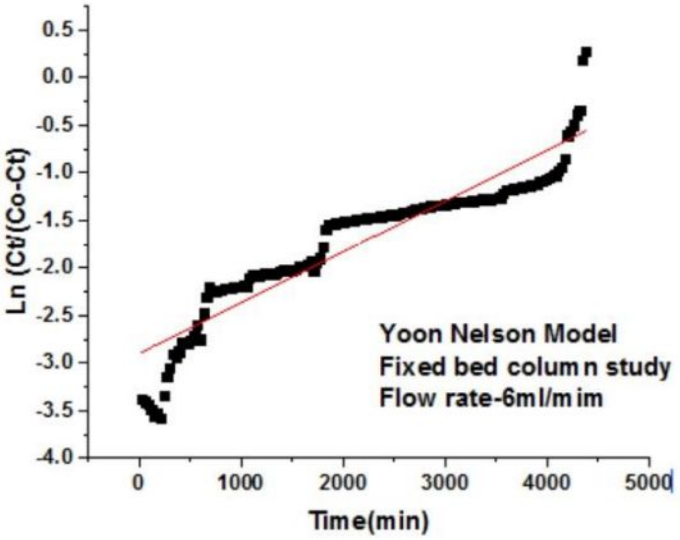


Fig. 23: Yoon–Nelson Model plots for the adsorption of F^- in the fixed-bed column, adsorbent material: Red Laterite

- **Thomas Model:**

Thomas rate constant (k_{TH}) and equilibrium compounds uptake per gm (q_{TH}) are determined by plotting the ln $[(C_0/C_t)^{-1}]$ against the time (t) graph. Calculated k_{TH} is 0.0002 L min^{-1} mg^{-1} and q_{TH} is 180.31 mg gm^{-1}. The correlation coefficient (R^2) value is 0.868 (Fig. 24).

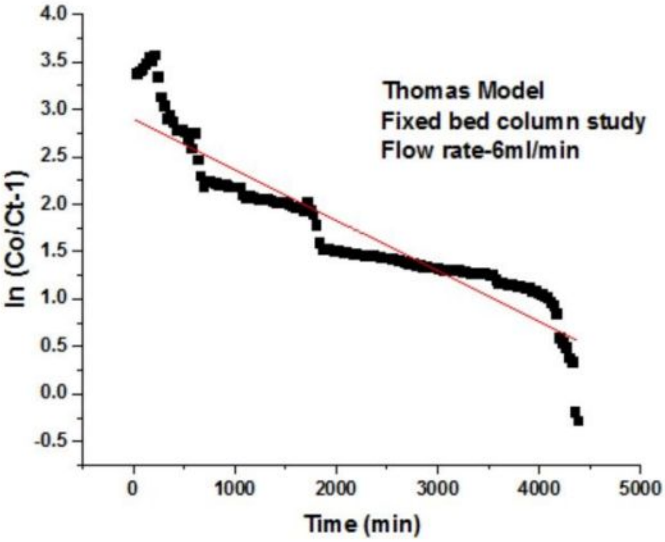


Fig. 24: Thomas Model plots for the adsorption of F^- in the fixed-bed column, adsorbent material: Red Laterite

Table 14 Parameters for each isotherm model in the studies for fixed bed column

Model	Constants	Value
Bohart – Adams	K_{BA} (L mg^{-1} min^{-1})	0.000189
	N_0 (mg gm^{-1})	91.773
	R^2	0.854
Yoon – Nelson	k_{YN} (min^{-1})	0.00052
	τ (min)	5795.8
	R^2	0.868
Thomas	K_{TH} (L mg^{-1} min^{-1})	0.0002
	q_{TH} (mg gm^{-1})	180.313
	R^2	0.868

7.2.2 TDS variation with respect to Time in filtered water:

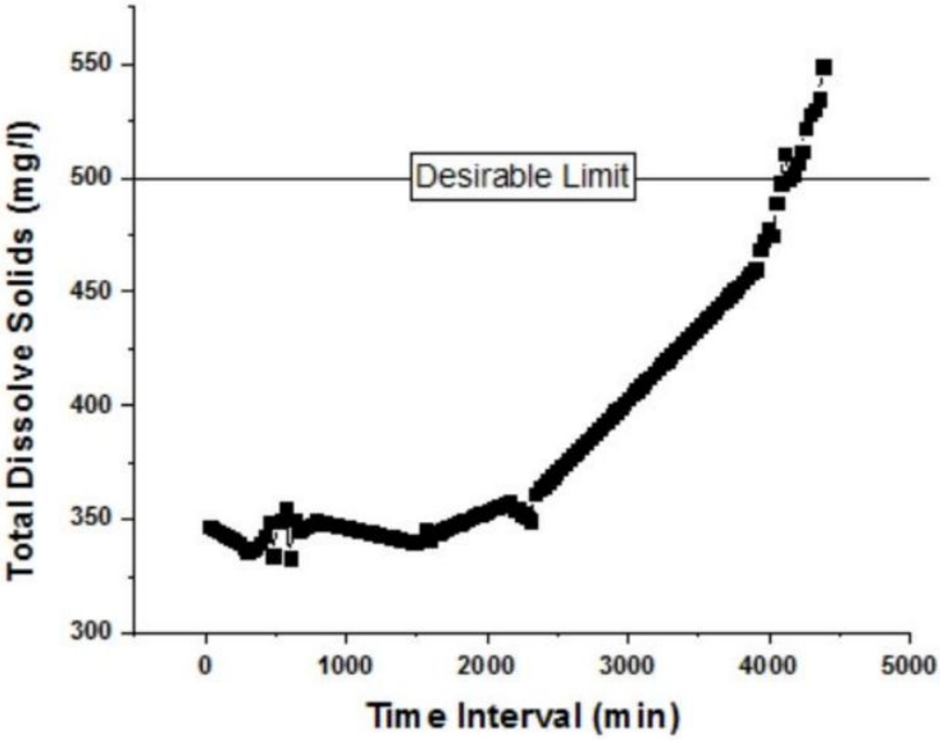


Fig. 25: Total Dissolved Solids (TDS) variation with respect to Time in filtered water collected from Fix-bed Column Filter

7.2.3 Iron variation with respect to Time in filtered water

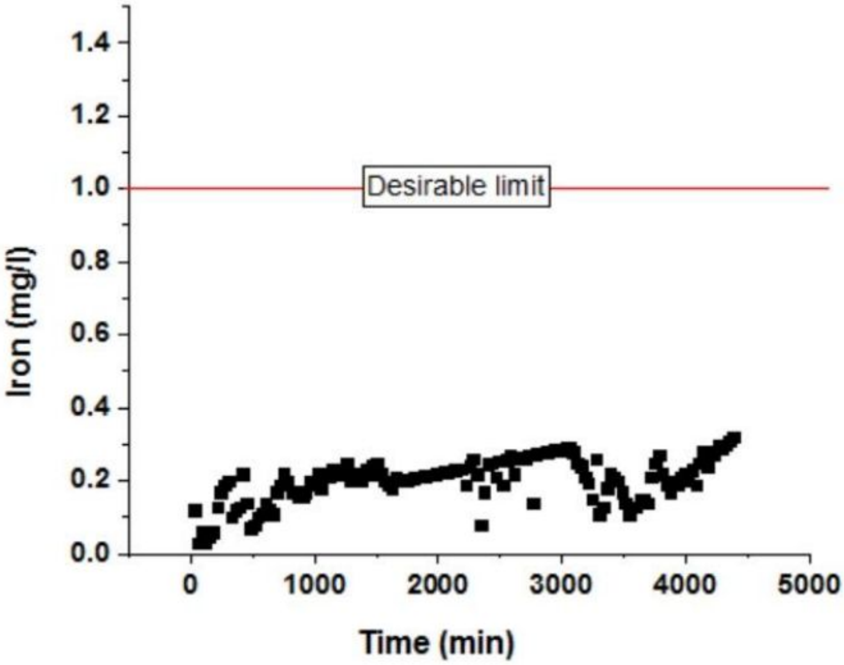


Fig. 26: Iron (Fe) variation with respect to Time in filtered water collected from Fix-bed Column Filter

7.2.4 pH variation with respect to Time in filtered water

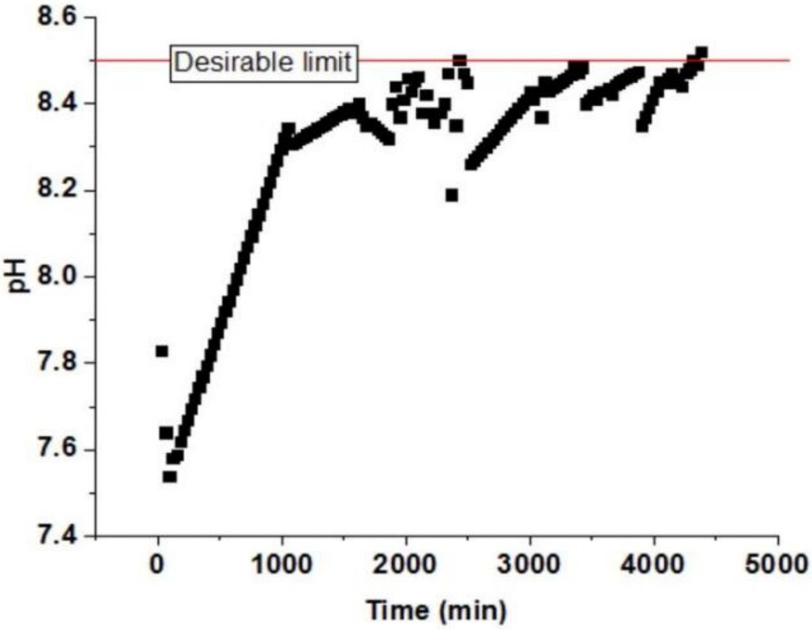


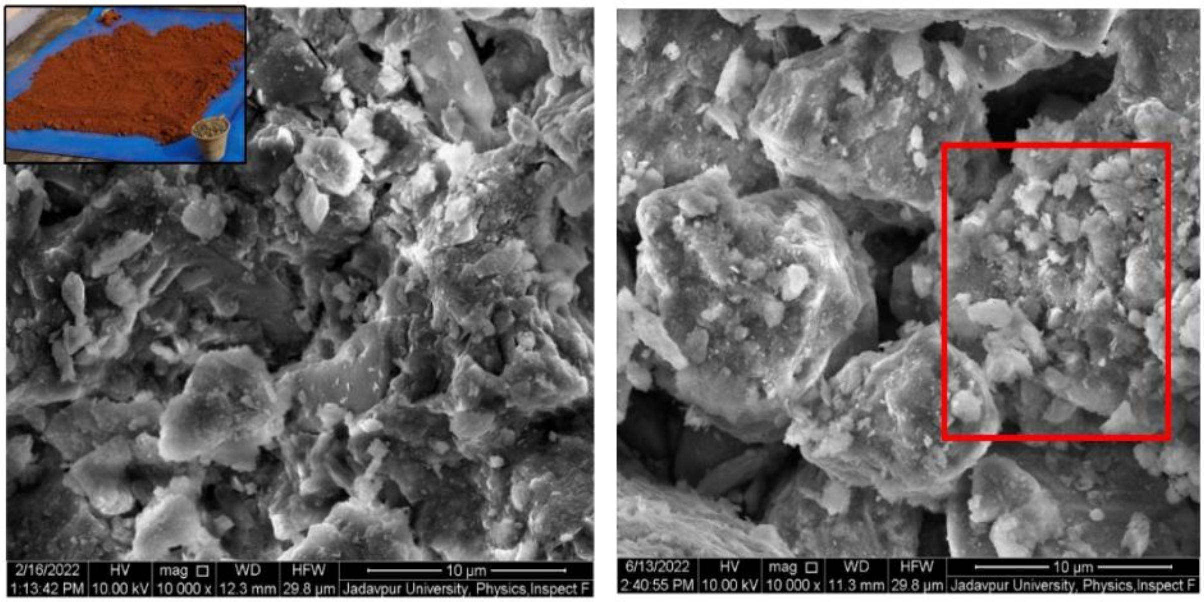
Fig. 27: pH variation with respect to Time in filtered water collected from Fix-bed Column Filter

7.3 CHARACTERIZATION STUDY OF THE ABSORBENT

7.3.1 FESEM & EDX Study

Laterite is mainly found in humid tropical weathering predominantly composed of hematite, goethite, quartz, kaolin, and other clay minerals. It is red, whitish brown to chocolate colored at the top showing hollow, vesicular, and botryoidal structure. The Field Emission Scanning Electron Microscopic image (FESEM) of the laterite soil with and without fluoride loaded are presented in Fig. 27. FESEM has been used here to show the changes in the surface morphology of the absorbent surface due to the addition of the fluoride ion. It also proofs the accuracy of the batch adsorption process and the ability of the material to remove the contaminant. FESEM has been made for both the untreated red and white laterite soil as collected from field. A Montmorillonite clay structure can be observed from FESEM. Fig.28 shows the FESEM of the fluoride mixed laterite sludge as taken out from the column bed filter system. There has been a remarkable change in the morphology and surface structure heterogeneity of the material when loaded with fluoride. Crystal formation is clearly evident from the images after the load of the fluoride into the soil. Laterite carry enriched grade of Fe, Al, Si, Na, K, Ti etc. Fig show the EDX (Energy Dispersive X-ray Spectroscopy) visualizing the elemental composition of the material at different condition. The corresponding EDX spectrum shows the inclusion of fluoride into the elemental composition after the absorption and filtration process.

a) Red Laterite soil before absorption **b) Red Laterite soil after absorption**



c) White Laterite soil before absorption **d) White Laterite soil after absorption**

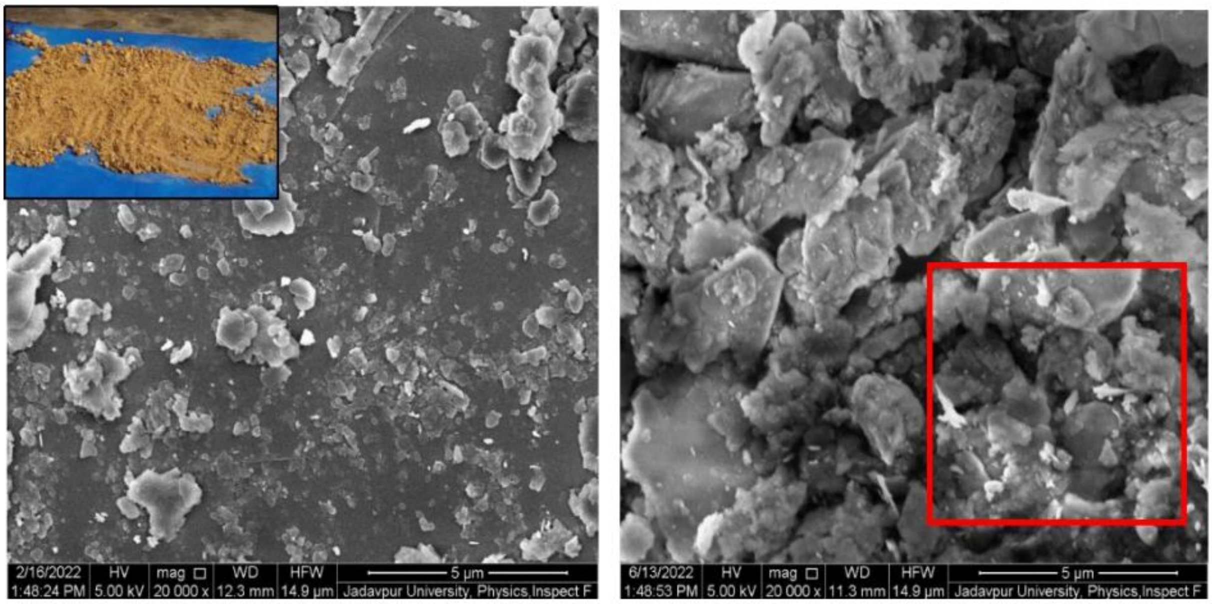


Fig. 28: FESEM characterizations of red and white laterite soil adsorbent, (a) Red laterite-before (b) Red laterite-after adsorption c) White laterite –before and d) White laterite- after

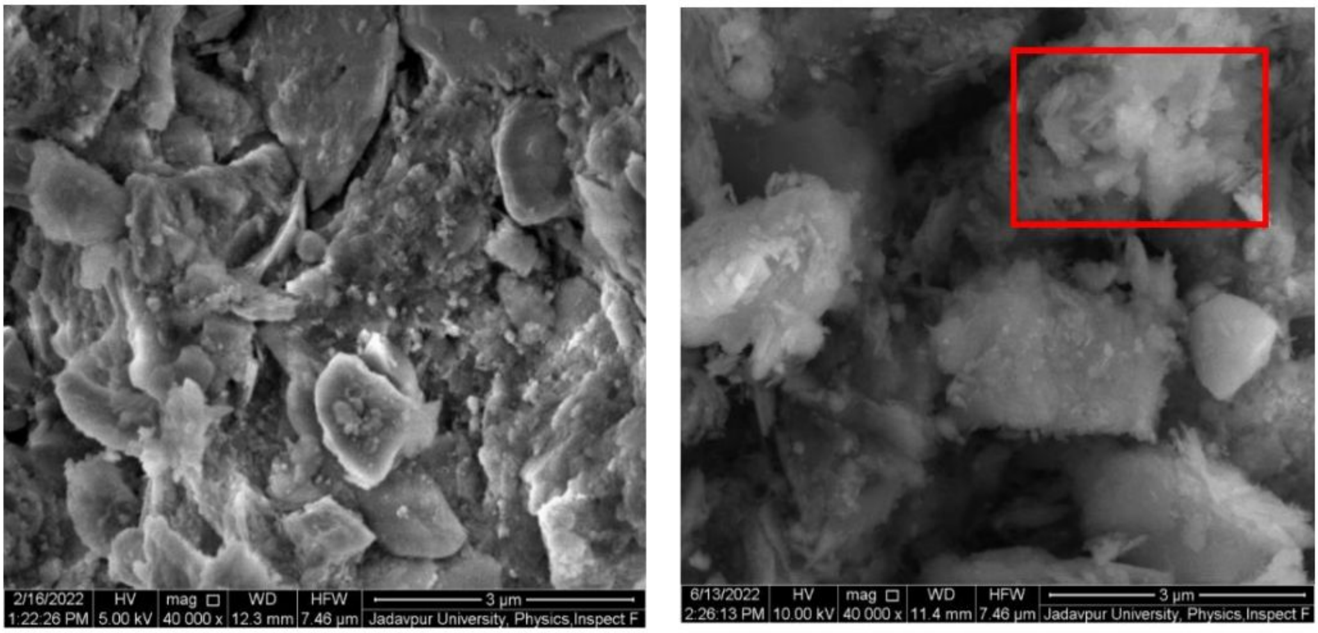


Fig. 29: FESEM characterizations of red laterite soil at 3µm scale- before (a) and after (b) fixed column bed filtration study

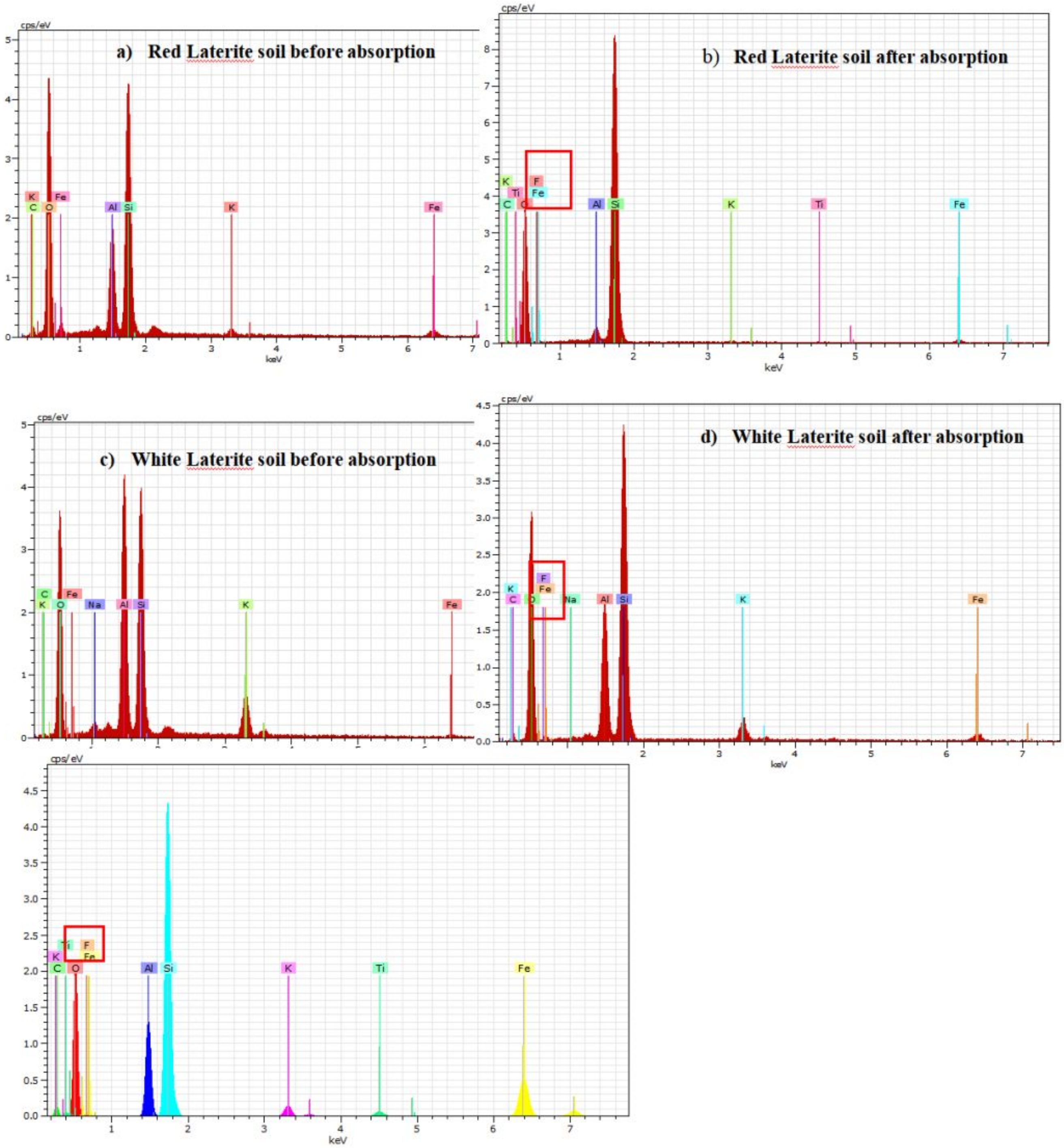


Fig. 30: EDX characterizations of red and white laterite soil adsorbent, (a) Red laterite-before (b) Red laterite-after adsorption c) White laterite –before d) White laterite- after and e) filter sludge

Table 15: Elemental composition of the material based on EDX

Red Laterite	Before absorption		Red Laterite	After absorption	
Element	Weight %	Atomic %	Element	Weight %	Atomic %
Oxygen	47.38	63.74	Oxygen	51.88	66.01
Silicon	30.95	23.47	Silicon	43.04	31.2
Aluminum	10.68	8.43	Aluminum	2.23	1.68
Iron	7.81	2.98	Iron	2.36	0.86
Potassium	1.92	1.05	Potassium	0.26	0.14
Titanium	0.78	0.3	Titanium	0.18	0.18
			Fluoride	**0.03**	**0.04**
White Laterite	Before absorption		White Laterite	After absorption	
Element	Weight %	Atomic %	Element	Weight %	Atomic %
Oxygen	48.65	63.42	Oxygen	48.65	63.42
Silicon	3.45	22.31	Silicon	3.45	22.31
Aluminum	13.66	10.56	Aluminum	13.66	10.56
Iron	3.58	1.34	Iron	3.58	1.34
Potassium	3.33	1.48	Potassium	3.33	1.48
Sodium	0.31	2.80	Sodium	0.31	2.80
			Fluoride	**0.02**	**0.02**
After column bed filtration					
Element	Weight %	Atomic %			
Oxygen	42.44	63.62			
Silicon	21.16	23.81			
Aluminum	9.48	7.54			
Iron	9.72	3.73			
Potassium	1.25	0.69			
Titanium	0.69	0.31			
Fluoride	**0.26**	**0.29**			

7.3.2 FTIR Study:

Fourier Transformation Infrared (FTIR) spectral data is a simple way to gain understanding about the octahedral, tetrahedral and hydroxyl structural units of minerals and clays. It involves in the identification of functional groups in clay minerals and compounds based on their Infrared (IR) spectra characterization and whose features could easily identify the structural groups within the clay and minerals. From the FTIR analysis the peak at 3695.6 cm^{-1} and 3622.39 (red) and 3695.6 and 3620.39 (white) signifies the AI-O-H stretching. The OH group of AI, Fe and Si comes within the range of this values. Such ranges signifies condensation of OH stretching vibration, stretching vibration of Si-O and have wide peak.

The peak value at 1872.88 for both the type shows the C=O stretch of anhydride group. The peak at 1612.49 (red) and 1610.56 (white) for both the type can be due to the presence of inner layers of H_2O molecules and is associated with H-O-H bending of water. The peak for the range 1000-600 specifies the presence of Si-O-Fe, AI-OH and Fe-OH band stretching. The peak at 538. 14 (red) and 536.14 (white) signifies the presence of Fe-O band stretching. The FTIR peaks of the three laterite samples (red, white and fixed bed column) after absorption has been shifted indicating that hydroxyl and carbonyl participated in the experimental process as the removal of fluoride directly depends on the persistent of these sites on the laterite. Beside the shift of peaks, occurrence of new peaks has also been observed clearly indicating the interaction between the fluoride and metal ions in the absorption process.

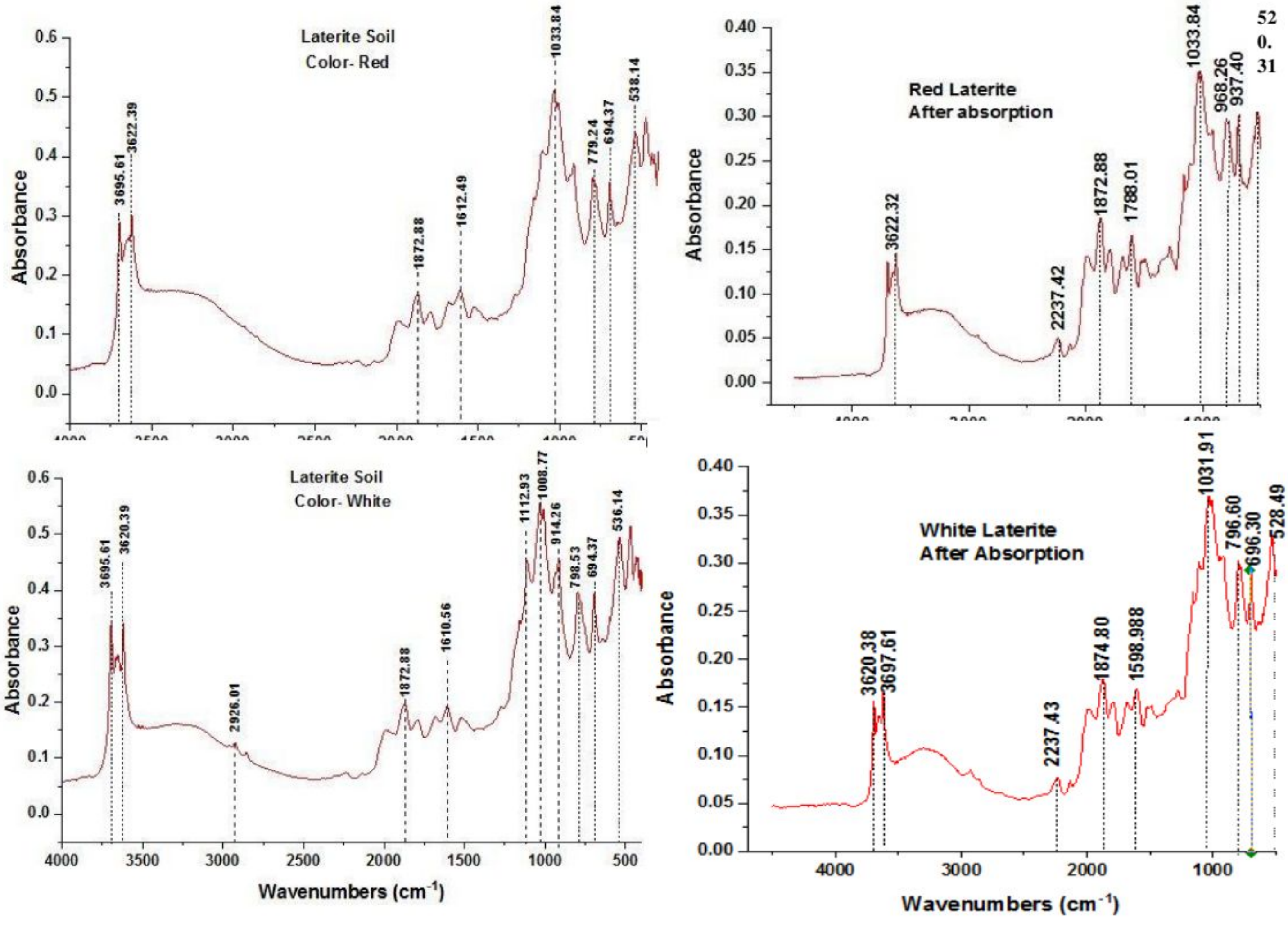


Fig. 31: Fourier Transformation Infrared (FTIR) spectral data of before and after application of white laterite

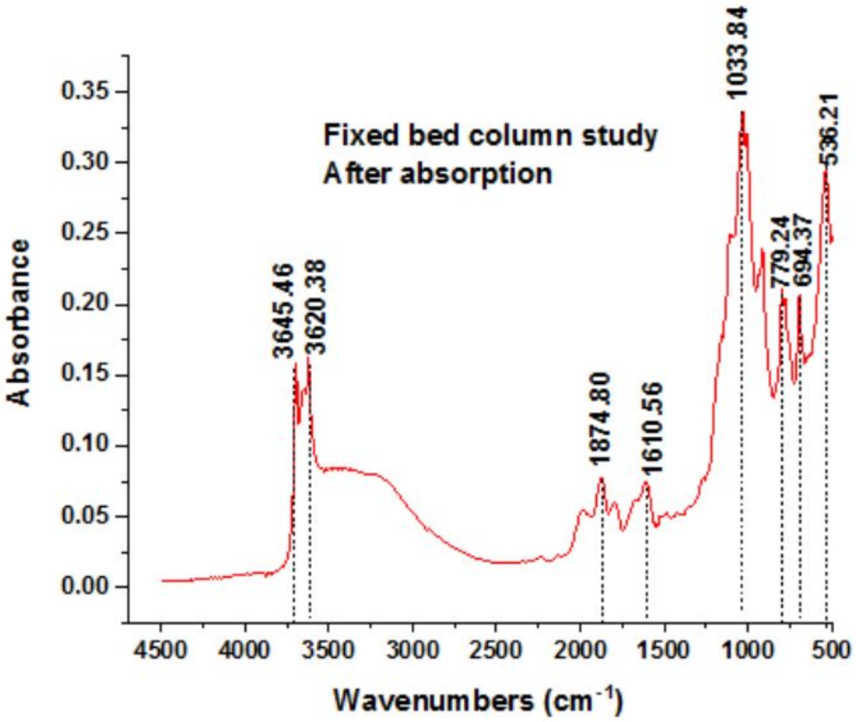


Fig. 32: Fourier Transformation Infrared (FTIR) spectral data of before and after application of fixed bed column study

7.4 DISCUSSION:

In various parts of India, laterite, or red soil, is readily available. The use of it as an adsorbent to remove fluoride from drinking water can be recommended. Adsorbents used in construction of defluoridation units incur the cost of adsorbents, activation and processing, as well as transportation costs. As adsorbent, laterite is widely available as natural soil, and only transportation costs are necessary since it does not require any typical processing or activation. In this study application of laterite of two different samples gave good results. From the batch experiment data, it can be said laterite soil exhibits a satisfactory efficiency for the removal of fluoride. It can be achieved more than 90% if a certain amount (20gm) of laterite is applied at 28°C and agitation speed 150 rpm. Sarkar *et al.*2006 reported 78.2% removal efficiency using 10 gm of laterite. The removal efficiency differs because of the difference of agitation time (reported 195 min) and temperature differences (reported 30°C).
In this study, point of zero charge was found at pH 5.67. Sarkar *et al.*2006 was reported point of zero charge at pH 3.98. The difference is because of different amounts of other oxides present along with silica and alumina. With the increase of agitation time the removal

capacity of laterite is increased. After 5 hours it has been observed that removal efficiency is almost constant. In case of white laterite soil, the TDS level of the water is comparatively high than red laterite. In this adsorption process the pH level of the water after fluoride removal is found low (pH 5-6).Red laterite has shown a better removal capacity than white laterite, that's why red laterite is used for column study. In the column filter, first 30 min the removal efficiency of the fluoride is not great. It started to show the good result after 30 min. The other general parameters of water quality (like pH, TDS, iron) of filtered water gradually increase with time in case of column filter. Regeneration of the media is required when the fluoride level of filtered water will exceed 1.0 mg/L

CHAPTER- 7

8.1 CONCLUSION & RECOMMENDATION

8.1.1 Conclusion:

The presence of fluoride in drinking water causes main health hazards like skeletal and non-skeletal fluorosis and dental fluorosis etc. Therefore removal of fluoride is essential before human consumption. Efforts were made in this investigation to remove fluoride using laterite soil. Finding. The water samples collected from Lakshmisagar found fluoride concentration as high as 2.38 mg/l. Many patients were diagnosed with fluorosis. Removal of fluoride from water by adsorption using laterite soil is depends on initial concentration of fluoride, agitation time and initial pH of solution. It has been found that red laterite shows better removal capacity along with low TDS level than weathered laterite (white laterite). Thereby red laterite was chosen for column study. In adsorption study, the equilibrium data is fitted with Langmuir, Freundlich and Temkin model. In kinetic study indicated that adsorption of fluoride using laterite is best fit with pseudo second order reaction in case of both red and white laterite soil. In fixed-bed column study 26.28 liters of water was filtered with fluoride concentration below the permissible limit. The capacity of red laterite soil was found 111.826 mg/kg and having average removal efficiency 82.411% in column study. In FESEM and EDX analysis confirmed that fluoride was removed using laterite soil. The use of laterite as an adsorbent for fluoride removal is found to be cost effective and hence can be considered as an alternative for defluoridation.

8.1.2 Recommendation:

1. Effort should be taken to supply surface water (River) after proper treatment in the excess Fluoride affected areas. The river water generally contains fluoride less than 1 mg/l.
2. Fluoride adsorption using column filter using laterite soil is a very cost-effective technique. So, it can be adopted for rural areas where laterite soil is easily available. Another advantage of this filter is no technical expertise is required to run the filter.

3. At Lakshmisagar, (in Bankura district) deep tube wells may be installed to abstract groundwater from the fluoride-safe aquifer, where feasible.
4. Regular water quality monitoring need to be carried out for all ground water sources (dug well/ tube well/ bore well).
5. Awareness and motivation campaign should be organized in fluoride affected areas.
6. Proper health care services with infrastructural facilities need to be extended for proper diagnosis and treatment for fluoride patients.

8.1.3 Limitation of the study

Laterite is a low cost natural filter medium for fluoride removal, at small scale water treatment. However it is worthwhile investigating the application of this technology at medium scale. Thereby large scale application and optimisation of parameters is required which has not been considered in this study because of short tenure of the course.

8.1.4 Future works

It was concluded that the use of lateritic soils for fluoride removal is very promising on a domestic scale where drinking, even in the presence of another ions such as Cl^- ; SO_4^{2-}, NO_3^- etc. But such ions have some health implications which whose concentrations is also needed to be optimised in future study. More optimisation for the fixed bed columns study is required with analysis of the regeneration of repetitive cycles of laterite for fluoride removal.

REFERENCES

1. S.M. Maliyekkal, A.K. Sharma, L. Philip, Manganeseoxide-coated alumina: a promising sorbent for defluoridation of water, Water Research 40 (19) (2006) 3497–3506.
2. L.N. Affonso, J.L. Marques Jr., V.V.C. Lima, J.O. Gonçalves, S.C. Barbosa, E.G. Primel, T.A.L. Burgo, G.L. Dotto, L.A.A. Pinto, T.R.S. Cadaval Jr., Removal of fluoride from fertilizer industry effluent using carbon nanotubes stabilized in chitosan sponge, J. Hazard. Mater. 388 (2020) 122042.
3. World Health Organization (WHO), Guidelines for Drinking water Quality: Incorporating the First and Second Addenda, 3rd edition vol. 1, World Health Organization (WHO), Geneva, Switzerland, 2008.
4. Ghosh A, Mukherjee K, Ghosh SK (2013) Sources and toxicity of fluoride in environment. Res Chem Intermed 39:2881–2915
5. Haguenauer D, Welch V, Shea B, Tugwell P, Wells G. 2000. Fluoride for treating postmenopausal osteoporosis. Cochrane Database Syst Rev 2000: CD002825
6. Project Report, Depleting Groundwater Levels and Increasing Fluoride Concentration in Villages of Mehsana District, Gujarat, India: Cost to Economy and Health, Report Prepared by S.K. Gupta and R.D. Deshpande (May, 1998)
7. S. Jagtap, M.K. Yenkie, N. Labhsetwar, S. Rayalu, Fluoride in drinking water and defluoridation of water. Chem. Rev. 112, 2454–2466 (2012)
8. K. Singh, D.H. Lataye, K.L. Wasewar, Removal of fluoride from aqueous solution by using bael (Aegle marmelos) shell activated carbon: kinetic, equilibrium and thermodynamic study, J. Fluor. Chem. 194 (2017) 23–32.
9. Meenakshi, R.C. Maheshwari, Fluoride in drinking water and its removal. J. Hazard. Mater. 137, 456–463 (2006)

10. S.C. Lung, P.K. Hsiao, K.M. Chiang, Fluoride concentrations in three types of commercially packed tea drinks in Taiwan. J. Expo. Anal. Environ. Epidemiol. 13, 66–73 (2003)

11. A.K. Yadav, C.P. Kaushik, A.K. Haritash, B. Singh, S.P. Raghuvanshi, A. Kansal, Determination of exposure and probable ingestion of fluoride through tea, toothpaste, tobacco and pan masala. J. Hazard. Mater. 142, 77–80 (2007)

12. F.V. Zohoori, P.J. Moynihan, N. Omid, A. Maguire, Impact of water fluoride content of infant foods and drinks requiring preparation with liquids before feeding. Community Dent. Oral 40, 432–440 (2012)

13. Project Report, Depleting Groundwater Levels and Increasing Fluoride Concentration in Villages of Mehsana District, Gujarat, India: Cost to Economy and Health, Report Prepared by S.K. Gupta and R.D. Deshpande (May, 1998)

14. C.D. Klaassen, Casarett and Doull’s Toxicology—The Basic Science of Poisons, 7th edn. (McGrawHill, New York, 2008), pp. 965–966

15. L.H. Weinstein, A. Davison, Fluorides in the Environment (CABI Publishing, Oxford, 2004)

16. http://www.dealmortgage.net/fluoride-class-action/unicef-1999-fluoride-harmful removal.pdf

17. Shortt HE, Pandit CG, Raghavachari TNS (1937) Endemic fluorosis in the Nellore District of South India. Indian Med Gaz72:396–398.

18. Rao NS, Rao PS, Dinakar A, Rao PVN, Marghade D (2015) Fluoride occurrence in the groundwater in a coastal region of Andhra Pradesh, India. Appl Water Sci. doi:10.1007/s13201-015-0338-3

19. http://cgwb.gov.in/wqoverview.html

20. Public Health Engineering Department. Government of West Bengal. A Note on Fluoride Contamination of Ground Water in West Bengal,2008 (http://www.wbphed.gov.in).

21. Piddennavar R, Krishnappa P. Review on Defluoridation techniques of water. Int J Eng Sci 2013;2:86-94.

22. Modi S, Soni R. Merits and demerits of different technologies of defluoridation for drinking water. J Environ Sci Toxicol Food Technol 2013;3:24-7

23. Razbe N, Kumar R, Pratima, Kumar R. Various options for removal of fluoride from drinking water. Int Organ Sci Res J Appl Phys 2013;3:40-7.

24. Mckee R, Johnston WS. Removal of fluorides from drinking water using low-cost adsorbent. Indian J Environ Health 1999;41:53-8.

25. Gunnar J, Bhattacharya P, Chaudhary V,Singh K.P. Controls on the genesis of some high-fluoride groundwaters in India. Applied Geochemistry (2005) 221–228

26. He X, Ma T,Wang Y, Shan H, Deng Y. Hydrogeochemistry of high fluoride groundwater in shallow aquifers, Hangjinhouqi, Hetao Plain. Journal of Geochemical Exploration 135 (2013) 63–70

27. Belkhalfa H,Gana M.Fluoride concentrations in drinking water and health risk assessment in the south of Algeria. DOI: *10.1016/j.yrtph.2021.105086*

28. Mondal D, Gupta S, Reddy D.V, Dutta G. Fluoride enrichment in an alluvial aquifer with its subsequent effect on human health in Birbhum district, West Bengal, India.Chemosphere 168 (2017) 817-824

29. Karunanidhi D,Aravinthasamy P, Kumar D,Subramani T, Roy P.D. Sobol sensitivity approach for the appraisal of geomedical health risks associated with oral intake and dermal pathways of groundwater fluoride in a semi-arid region of south India, Ecotoxicology and Environmental Safety 194 (2020) 110438

30. Choubisa SL. Status of industrial fluoride pollution and its diverse adversehealth effects in man and domestic animals in India. Environ Sci Pollut Res (2016) 23:7244–7254

31. Huimei C, Lingyun X , Guijie C, Chuanyi P, Fei K, Zhengquan L , Daxiang L, Zhengzhu Z , Xiaochun W. Removal of fluoride from drinking water using modified ultrafine tea powder processed using a ball-mill. Applied Surface Science, Volume 375, p. 74-84.

32. Zhang K ,Wu S, He J, Chen J , Cai X, Chen K, Li Y, Sun B, Lin D , Liu G, Kong L, Liu J. Development of a nanosphere adsorbent for the removal of fluoride from water. doi: 10.1016/j.jcis.2016.04.037.

33. Wu S, Zhang K, He J, Cai X, Chen K, Li Y, Sun B. High efficient removal of fluoride from aqueous solution by a novel hydroxyl aluminum oxalate adsorbent. Journal of Colloid and Interface Science 464 (2016) 238–245

34. Bharali R.K., Bhattacharyya G.K. Biosorption of fluoride on Neem (Azadirachta indica) leaf powder. Journal of Environmental Chemical Engineering 3 (2015) 662–669

35. Sarkar M, Banerjee A, Pramanick P.P. , Sarkar A.R.Use of laterite for the removal of fluoride from contaminated drinking water.Journal of Colloid and Interface Science 302 (2006) 432–441

36. Gomoro K., Zewge F, Hundhammer B. FLUORIDE REMOVAL BY ADSORPTION ON THERMALLY TREATED LATERITIC SOILS . Bull. Chem. Soc. Ethiop. 2012, 26(3), 361-372.

37. A. Maiti, J.K. Basu, S. De, Experimental and kinetic modeling of As(V) and As(III) adsorption on treated laterite using synthetic and contaminated groundwater: effects of phosphate, silicate and carbonate ions, Chem. Eng. J. 191 (2012) 1–12.

38. B.-Y. Zhu, T. Gu, Surfactant adsorption at solid-liquid interfaces, Adv. Colloid Interface Sci. 37 (1991) 1–32.

39. J.A. Schwarz, C.T. Driscoll, A.K. Bhanot, J. Colloid Interface Sci. 97 (1984) 55.

40. T.W. Weber, R.K. Chakravorti, Pore and solid diffusion models for fixed bed adsorbents, J. Am. Inst. Chem. Eng. 20 (1974) 228–238.

41. Govindarajan C, Ramasubramaniam S, Gomathi T and Sudha P N 2011 *Arch. Appl. Sci. Res.* **3** 572-80

42. Nita I, Iorgulescu M, Spiroiu M F, Ghiurea M, Petcu C and Cintezã O 2007 Analele Universitatii din Bucuresti-Chimie **1** 59-67

43. Z.A. ALOthman, M. Naushad, R. Ali,Environ Sci Pollut Res. (2013) https://doi.org/10.1007/s11356-012-1259-4

44. S. Lagergren, Zur theorie der sogenannten adsorption gelo ster stoffe. Kungliga Svenska Vetenskapsakademiens Handlingar, Band 24 (1898) 1–39.

45. J.P. Simonin, ChemEngJ. (2016). https://doi.org/10.1016/j.cej. 2016.04.079

46. H. Moussout, H. Ahlaf, M. Aazza, H. Maghat, Karbala Int J Mod Sci. (2018). https://doi.org/10.1016/j.kijoms.2018.04.001

47. G. McKay, Y.S. Ho, Pseudo-second order model for sorption processes, Proc. Biochem. 34 (1999) 451–456.

48. W.J. Weber, J.C. Morris, Equilibria and capacities for adsorption on carbon, J. San. Engg. Div. 90 (1964) 79–107.

49. Han, R.; Wang, Y.; Zhao, X.; Wang, Y.; Xie, F.; Cheng, J. Adsorption of methylene blue by phoenix tree leaf powder in a fixed-bed column: Experiments and prediction of breakthrough curves. *Desalination* 2009, *245*, 284–297.

50. Bohart, G.S.; Adams, E.Q. Some aspects of the behavior of charcoal with respect to chlorine. *J. Am. Chem. Soc.* 1920, *42*, 523–544.

51. Vilvanathan, S.; Shanthakumar, S. Column adsorption studies on nickel and cobalt removal from aqueous solution using native and biochar form of *Tectona grandis*. *Environ. Prog. Sustain.* 2017, *36*, 1030–1038.

52. Thomas, H.C. Heterogeneous Ion Exchange in a Flowing System. *J. Am. Chem. Soc.* 1944, *66*, 1664–1667.

ANNEXURE

Fig. 33 **:** An interview with Fluorosis affected patients (from left 2nd and 3rd) in presence of ASHA ma'am (right) at Lakshisagar in Bankura district, West Bengal, India (Latitude: N22˚55'28'', Longitude: E87°0'27'')

Fig. 34: Sources of Fluoride contaminated drinking water at Lakshisagar in Bankura district, West Bengal, India (Latitude: N22˚55'28'', Longitude: E87°0'27'')

Fig. 35**:**Water Sample Collection for Fluoride test from different Mark-II tube well at Lakshisagar in Bankura district, West Bengal, India.

[Lakshisagar P.H, Lakshisagar Bus stop (top), Lakshisagar Village-1, Lakshisagar Village-2 (bottom)]