Fluoride Removal from Water Environment by Acid Modified Fish Scale Biochar

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CERTIFICATE FROM THE SUPERVISORS

*This is to certify that the thesis entitled "**Fluoride Removal from Water Environment by Acid Modified Fish Scale Biochar**" submitted by **Ms. Disha Asaram Khandre** who got her name registered on 30th April 2019 for the award of Ph.D. (Engg.) degree of Jadavpur University is absolutely based upon his own work under the supervision of Prof. (Dr.) Somnath Mukherjee, and that neither his thesis nor any part of the thesis has been submitted for any degree/diploma or any other academic award anywhere before.*

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Chapter 1
Introduction

1.1 Background of the study

Natural water bodies have impurities from various sources. The most common contaminants are microorganisms, suspended particles, colloidal materials, pesticides and various dissolved metallic and non-metallic substances. The quality of water in rivers and subsurface source is being deteriorated continuously, due to release of contaminants from cities, industries and agriculture together with decomposition of rock forming minerals as natural pollution. Among these compounds, anionic pollutants like fluoride, arsenic and nitrate contamination in groundwater has been recognized as one of the most serious challenges to render fit for potable purpose worldwide (Kaushik et al., 2004; Ahmad et al., 2022).

Fluoride is often described as a "double-edged sword" as inadequate ingestion is associated with dental caries, where as excessive intake leads to dental, skeletal and soft tissue fluorosis almost non curable. Fluorosis is becoming a global environmental toxicological problem and is most commonly found in water-stressed regions. (Fawell *et al*. 2006; Raju 2017). Fluoride contamination in drinking water sources has been a major problem in many countries, especially in several parts of India, China, Sri Lanka, South Africa, Tanzania, Argentina, East Africa, part of South Africa, Turkey and some part of South America. (Srimurali *et al*, 1998; Barati *et al.* 2014)

It is revealed from published literature that, India is among the 25 nations around the globe, where health problem occurs due to the consumption of fluoride-contaminated water. In India, 18 states have been identified as epidemic for fluorosis (Raju , 2017). The severe cases of fluorosis were reported in part of North-Western part of India exceeds fluoride concentration of 0.4-19 mg/L (Yadav et al., 2009; Dhiman and Kesari, 2006). Few literatures have reported fluoride concentration of 0.2-20 mg/L in parts South India (Shaji et al., 2007; Karthikeyn et al., 2010; Mamatha and Rao 2010). Central India and Deccan Province have also reported moderated fluorosis due to fluoride concentration of 0.2-10 and 0.4-8 mg/L respectively(Mobeen and Kumar 2017; Sivarajasekar et al., 2017; Yadav et al., 2019,) . Nearly 200 districts of 18 Indian states have reported fluoride associated problems affecting around with 200 million people

(Mondal and George 2015; Das 2017). It is well known that F^- contamination is present in the ground water in the western part of West Bengal. Districts like Birbhum, particularly Nalhati, Bankura, Purulia, parts of Midnapore, and Bardhaman suffers through high fluoride contamination of groundwater sources (Mondal *et al.*, 2014; Das, 2017). The severe cases of fluorosis were observed in North-West India with fluoride concentration of 0.4-19 mg/l and South India with fluoride concentration of 0.2-20 mg/l, and moderated fluorosis was reported in Central India and Deccan Province with fluoride concentration of 0.2-10 mg/l and 0.4-8 mg/l, respectively. (Mobeen *et al*., 2017)

Water defluoridation techniques are recognized as chemical precipitation/coagulation, ion exchange, adsorption, reverse osmosis, and electro-dialysis. Many of these methods possess limitations on large scale application for various unfavorable factors such as high chemical, operational and maintenance cost. The generation of toxic byproducts (pollution) and sometimes makes the process more complex. Among these methods, adsorption is the most suitable and widely used engineering tool due to its simple operation, and the availability of a wide range of adsorbents. (Suriyaraj *et al.*, 2015; Thakre *et al*., 2015).

Fluoride removal by adsorption has been widely explored with various adsorbent, still there exist a great gap between developed technology and its application. There is a further scope of searching out new material that to be low cost easily available, efficient and compatible with existing technology. With a view to explore to achieve sustainable and low cost solution scientist and engineers still carrying out extensive research work in this area in pursuit of these objectives.

Solid waste management is another major problem being faced by all nations across the globe. Wastes generated at fish markets and fish industry are considered as an important pollutant having a serious impact on the environment. The worldwide consumption of fish per capita nearly doubled over the last 45 years, leading to larger quantities of fish processing wastes (Ward and Loes, 2011). A large amount of fish waste, about 50-70% of original materials is generated in Fish markets and Fish Processing units everyday worldwide. (Kafle *et al*, 2013) About 18 - 30 million tons of fish wastes is generated at fish processing industries and markets of which 4% are fish scales. (Muhammad *et aL*, 2016) It is observed that, scales-a major component of fish processing waste, is often discarded together with other fish wastes.

Biosorbents prepared from fish scales has been used to treat wastewaters containing heavy metals, dyes and pharmaceuticals (Marrakchi *et al*, 2017).

1.2 Statement of the problem

Consumption of water with high levels of fluoride is causing great concern across the globe. India has 29 states and more than 18 states are affected by fluorosis. The excessive consumption of Fluoride resulting in fluorosis. The disease caused due to excessive intake of fluoride has great impact on physical and mental health in persons affected by fluorosis. The health effects of fluoride in drinking water are not only irreversible but also detrimental. Preventing people from consumption of water laden with excessive fluoride is the only possible cure for this problem. Defluoridation of such contaminate water is the only sustainable approach. Among all the methods of defluoridation, adsorption is the most convenient method. Many adsorbents have been used by the adsorption method, but they have limited use due to their high cost, less adsorption capacity and less regeneration capacity.

On the other hand consumption of fish and shrimp worldwide is increased over the last decade. As an outcome of these activities a huge production of fish scale is salvaged globally. In India, this waste is discarded as garbage and indiscriminately disposed without recovery of any useful product. This formed the base and need of the present study, focusing on using fish scale waste based adsorbent materials to remove fluoride ions from water which will give sustainable solution to the problem. In terms of the magnitude of fluoride contamination problem, exploring the novel, economic and environment friendly Fish scale Biochar and composite material will be a small attempt for a big problem. It will a veil some of the existing problem of Solid waste management, will also reduce the burden of environmental pollution due to fishery waste.

1.3 Motivation

It is a challenging task to establish a low-cost technology to minimize the acute fluoride damage to mankind and the environmental risks that it induces and relevant treatment option. Utilization of fish scale for water remediation is a recent outcome of innovative endeavor. The literature addressed that, fish scales and their derivatives have been examined earlier for removal of Heavy Metals and dyes from water environment however no study has been performed previously to investigate potential performance of Fish Scale Biochar (FSB) and Acid modified fish scale biochar(AMFSB) for Fluoride removal from water environment. This aspect prompted to undertake the present research work and motivated the candidate for evaluation of waste based fish scale biochar as a useful adsorbent for fluoride removal form water environment..

Chapter 2

Literature review

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2. 1 Fluoride removal technologies

Various technologies are exhibited or used to remove fluoride from water. Out of all the process but the adsorption process is generally accepted as the economically attractive and most effective for removal fluoride from water. Defluoridation of water can be done by different methods. The technologies currently available to people are Precipitation/coagulation techniques, Ion-exchange techniques, Membrane techniques electrochemical treatments , Nano-filtration, and Adsorption techniques (Rao 2003; Shen et al.,2003; Sujana et al.,2009; Khatibikamal et al.,2010; Bhatnagar et. al.,2011; Diawara et al.,2011; Bhaumik and Mondal 2015;Jadhav et al., 2015; Waghmare et al., 2015; Mobeen and Kumar 2017; Yadav et al., 2018; Sabti, et al 2023). However, the shortcomings of most of these methods are high operational and maintenance costs, secondary pollution and complicated procedure involved in the treatment (Singh et al., 2018; Kumar et al., 2022)

2.2 Fluoride removal by adsorbent

Adsorption techniques have been quite popular due to their simplicity and availability of wide range of adsorbent materials. Many bio-sorption techniques have been employed for the treatment of drinking water. Researchers worked on various locally and abundantly available materials like Leaf powder (Tembhurkar and Dongre, 2006), Activated rice husk (Vardhan et al., 2011), Barks (Jamode et al., 2004), Tamarind seeds (Karthikeyan et al., 2010), seed extracts of Moringa oleifera (Parlikar et al., 2013), tea ash (Monadal et al., 2012), egg shell (Mann et al., 2014; Bhaumk et al., 2017) are few among them. A number of agricultural and forest wastes/byproducts and industrial waste products have been proposed by a number of researchers for the fluoride removal from aqueous wastewater. The biosorbents and various materials for preparing biochar are abundant in nature, inexpensive, require little processing, and are effective for fluoride removal (Mohan D. *et al*., 2012; Tomar and Kumar, 2013, Sivarajasekar N. et *al.* 2017).

2.3 Fish Scale for Water /Wastewater treatment

One of the in wastewater treatment by the adsorption is the utilization of living and non-living biomass; this is known as biosorption (Demirbas, 2008). Biosorbents prepared from fish scales was utilized to treat wastewaters containing heavy metals, dyes and pharmaceuticals. Biosorbent from fish scales are usually produced from fish market and can be prepared as adsorbent. The major sources as of fish scale are found in the market, fish industries and large culinary establishments. Some of the scales are prepared and used directly while others are impregnated with additives, calcined or used as source for deriving hydroxyapatite and was used as modified surface treatment.

The available scientific literatures reveals that fish scale derived adsorbents have been successfully explored for removal of heavy metals (Cr, Cu, Mn, Pb, Se, U, Zn, etc), textile dyes, pharmaceutical compounds and inorganic pollutants like arsenic and fluoride. Recent researches on removal of these pollutants using fish scale based adsorbent are briefly discussed below. Various heavy metals and dyes removed from water environment with the help of Fish scale based adsorbent are listed in **Table 2.1.**

2.4 Earlier studies on waste based adsorbent for Fluoride removal from water environment

i) Bhargava and Kiledar (1995) studied potential of Fishbone charcoal for fluoride removal from aqueous solutions. Columns containing 45 g fishbone charcoal were tested in laboratory column bed with a continuous feed of water containing 2.5-20 mg fluoride /L. The useful capacity of the medium was defined as the volume of treated water or the amount of fluoride removed before the breakthrough at concentrations of 1 mg/L. It was observed that influent water containing 5 mgF^-/L resulted in useful volumes of 9.5 to 3 L, depending on the loading utilised (about 0.3 –1.7 mL/min/g). Useful removal capacities between 0.3 and 1.4 mg/g were obtained, the highestcapacity being observed for lowest flow rate and highest initial fluoride concentration.

Table 2.1:- Pollutant removal efficiency of fish scales as reported in the literature

Metal	Heavy metal Removal efficiency (%)	Reference
As(III) and As(V)	94.00	Rahaman M. & Basu (2008)
Fe (III)	80.00 90.00	Amjad & Jamal, (2008) Prabhu *et al*, (2012)
Cd (II)	98.00 86.00	Amjad & Jamal, (2008) Prabhu et al, (2012)
Cr(VI)	60.89	Kondapalli & Mohanty , (2009) Bamukyaye S,et al., *(*2017)
As (III)	99.83	Mustafiz et al., (2012)
Mn (II)	84.00	Prabhu et al, (2012)
Fe Zn Pb	64.20 91.00 86.00	Zayadi & Othman, (2013)
Pb	Almost 100	Bawadi Abdullah, et al. (2014)
Mn(II) and Cd(II)	81-87	Burham and Aly (2014)
Cr(VI)	about 22 mg/g	Moura (2012)
Cr(VI)	2.51 to 4.28 mg/g.	Kondapalli et al., (2011)
Uranyl ions	82	Hastenreiter et al., (*2011)*
Zinc, Iron	About *70*	Darge A. , (2013)
Chromium (VI)	40.51%,	Bamukyaye et al., (2017)
Azo dye, Ponceau 4R	134.40 mg g/1.	Zhu and Xiao (2013)
Reactive blue 5G dye	253.8 mg g/1	Ribeiro et al., (2015)
Reactive orange 16 adsorption	114 .20 mg /g	Marrakchi F., *et al* ., (2017)
Malachite Green dye	97.41	Chowdhury S. *et al.(* 2012)
Methylene blue	555.55 mg g/l	Zhe Huang , (2014)
Brilliant Red	3.199 mg g/l	Hosne Ara Begum, (2013)
Dichlorophenol	--	Mota J.A. et al. (2012)
Arsenic (As)	--	Rahaman et al.(2015)
Sulfamethoxazole and trimethoprim	--	Nielsen and Bandosz (2016)
Fluoride (F)	4.69 mg/g	Bhaumik R. , et al (2017)

Abe et al, (2004) have investigated six different carbonaceous materials for fluoride removal. The materials investigated are carbon block (CB), four kinds of coal charcoals (CC) and bone char (BC). They found that the fluoride removal efficiency of thse materials was in the order of BC > CC > CB > AC . the bone char reported highest fluoride removal of 82% at pH 4.6. The adsorption through BC flowed Freundlich isotherm with coefficient (r) 0.998. The adsorption was reported to be an ion exchange between fluoride and phosphate ions present in BC.

Deshmukh et al., (2009) investigated adsorbent prepared from agricultural waste rice husk. Chemical impregnation by physical activation was used for adsorbent preparation. Batch studies were conducted to evaluate effect of pH, contact time , dose of adsorbent and initial adsorbate concentration. The optimum adsorbent dose was found to be 10g/L. Maximum fluoride removal was observed to be 75%.

Bhaumik et al., (2017) explored the feasibility of fish scale dust for removal of F from aqueous solution. The adsorbent was characterized by SEM, FTIR and pHZPC. The value of pHZPC of fish scale powder is 6.5 . The porous and irregular surface structure of fish scale powder was observed under SEM. Effect of various operating variables such as pH, adsorbent dose, initial fluoride concentration, agitation speed, contact time and temperature on fluoride removal efficiency was observed by bacth adsorption studies. Optimum fluoride removal was occurred at pH 6.0 at 60 min contact time and 20gm / L adsorbent dose. The combined effect of these parametrs on removal of fluoride was assessed by using computerise software model known as Response Surface Methodology (RSM) based on Box-Behnken design (BBD). The optimized values of initial concentration, pH, adsorbent dose, and contact time for fluoride adsorption were found as 8.49 mg/L; 9.93; 22.6 g/L and 179.72 min, respectively. Among the equilibrium isotherms, Langumir model was found to be the best fitted one suggesting homogeneous mode of F biosorption on fish scale. Kinetic studies showed better applicability of pseudo-second-order model

Choudhary et al., (2023) studied Chicken feathers derived from poultry waste were employed as an adsorbent in this study to get rid of fluoride from aqueous solutions. FTIR, XRD, SEM–EDX, and BET analysis were used to characterize the adsorbent. The influence of initial sample pH, a dosage of adsorbent, contact time, and initial fluoride concentration on the capacity of adsorption by modified chicken feathers (MCFs) was explored in the batch test. The batch adsorption findings show optimized equilibrium at pH 6, dose 6 g/L, and contact time of 60 min.

The experimental data were found best suited to the Freundlich adsorption isotherm ($R^2 = 0.911$) among the three isotherms used. The highest adsorption capacity of the sorbents for fluoride was measured using the Langmuir isotherm ($Q_o = 4.78$ mg/g). The pseudo-second-order; PSO model with a more significant correlation ($R^2 = 0.9809$) and sorption capacity of 1.555 mg/g was in good agreement for fluoride uptake than other employed kinetic models according to kinetic statistics.

2.5 Limitations of earlier work

- Though Fluoride removal by adsorption is hugely explored and exploited with various adsorbent, there exist a great gap between developed technology and its application where required
- Methods developed for defluoridation so far are either not sustainable or economical for various unfavorable factors.
- With a view to explore to achieve sustainable and low cost solution scientist and engineers still carrying out extensive research work in this area in pursuit of these objectives
- The existing literature reveals that, Fish scales and their derivatives have been explored for removal of Heavy Metals and dyes from water environment but no such previous study has been performed to explore the potential of Fish Scale Biochar (FSB) for Fluoride removal from water environment

2.6 Critical Review of Literature

Fluoride is recognized as emerging pollutant in water environment particularly for sub-surface water resources. Removal of Fluoride from water environment is utmost important for potable water supply. Developing an effective and robust technology for removal of excess fluoride from water environment becomes a challenging task especially for developing countries. Most of the publications dealt with Fluoride removal with physicochemical methods predominantly with adsorption process. The serious drawback of all these methods leads into generation of secondary pollution mostly as sludge. Application of biosorption is an environmentally friendly approach for fluoride removal. However, there are some limitations over its use in real life scenario and treatment of industrial waste containing fluoride. Recently nano-adsorbents have been attracted considerable attention for defluoridation of water. These adsorbents have reported to have higher fluoride uptake capacity. Many researchers have investigated influence process parameters like pH, adsorbent dose, agitation time, initial fluoride concentration, temperature, particle size, presence of co-ions for defluoridation with various adsorbents. Existing literature indicates that many adsorbents obeyed pseudo-second order or pseudo-first order of rate kinetics. The equilibrium data was also tested by many researchers for adsorption isotherm modeling.

From the literature, it is also evident that biochar would be a preferred adsorbent in recent years in water pollution control and environmental remediation. Numerous biochars developed from natural resources played unique roles in field of defluoridation and water pollution control as they manifest the advantages of low cost and ease of operation. Many such literatures the column analysis, breakthrough studies and kinetic evaluation are not addressed to validate appropriate method of treatment. Literature back up also did not present / exhibit any relevant research work with fish scale charcoal or coupled with any kind of composite material. Hence it is felt by the researcher to carry out further study in details in the level of doctoral work for removal of fluoride from water environment by Fish Scale Biochar.

Chapter 3

Objective and scope of Present Work

3.1 Objective of research work

The objective of present research investigation is to explore potential application of a novel, feasible and cost effective Fish Scale based Biochar for removal of fluoride from water environment. The major focus of the research is to develop an engineering reactor considering economics, efficiency, and environment friendly approach by using the above as an alternative and substitute of traditional adsorbent material for fluoride removal. In terms of the magnitude of fluoride contamination problem, exploring the novel, economic and environment friendly fish scale biochar and its composite forms will veil some of the existing problem in drinking water treatment as well a the burden of environmental pollution. It s apprehended that the outcome may be applied for wastewater treatment with fluoride contamination.

3.2 Scope of the present work

The scopes of the present investigation work considered are as follows:

1. Selection and collection of appropriate Fish Scale from market place, synthesis of biochar and alternative chemicals for its surface modification for enhancing adsorptive capacities.
2. Synthesis of selected Fish scale biochar and its composites.
3. Characterization of material with various standard techniques (BET, FITR, SEM, XRD, EDX etc).
4. Batch sorption studies with synthetic samples.
5. Study of different influencing process parameters such as pH, initial fluoride concentration , adsorbent dose, agitation speed and contact time.
6. Removal kinetics and adsorption isotherm studies.
7. Optimization of different process parameters.
8. Rate limiting step determination including estimation of kinetics order.
9. Column performance study for determining breakthrough service time.
10. Validation of column modeling with kinetic data with performance study.

11. Performance optimization by usage of statistical tool Response surface methodology (RSM) for batch experiments results.

12. Desorption and regeneration studies to be undertaken to maximise the material usage. This aspect could not be done in present study due to some problems imposed due to Covid-19 pandemic.

13. Real life sample would be also used for exploring the efficiency fluoride removal

Chapter 4

Materials and Methods

4.1 Materials

4.1.1 Chemicals & Reagents

A stock solution of fluoride concentration (F^-) 1000 mg/L was prepared by dissolving 2.21 gm analytical grade Sodium fluoride (NaF) [Make Merck, India] in 1L of Double distilled water. Subsequent dilution of different strength of F spiked solutions with stock solution were made by addition of double distilled water with pre determined volume. All the solutions utilized throughout the experiments were prepared in double distilled water (DW). For preparation of other chemicals and reagents standard procedures were followed as mentioned in existing literature.

4.1.2 Apparatus and Instruments used

Various instruments were used throughout the present research study. The major instruments along with their purpose and specification are listed **Table 4.1**

Table 4.1: Instruments Used

Process	Instrument	Make
pH determination	Digital pH meter	Deluxe , Model 101E,M.S. Electronics India Pvt Ltd.
Fluoride measurement	Ion Selective Electrode(ISE)	Orion Star™ A214 pH/ISE Bench top Meter
Weight measurements	High precision electrical balance	Wensar , Model PGB 300
Agitation of batch study samples	Orbital mechanical shaker	Remi , India make
Drying of washed adsorbent	Hot Air Oven	Scientific Industries, India
Carbonization of FSB	A muffle furnace	Sicco India furnace , India
BET surface area	BET surface analyser	Quantachrome NovaWin, Japan

Surface morphology and elemental composition	SEM (Scanning electron microscope), equipped with EDX	JSM-6490 V, JEOL, JAPAN)
FTIR analysis	Fourier Transform Infrared Spectrometer	Perkin Elmer Spectrum, United Kingdom
XRD analysis	X-ray diffract meter equipment	Bruker, D8 Advance, Germany
Fixed bed column study (up-flow mode)	A peristaltic pump	A peristaltic pump of Rivotek^{TM} supplied by Riviera Glass Private limited

4.2 Preparation of adsorbent material

4.2.1 Preparation untreated Fish scale biochar (FSB)

Labeo Rohita (Rohu) scales used were collected from the local fish market atf Kolkata). The dust, dirt and soluble impurities from the surface of fish scales were removed by washing them thoroughly with tap water as well as distilled water. Then the scales were sun dried in open to atmosphere for 2 days and subsequently derived to char in muffle furnace at 600ºC for 3 h. The resulting fish scale biochar was pulverized into biochar powder using a grinder. The grinded powder was sieved to obtain particle size of 125– 250µm and the resultant product was used adsorbent without any chemical modification. The biochar thus obtained was given a name as Fish scale biochar (FSB). The schematic representation of preparation of FSB is exhibited in **Figure 4.1 (a) though Figure 4.1(e).**

4.2.2 Preparation of acid treated fish scale biochar (AMFSB)

To prepare acid modified fish scale biochar , 20 gm of fish scale biochar(FSB) has been kept in diluted HCL solution (2 mol/L), and stirred for 3 h. After this the fish scale biochar was filtered and washed several times with distilled water till wash water reaches to neutral pH. The washed acid soaked biochar was then oven dried at 100^0 C till it reached to constant weight. This dry acid modified biochar was then stored in air tight container and used as adsorbent in fixed bed continuous column for fluoride removal studies. **The Figure 4.1** depicts the schematic of preparation of Acid modified fish scale biochar.(AMFSB).

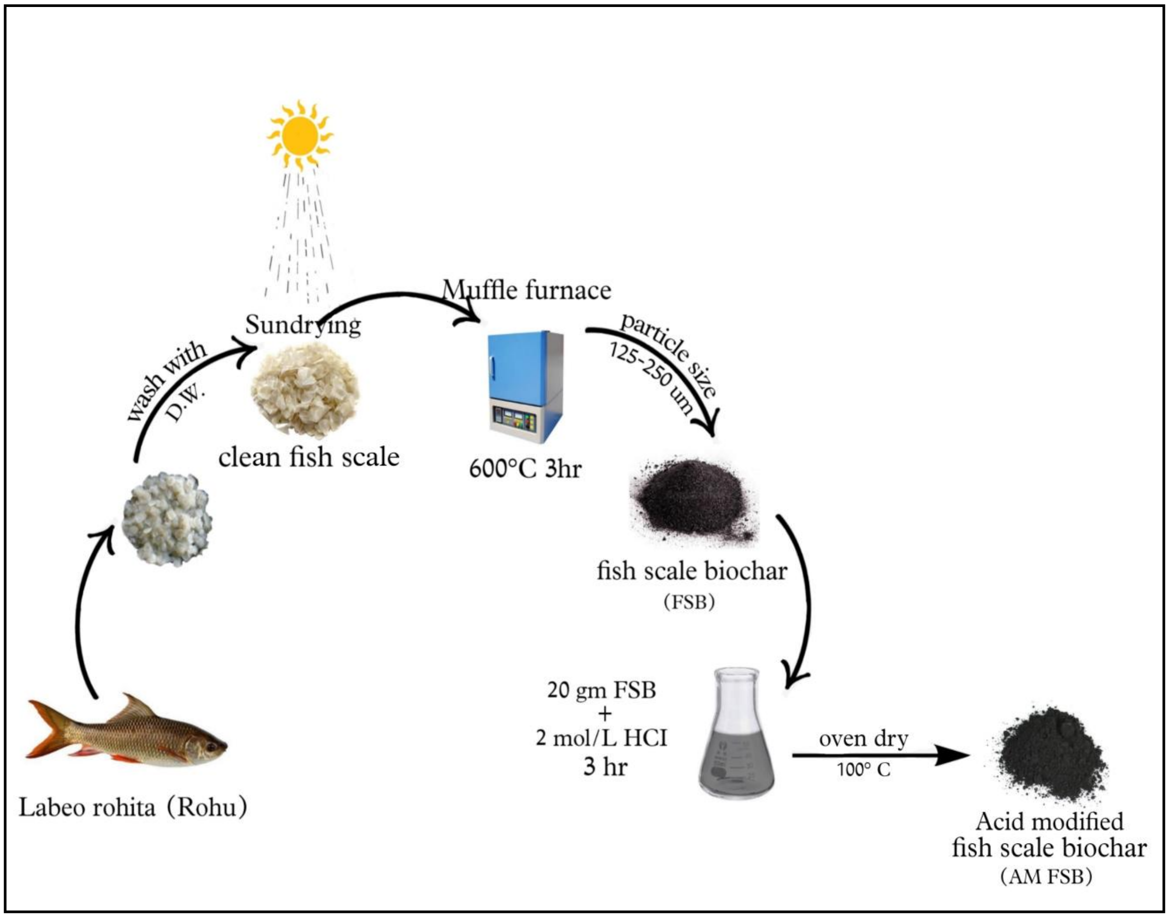


Figure 4.1: Schematic diagram of FSB and AMFSB synthesis

4.1.1.1 Preparation of Metal impregnated Fish Scale Biochar

For preparation Aluminum (Al), Iron (Fe) and Manganese (Mg) impregnated Fish Scale Biochar of Aluminium nitrate($Al(NO_3)_3$), Iron (III) chloride hexahydrate ($FeCl_3.6H_2O$) and Magnesium chloride hexahydrate ($MgCl_2.6H_2O$) having 99.99% purity was purchased from Merck and used without further purification. For the $Al(NO_3)_3$ doped Biochar sample, 20gm of the previously prepared biochar was mixed thoroughly with 5gm of $Al(NO_3)_3$ in a mortar pestle. The mixture was then heated in a muffle furnace at 550^{o}C for 4 hours at 5^{o}C/min heating rate in air atmosphere. A black colored powder sample was obtained after cooling down to room temperature. This was named as Al –Fish scale biochar (Al-FSB). For the Iron and Magnesium impregnated biochar synthesis, the same procedure was followed with $FeCl_3.6H_2O$ and $MgCl_2.6H_2O$ as the precursor respectively. The black powder obtained in this case was named as Fe- fish scaled biochar (Fe-FAB) and Mg-fish scale biochar(Mg-FSB) respectively.

4.3 Material characterization

Material characterization was done using X-ray Powder Diffraction (XRD), Scanning Electron Microscopy (SEM), Fourier-transform infrared spectroscopy (FTIR) and Energy Dispersive X-ray Analysis (EDS) has been done to investigate the properties and compositions of selected adsorbent material. Energy Dispersive X-ray (EDS) is an integral part of SEM analysis. In SEM-EDX , a focused beam of electrons is bombarded on sample to obtain a localized chemical composition. EDX can detect all elements.

The FTIR technique used in the present study identifies resonance frequency characteristics of functional groups present in the sample. This technique widely used for identification of functional groups of any mixtures or compounds to be analyzed. using X-ray Powder Diffraction (XRD analysis evaluates the atomic arrangement, crystallite size of sample. X-ray diffraction (XRD) patterns of AMFSB was recorded using an advance X-ray diffractometer (Philips Analytical PW-1710) which was equipped with Cu-Kα radiation of λ=1.5418 Å. These investigations were done at sophisticated test and instrumentation centre (STIC), located at Cochin .

Surface area and porosity are two important physical properties for any adsorbent. The Brunauer, Emmett, and Teller (BET) theory for gas adsorption was used for the measurement of surface area of FSB. The analysis was done at laboratory of Jadavpur University, Kolkata.

4.4 Adsorption experiments

A series of batch experiments were conducted to evaluate the effect of process influencing parameters viz., adsorbent dose, pH, initial fluoride concentration, contact time, agitation speed and co-existing ions. a series of batch adsorption process was carried out by mechanical agitation. All adsorption batch study experiments were performed in triplicate. One factor at a time (OFAT) approach was used for optimizing the process parameters. To determine optimum pH for removal of fluoride pH of water sample was varied from pH 2-12. The adsorbent dose was varied from 2-12 gm/L. The contact time for batch study was varied from 60 to 210 min. The initial fluoride ion concentration was varied from 2mg/L to 10 mg/L. To observe the effect of agitation speed on fluoride removal the orbital mechanical shaker was rotated at varying speed from 60rpm to 180rpm. The effects of co–existing anions like bicarbonates, chlorides, sulphates and nitrates were also observed After every batch experiment the sample was allowed for the gravitational settlement of adsorbent and then the solution was filtered using Whatman filter paper (No 1). This sample was used for estimation of fluoride ion concentration The remaining fluoride ion concentration in the sample was estimated by an ISE meter(Orion fluoride ion selective electrode (Thermo Scientific Orion, USA). All the experiments were conducted at ambient temperature. The experimental data obtained was for adsorption isotherm analysis and to determine rate order kinetics. An empirical statistical technique Response surface methodology (RSM) was used with Box-Behnken design approach for designing experiments and finding the optimum conditions for various process parameters

4.5 Fixed Bed Column Study

To evaluate the performance of the prepared acid modified fish scale biochar for removal of fluoride from water, continuous fixed bed column experiments were conducted. The effects of different bed depths, flow rate and initial F^- concentrations were analyzed using breakthrough curves. The adsorption experiments were conducted at a neutral pH 7.0 ± 0.1 and room temperature (30^0C). A vertical Acrylic column of 2cm diameter and 40cm height was used for performing the fixed bed column studies. The column study was conducted with synthetic fluoride water sample at ambient temperature. Acrylic columns were wet-packed with glass beads at the bottom. Then a thin layer of glass wool (Sigma Aldrich) was place just below and above acidified fish scale biochar as per experiment design. An influent tank of 10 lit capacity of the was used for the column to run in up-flow mode and the peristaltic pump was connected to it with pipe. The influent fluoride solution from the model water tank was allowed to pass through an inlet placed at the packed bed column in a up-flow direction at a design flow rates. At fixed interval , the treated effluent is collected at the outlet placed above the packed bed.. Breakthrough curve analysis was performed on the results obtained for fixed bed column study. Mathematical modeling of fixed bed column data was done by using Thomas model, Yoons – Nelson model and bed height service time (BDST) model.

4.6 Isotherm modeling and Kinetic order study and optimization

Experimental results were tested with various available adsorption isotherm models to validate adsorption phenomenon. Kinetic order study is conducted to determine various reaction rate constants and to describe the adsorption mechanism. Application of statistical tool Response surface Methodology RSM) technique with Box-Behnken design of experiments for batch test data. The optimum performance of the experimental output has been predicted.

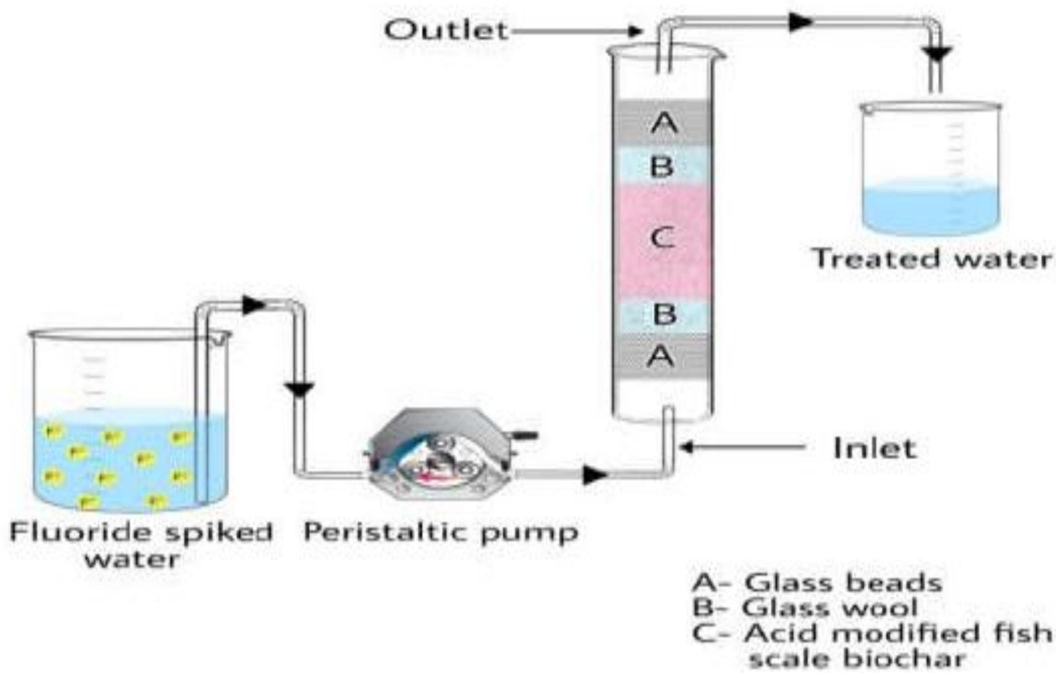


Figure 4 2 Schematic of Column study

Chapter 5

Theoretical considerations

The present research investigation is based on various theoretical considerations of Adsorption process. Based on which the evaluation of batch adsorption and column adsorption data is performed. The various mathematical equations used in the present study are as follows:

5.1 Adsorption isotherm

An adsorption isotherm model gives a better understanding of mechanism of adsorption. It also determines type of interaction between adsorbate and adsorbent at its equilibrium state. The batch experimental data obtained is analyzed using existing established isotherm models. For adsorption isotherm study Langmuir, Freundlich and Intra-particle diffusion models were studied.

5.1.1 Langmuir isotherm

Irving Langmuir in 1932, proposed an empirical isotherm for gases adsorbed on solids. The Langmuir isotherm models is expressed in linearized equation forms as equation (1) .

$$\frac{\mathbf{Ce}}{\mathbf{q_e}} = \frac{1}{K_l\, q_{max}} + \frac{Ce}{\mathbf{q_{max}}} \qquad (1)$$

where, $q_{e=}$ the amount of fluoride adsorbed per unit mass of Fish scale biochar (FSB) (mg/g)

C_e = equilibrium concentration of fluoride(mg/L)

q_{max} = maximum amount of the fluoride ions per unit mass of FSB

K_L = Langmuir constant representing the binding sites affinity (L/mg).

A dimensional equilibrium parameter (R_L) is a characteristic of Langmuir model and it is expressed as equation (Ho and McKay, 1999)

$$R_L = \frac{1}{(1+c_0 * k)} \qquad (2)$$

Where, *k* = constant (Langmuir) Co = concentration of fluoride (mg/l). When the R_L value is greater than 1, then it indicates the adsorption isotherm type supposedly to be unfavorable and if R_L = 1, then type is linear. When value of R_L ranges within 0 to 1 ($0< R_L <1$), it is considered as favorable and R_L equals to 0 then, its irreversible.

5.1.2 Freundlich isotherm

Freundlich and Kuster earlier in 1894 suggested an empirical isotherm model known as Freundlich isotherm. Freundlich isotherm describes the non-ideal and reversible adsorption. It is mostly early applicable to physico-chemical adsorption on heterogeneous surfaces (Ho and McKay, 1998). It is based on the assumption that adsorbent surface is heterogeneous for adsorption of adsorbate. In this model, adsorption takes place at all active sites of adsorbent surface. Freundlich isotherm model is expressed as:

$$ln\ q_e \ln K_f \ + \frac{1}{n} ln\ C_e \quad (3)$$

where, K_F ((mg g^{-1})(L mg^{-1})1/n) is a parameter of relative adsorption capacity of the adsorbent and 1/n gives an indication of the favorability of adsorption. Values of n > 1 represent favorable adsorption condition (Langmuir , 1918).

5.2 Adsorption kinetics and mechanisms

The kinetic behavior of an adsorbate removal or the absorption of a particular compound on to the adsorbent surface follows three main steps (Ho and McKay, 1999; Salameh et al. 2015)

The sorption kinetics provides insight into mechanism of adsorption reaction, Pseudo first order kinetic model and pseudo second order were used in the present study.

5.1.2.1 Pseudo-First-Order Kinetics

Different kinetic reactor model are used to determine the mechanism of adsorption and estimating reactor order. Bhattacharyya and Sengupta, (2006) suggested Lagergren model is most useful. The pseudo-first-order kinetic model is based on the assumption that solute sorption process is first-order in nature and it is only dependent on the number of fluoride ions present in the solution at any specific time (Langmuir, 1918; Bellack 1971; Dayanada et al., 2014)

Pseudo first order kinetic model is expressed as:

$$Log(q_e - q_t) = logq_e - \frac{K_1 t}{2.303} \quad (4)$$

Where, qe and qt are uptake capacity (mg/g) at equilibrium and at any time t , respectively. K_1 is first order kinetic rate constant. (min/L)

5.1.2.2 Pseudo-second-order kinetics

A second order rate law considers that the rate of removal depends on the sorption capacity and not the concentration of the sorbate (Ho and Mackay, 1998; Singh et al, 2022) Pseudo-second-order kinetic model assumes that the fluoride adsorption process is dependent on the number of fluoride ions present in the solution as well as available adsorption sites on the adsorbent surface (Ho and McKay, 1999). The Pseudo-second –order equation is expressed as

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \qquad (5)$$

Where K_2 is rate constant, q_t is uptake capacity (mg/g) at any time t.

5.1.2.3 Intra particle diffusion:

In adsorption process, there are several steps that that enhances the movement of adsorbate from solution on the adsorbent surface. The steps are governed by various factors like surface diffusion, film or external diffusion, pore diffusion or combination of more than one step (Ho and McKay, 1999). This kinetic model had been suggested by Weber and Morris and possibility of intra-particle diffusion can be described using following formula:

$$q_t = k_d t^{0.5} + C \qquad (6)$$

where, k_d = diffusion rate constant (mg/g. $h^{0.5}$), C = intercept and represents boundary layer thickness and qt = the amount of adsorbed compound (mg g/L) to the adsorbent at time t (min).

5.2 Column studies

The fixed bed column adsorption method allows the solute solution to flow continuously through a packed bed of adsorbent. The bed height, the rate of flow and initial concentration are varied to see their effect on adsorption. The performance of column adsorption is continuously monitored by measuring the effluent concentration with predetermined interval of time.

The efficiency of the column can be explained by means of the breakthrough curves (Onyangoa et al., 2004; Ofomaja et al., 2005).A breakthrough curve is plotted between column effluent concentration vs treated volume or treatment time (Fawell, 2004). The shape of breakthrough curve the graph is in general S- shaped.

Breakthrough is deemed to have occurred at some time t_b, break point time, when the concentration of the adsorbate leaving the bed increases to an arbitrarily defined value, C_e, break point concentration, which is often the minimum detectable or maximum allowable concentration of the component to be removed. In other words, the breakthrough point can be defined as the point at which the effluent concentration increases rapidly (Chen et al., 2001; Ramesh et al., 2012). The **Figure 5.1** shows a typical adsorption column breakthrough curve and movement of MTZ in fixed column

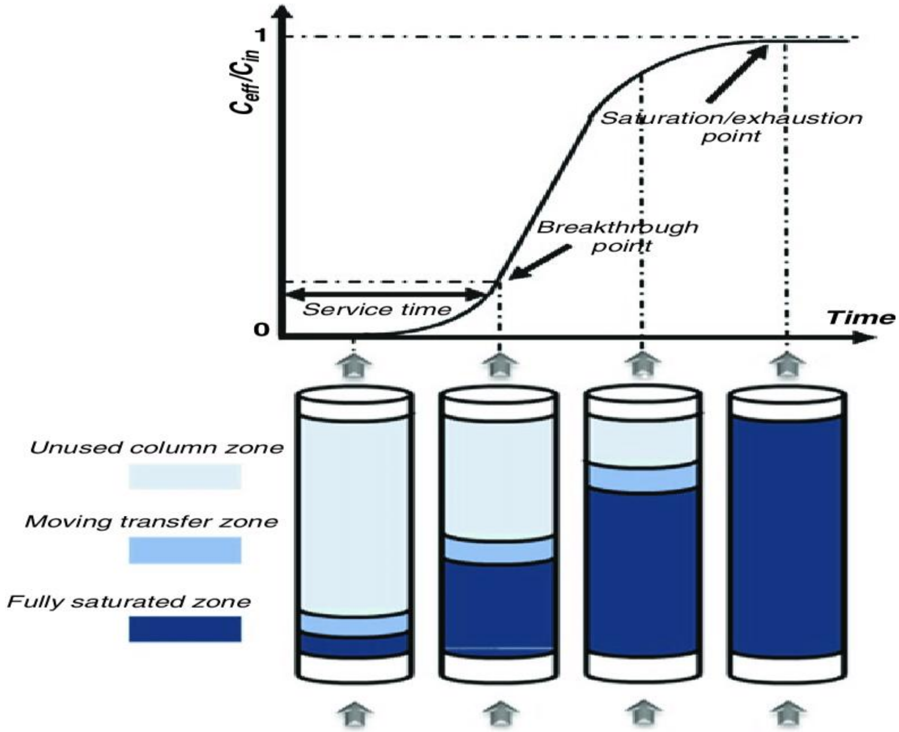


Figure 5.1 Schematic of adsorption column breakthrough curve and MTZ in fixed column

Chapter 6

Result Discussion

6.1 Characterization of selected material

Bulk density, Moisture content and biochar yield of Fish scale biochar were determined by was determined by following standard method. The result obtained are given in Table 6.1.

Table 6.1 Physical Characteristics of Fish Scale Biochar

Parameter		FSB	AMFSB
Bulk density (g/ml)		1.08	1.02
pH		7.84	6.62
Moisture content (%)		0.982	1.14
Biochar yield (wt%)			
	FSB @ 400	51	-
	FSB @ 600	48	-
BET surface area(m^2/g)		--	37.967
Pore Volume(cc/g)		--	0.108
Pore Diameter(nm)		--	3.618

The detailed physiochemical characterization of adsorbent material was done. The BET surface analysis showed good surface area of 37.967 m2/ gm. The biochar yield of fish scale biocahr (FSB) was found to be 51 and 48 % at 400 and 600 °C respectively. The biochar yield observed to decrease with increase in temperature. The SEM-EDS , FTIR and XRD analysis was performed on AMFSB and it was confirmed the mesoporous structure acid modified biochar and presence of Fluoride binding constituents in the prepared biochar. **Table 6.2** gives the elemental composition of AMFSB before and after adsorption of fluoride.

Table 6.2: Elemental composition of AMFSB

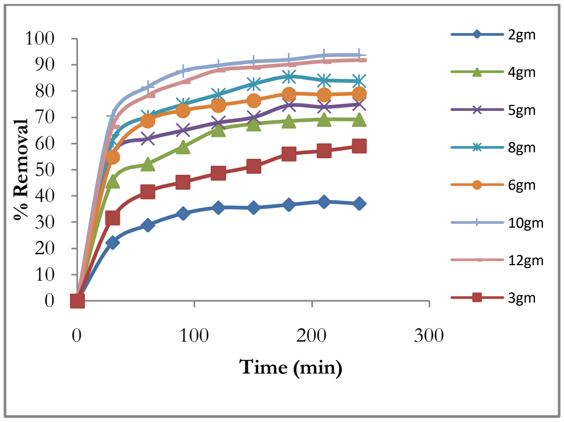
	Composition by wt %						
Element	**C**	**O**	**N**	**Ca**	**P**	**Mg**	**F**
AMFSB before adsorption	63.1	16.8	16.7	2.1	1.3	0.1	ND
AMFSB after adsorption	63.0	14.7	13.1	5.8	3.1	0.1	0.2

6.2 Batch studies:

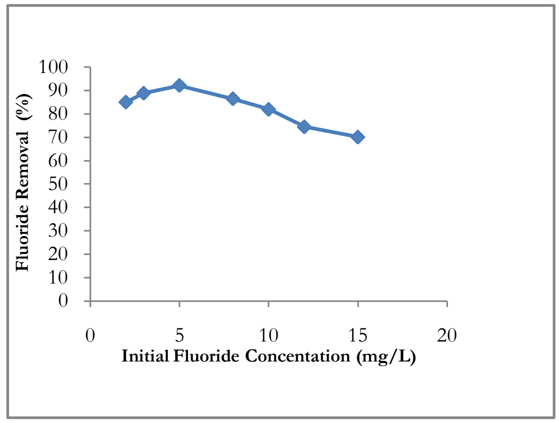
The batch studies were conducted to investigate the effect of different process parameters for removal of fluoride form water environment. It was found that the removal of fluoride with FSB and AMFSB was greatly influenced by pH, initial concentration of Fluoride, contact time and adsorbent dose. The effect of various parameter on % removal efficiency of fluoride by FSB and AMFSB are shown in **Figure 6.1and Figure 6.2.**

As shown in **Figure 6.1and Figure 6.2,** the adsorption rate of fluoride on FSB increases with time and eventually reaches to equilibrium after 180 min. At the start of FSB and F– interaction initial more number of active sites are available favorably for adsorption but with progress of time active adsorption sites was decreased and hence after equilibrium time no significant increase in removal of fluoride is observed. (Meenakshi and Sukumar, 2008; Bhumik *et al.*, 2016; Marrakchi *et al.*, 2017; Ayalew A., 2023). The results proved that at lower initial F- concentrations the sites available for adsorption are more whereas at higher F- concentrations most of the F- are left unabsorbed due unavailability of active adsorption sites onto the adsorbent surface. The obtained result concludes that % removal of F- was directly proportional to the initial F- concentration of water sample. For FSB and AMFSB both , fluoride removal increases with the increase in the speed of agitation. This is because, at higher agitation speed adsorbate can make proper contact with adsorbent surface (Tembhurkar et al., 2006 ; Roy et al., 2013)

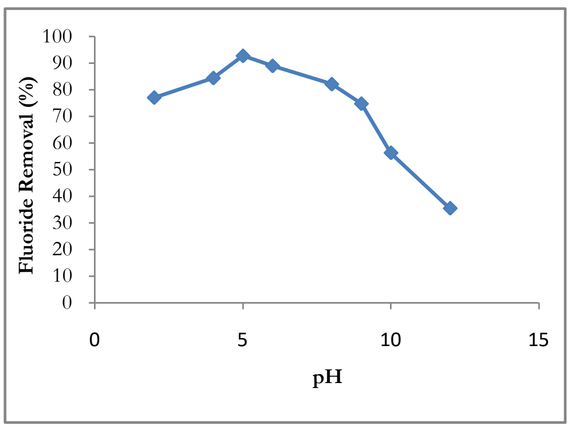
The effect of co-ions on fluoride removal by AMFSB was observed and was found that adsorption of F- was greatly affected by the presence of phosphate ions. In real life, groundwater with such high concentrations of ions are seldom present in drinking water. The experimental result showed that interference by competing ions followed the following order: nitrate < chloride < sulfate < bicarbonate < phosphate, from lower to higher concentrations in aqueous medium. The results obtained are in good agreement with results obtained for hydroxyapatite-based biochar materials reported by other authors to (Monal and George 2015, He , *et al.*, 2016).



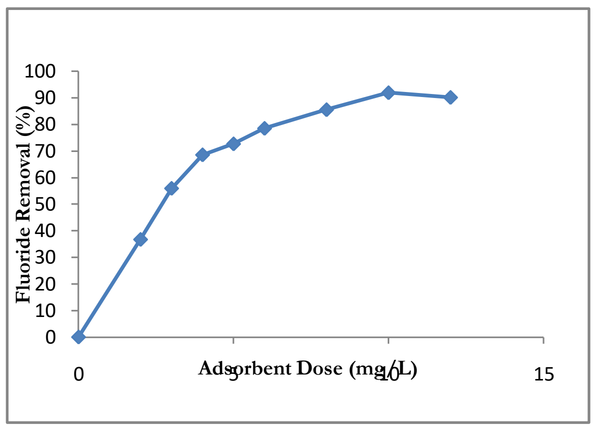
(a) Effect of contact time



(b) Effect of initial F- ion concentration



(c) Effect of pH



(d) Effect of dose of adsorbent

Figure 6.1: Effect of various parameters on fluoride removal (%) by FSB

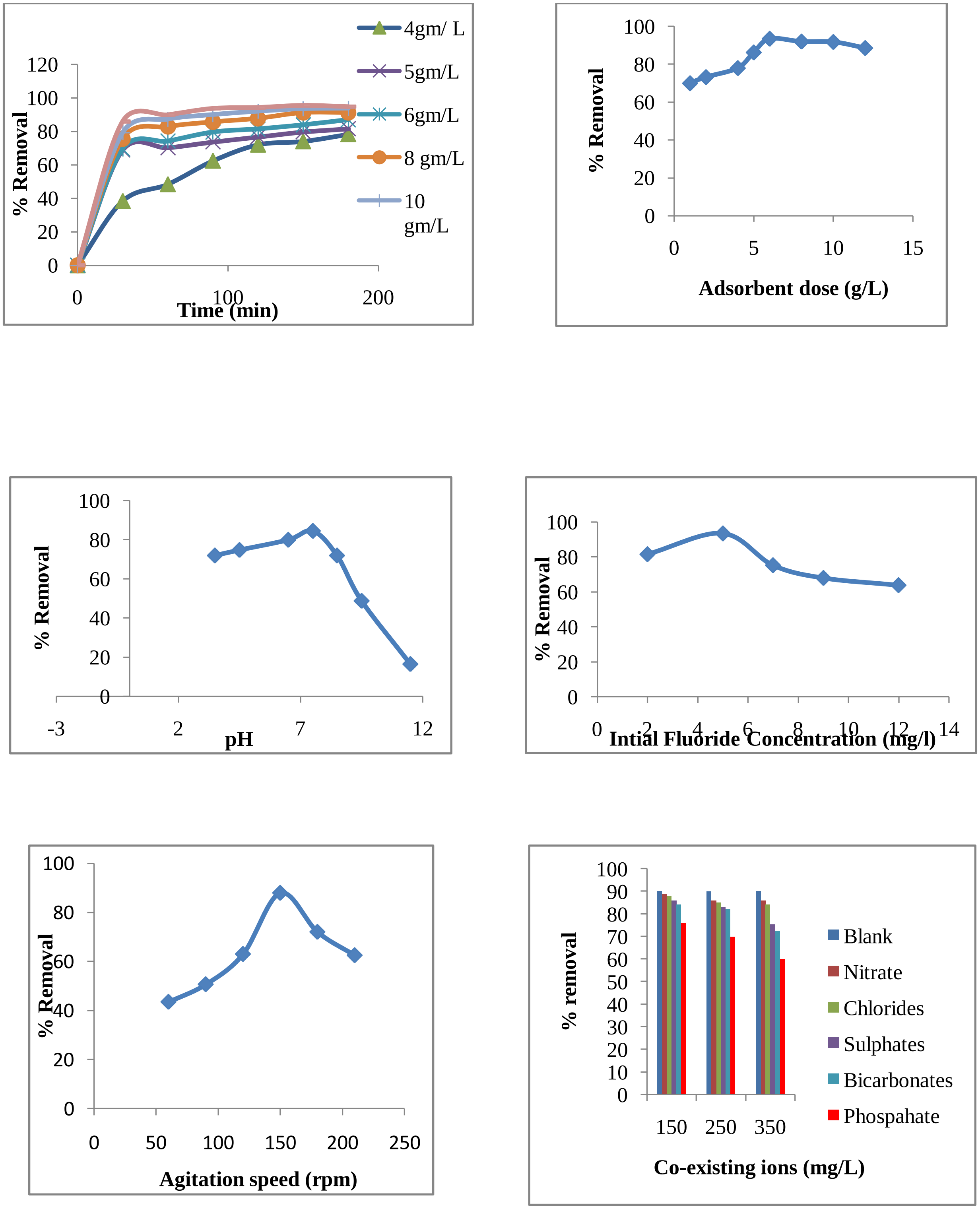
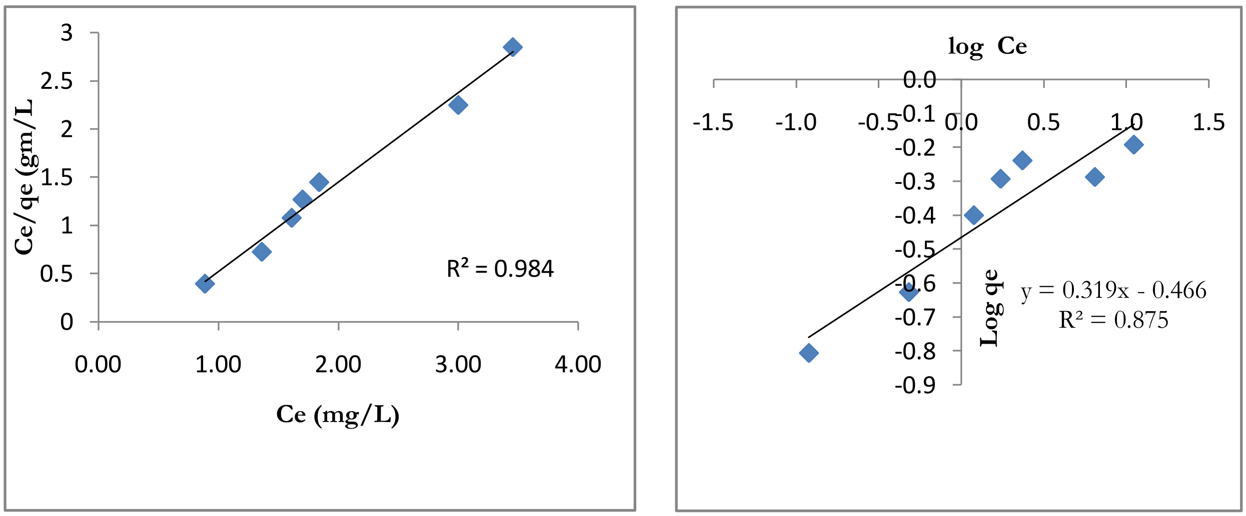


Figure 6.2 : Effect of various parameter on fluoride removal (%) by AMFSB

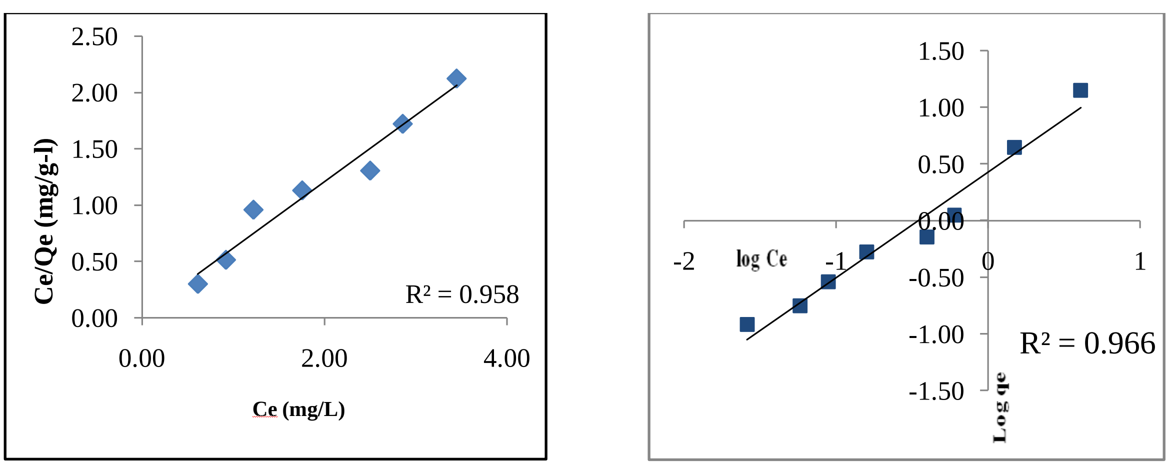
6.3 Adsorption Isotherm

To recognize the adsorption potential and adsorption mechanism of FSB and AMFSB different adsorption isotherm models were employed in the present study. Langmuir and Freundlich are isotherm models were used to illustrate the surface properties and adsorption mechanism The Langmui anf Freundlich r adsorption isotherm for FSB **Figure 6. 3** wheras **Figure 6.4** shows adsorption isotherms for AMFSB . The adsorption coefficients for FSB and AMFSB are calculated from the graphs plotted are gven in **Table 6.4 and Table 6.5.**



(a) Langmuir isotherm for FSB **(b) Freundlich isotherm for FSB**

Figure 6. 3 Adsorption isotherms for FSB



(a) Langmuir isotherm for AMFSB **(a) Langmuir isotherm for AM FSB**

Figure 6.4 Adsorption isotherms for AMFSB

Table6.3: Langmuir adsorption constants for fluoride removal

Parameter	FSB	AMFSB
R^2	0.984	0.984
q_{max}(mg/gm)	2.16	6.12
b (L mg^{-1})	0.437	0.035
R_L	0.320	0.89

The value of R_L signifies the adsorption nature which can be either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$), or irreversible ($R_L = 0$). **Figure 6.20(a) and (b)** shows the Langmiur isotherm plot for FSB and AMFSB.

Table 6.4 : Frendulich adsorption parameters for fluoride removal

Parameter	FSB	AMFSB
R^2	0.872	0.980
1/n	0.319	0.895
n	3.135	1.11
K_f	2.92	2.66

The values of Freundlich constant (n and K_F) and regression coefficient (R^2) were calculated by using linear Freundlich isotherm equation as given in **Table 6.6.** Based on values of regression coefficient (R^2), It was observed that FSB and AMFSB equilibrium data fitted well with Langmuir model than Frendulich model.

The plot for AMFSB with high R^2 values suggests the good applicability of the model as compared with R^2 value for FSB. The value of 1/n less than 1 obtained for confirmed that the adsorption of fluoride prepared FSB and AMFSB surface was favorable.

6.4 Adsorption Kinetics

Kinetic rate order evaluation for FSB and AMFSB is also performed separately. Pseudo-first-order and pseudo-second-order model were used to elucidate rate limiting state of fluoride removal (Ho and McKay, 1998). It is observed that the pseudo-first-order equation gives a higher regression value of 0.964 and 0.990 for FSB and AMFSB confirming the adherence to the pseudo-first-order rate law. The excellent fit of experimental data into pseudo-first- order models suggest that the removal of fluoride onto the surface of FSB and AMFSB is favored by physisorption.

The linear plots for pseudo first order, pseudo second order and intra-particle diffusion were plotted and the kinetic rate order constants were calculated and are listed in **Table 6.5 .** It is observed that (K_2) values of AMFSB are larger than that of the FSB ,these results are in good agreement with observations made by of Sundaram et al., 2008, Imtiaz et al., 2022; Chaudhari et al., 2023. the R2 value for intra-particle diffusion model was found to be 0.962 and 0.977 for FSB and AMFSB respectively. It confirms that intra-particle diffusion also attributed to the rate determining step of fluoride removal by FSB and AMFSB(Ghorai et al., 2005; Biswas et al., 2007; Gupta et al., 2013; Chaudhari et al.2023).

Table 6.5 Kinetic parameters for adsorption of fluoride on CAC and FSAC

Adsorbent	**Pseudo-first-order model**			**Pseudo-second-order Model**		
	Calculated q_e (mg/g)	**K_1 (1/min)**	**R^2**	**Calculated q_e (mg/g)**	**K_2 (g/mg min)**	**R^2**
FSB	2.01	0.021	0.964	1.53	0.0041	0.771
AMFSB	5.15	0.562	0.99	5.78	0.0082	0.940

6.5 Fixed-bed column adsorption study

Removal of fluoride by batch adsorption studies by many adsorbents have been reported in large, but the practical utility of an adsorbent in removing the fluoride from the water is mainly assesed by column operation (Ghorai and Pant, 2004; Ghorai & Pant, 2005; Halder et al., 2015; He et al., 2017; Chatterjee et al., 2018). The column experiments were also performed to evaluate the effect of column design parameter i.e. initial fluoride concentration, adsorbent bed height and flow rate. The column performance was plotted with breakthrough curves. The kinetic modeling of the breakthrough curve was tested using Thomas model, Yoons – Nelson model and bed height service time (BDST) model.

6.5.1 Effect of adsorbent bed depth

To investigate the effect of bed height, there different bed heights i.e. 1, 2 and 3 cm were taken with initial F- concentration 7.5 mg/L and flow rate through fixed bed of 1.5 mL/min is represented in **Figure 6.5.** It is observed that with increase in bed height, the breakthrough time and exhaustion time were increased (Rout et al, 2014; Patel 2020). The empty bed contact time (EBCT) was found to be 8.73, 16.75 and 25 .12 min for 1 .0, 2.0 and 3.0 cm of bed depth respectively. At initial stage, breakthrough curve showed gradual increase in slope and high fluoride removal. This gradual increase continued till the adsorbent bed got exhausted. At breakthrough point the concentration of fluoride in effluent increased more quickly so as the slope of the curve. The columns with minimum bed height got saturated earlier than the columns with more bed heights

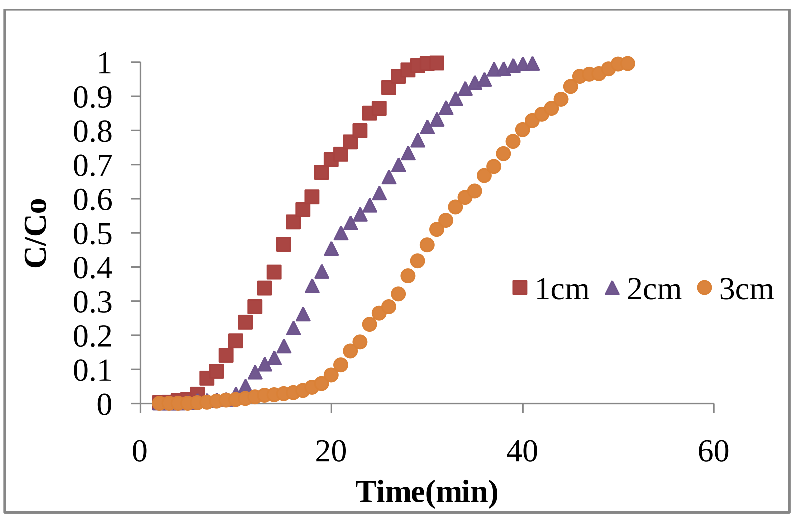


Figure 6.5 :Breakthrough curve of fluoride removal at different bed height

6.5.2 . **Effect of flow rate**

Figure 6.6 demonstrates the influence of influent flow rate on fluoride removal breakthrough curve at a fixed bed height 2 cm of column. From the evaluation of breakthrough data it is observed that with increase in the flow rate, breakthrough time (t_b), exhaustion time (t_e) and uptake capacity (q_b) was decreased whereas the treated volume with less removal was increased. This is due to, at lower flow rate F^- ions get longer contact time to diffuse with adsorbent surface (Maity, *et al.*2008; Mohan *et. al*., 2017).

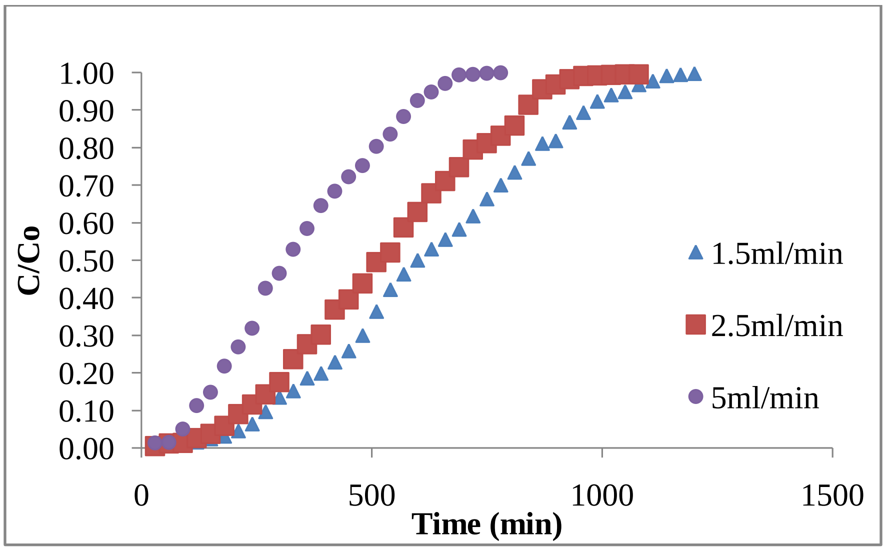


Figure 6.6 : Breakthrough curve of fluoride removal at different flow rate.

6.5.3 Effect of initial F- concentration

To investigate the effect of initial F- concentration on the adsorption by acid modified fish scale biochar with a constant flow rate (2.5 mL/min) and bed depth (2 cm) , the F-ion concentration was varied 5 mg/L, 7.5 m/L and 10 mg/L**. Figure 6.7** shows the breakthrough curve at varying F-ion concentrations. The results obtained are summarized in **Table 6.6** . The results also showed that the plateau of the breakthrough curve reached faster with increasing flow rate, which was due to the decrease of contact time between the solute in mobile phase and the surface of the stationary phase making quicker appearance of adsorption zone at the bottom of the column.(Ranjan et al., 2009; Mohan et al., 2017).

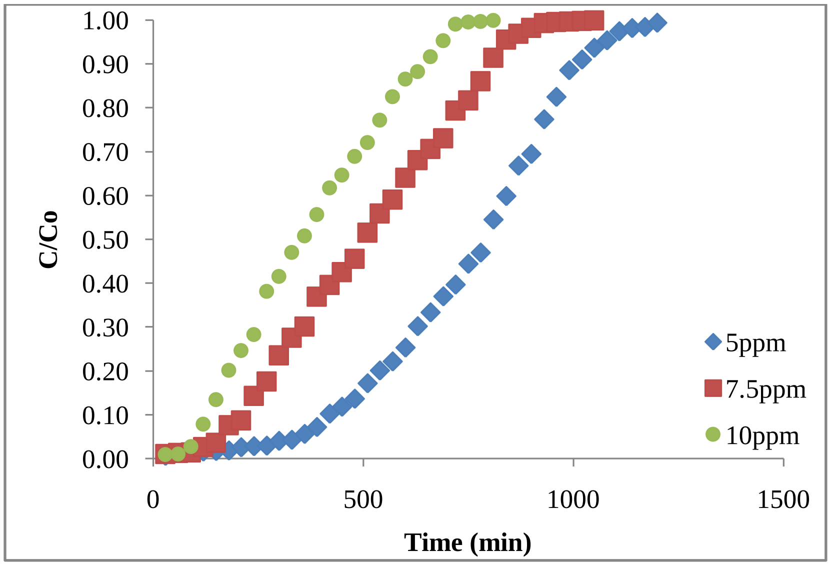


Figure 6.7 Breakthrough curve of fluoride removal at different F- ion concentration

Table 6.6 Experimental column parameters obtained from breakthrough curve

Ci (mg/L)	**Z** (cm)	**M** (gm)	**Q** (ml/min)	t_b (min)	t_e (min)	t_z (min)	**MTZ** cm	V_b (ml)	V_e (ml)	q_b (mg/gm)	**BV** cm3	**EBCT** (min)
7.5	1	2	1.5	283.64	734.48	450.84	0.61	425.46	1101.72	1.60	12.56	8.373
7.5	2	4.12	1.5	441	966.21	525.21	1.09	661.5	1449.32	1.20	25.13	16.75
7.5	3	6.2	1.5	673.53	1297.12	623.59	1.44	1010.3	1945.68	1.22	37.69	25.12
7.5	2	4.12	1.5	394	990.05	596.05	1.20	591	1485.08	1.08	25.13	16.753
7.5	2	4.12	2.5	314.23	832.45	518.22	1.31	785.575	2081.13	1.18	25.13	10.052
7.5	2	4.12	3.5	174.08	577.3	403.22	1.41	609.28	2020.55	1.28	25.13	7.18
5	2	4.12	2.5	630	1020	390	1.02	1575	2550	1.91	25.13	10.052
7.5	2	4.12	2.5	316.72	832.78	516.06	1.24	791.8	2081.95	1.44	25.13	10.052
10	2	4.12	2.5	183.19	645.72	462.53	1.43	457.98	1614.3	1.11	25.13	10.052

From the above **Table 6.6** it is evident that the Empty bed residence time was increased with increased in bed height of adsorbent in column. The volume of treated water was also increased with increased in bed height.

6.6 Breakthrough curve modeling

Breakthrough curve modeling of column data was done using Thomas model, Yoon-Nelson model and BDST model. The Thomas model plot showed in **Figure 6.8** the satisfactory correlation having R^2 values 0.96, 0.96 and 0.968 for 1cm, 2cm and 3 cm bed height respectively. Hence, it is evident that , Thomas model reasonably fits well and interpret the adsorption of fluoride on acid modified fish scale biochar (Ibrahim *et al*., 2016, Cruz *et. al*., 2020, Kumari *et. al*.,2021)

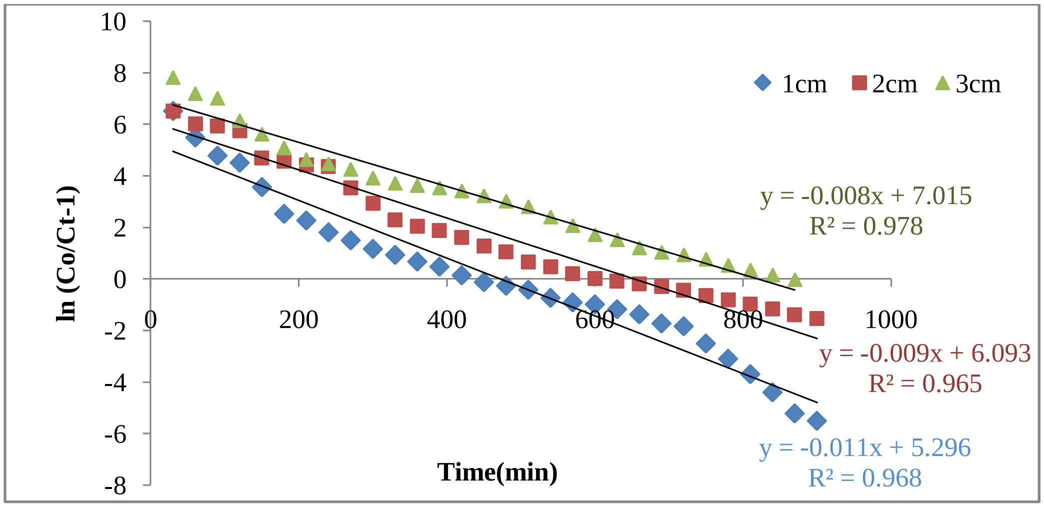


Figure 6.8: Thomas model plot of ln(Co/Ct - 1) vs time (t) at different Bed Depth

The **Figure 6.9** illustrates the plot of ln [C/(C_0- C)] against t is used to estimate the Ye-N constants (i.e., K_{yn} and τ). It is observed that the plots have good correlation coefficient 0.990, 0.96 and 0.98 for 5mg/L , 7.5 mg/L and 10 mg/L initial F- ion concentration. **Figure 6.10** depicts the BDST model plot for AMFSB. The data fits well in a linear graph with good R^2 value of 0.998 and 0.990 for breakthrough and exhaustion point of adsorbent respectively. The adsorption rate constant (K_o) and the dynamic bed capacity per unit volume of bed at breakthrough were calculated as 0.689 (L/mg/min) and 4,65(mg/L) respectively.

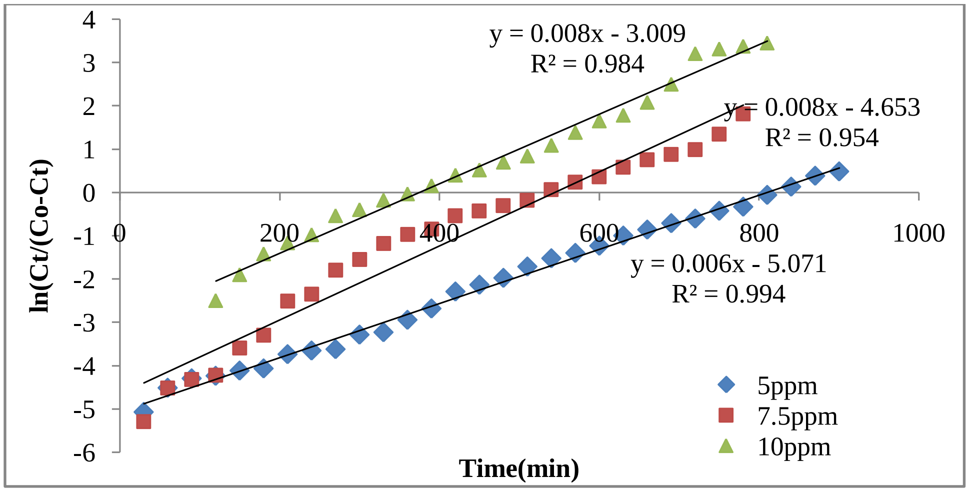


Figure 6.9 : Yoon-Nelson model plot at different F- ion concentration

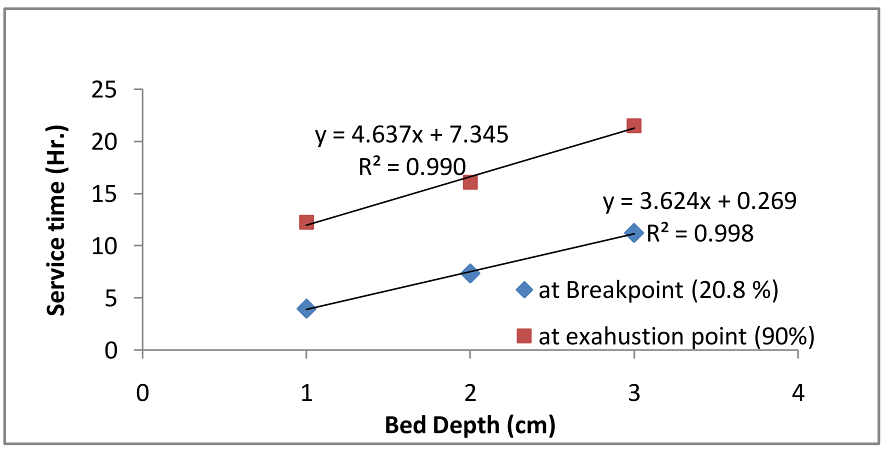


Figure 6.10: BDST model plot at C/Co

6.6 Response Surface Methodology

The Response Surface Methodology (RSM) is widely used statistical tool to understand the effect of individual and interactive effects of independent variables. Designing experiments can be easily done using statistical techniques such as response surface methodology (RSM) (Chatterjee *et al*.2012; Thakur et al., 2016; Halder et al., 2016; Bhaumik 2017; Mittal et al., 2020; Ahmadi et al., 2021; Shekhawat et al., 2023) . In the present study, statistical analysis using Design-Expert (Stat-Ease Inc.,version7.0.3, Minneapolis, USA, trail version) was employed for designing the experiments, data analysis, and interpretation According to The Box–Behnken design, 27 experiments were carried out to determine simultaneously the interaction effects. Response Surface Methodology was also used to explore optimal condition for fluoride removal.

The **Table 6.7** gives experimental levels and ranges of the independent parameters used in fluoride removal experiments. The input factors were pH, contact time (min), , initial fluoride concentration(mg/L), adsorbent dose (mg) .

Table 6.7: Experimental range and levels of the independent parameters

Coded variables	**Code notation**	**Coded Levels**		
		−1	**0**	**+1**
A	**pH**	2	6	10
B	**Time(min)**	60	120	180
C	**Initial F-(mg/L)**	2	7.5	10
D	**Dose(mg)**	2	5	8

The % of removal was treated as the response. In the present investigation the second-order polynomial equation by Box-Behnken design (BBD) was used to predict the response. Analysis of variance (ANOVA) was performed with a 95% confidence level. The fit of the model was determined by determination coefficient R^2 and adjusted R^2. (Ahmadi et al., 2021; Haldar et al., 2020; Mittal et al., 2020; Shekhawat et al., 2023; Buddharatna, 2016). **Table 6.8** shows the results obtained for ANOVA.

The RSM model equation in coded form obtained for fluoride removal by AMFSB is :

$$\text{Percent Removal} = 8.33-0.756\,A++0.5470\,B-0.2410\,C+0.2727\,D-0.4055AB+0.1029AC-0.0028AD+0.3104BC+0.1805BD-0.0317\,CD-0.0313\,A^2-0.1871\,B^2+0.1472\,C^2+0.4344\,D^2$$

It is to be written in input parameter form as:

$$\text{Percent Removal (\%)} = 8.33-0.756\,pH++0.5470\,time-0.2410\,Intial\,F^-+0.2727\,Dose-0.4055pH.time+0.1029pH.initial\,F^- -0.0028pH.dose+0.3104time.\,initial\,F^-+0.1805\,time.\,Dose-0.0317\,Initial\,F^-.Dose-0.0313\,pH^2-0.1871\,time^2+0.1472\,initial\,F^{-2}+0.4344dose^2$$

Table 6.8: Analysis of variance (ANOVA) for Response Surface Quadratic Model.

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	8.26	14	0.5902	36.89	< 0.0001	significant
A-ph	0.0686	1	0.0686	4.29	< 0.0006	
B-time	3.59	1	3.59	224.43	< 0.0001	
C-F	0.6971	1	0.6971	43.57	< 0.0001	
D-Dose	0.8922	1	0.8922	55.76	< 0.0001	
AB	0.6576	1	0.6576	41.10	< 0.0001	
AC	0.0424	1	0.0424	2.65	0.1297	
AD	0.0000	1	0.0000	0.0019	0.9659	
BC	0.3853	1	0.3853	24.08	0.0004	
BD	0.1303	1	0.1303	8.14	0.0145	
CD	0.0040	1	0.0040	0.2510	0.6254	
A^2	0.0052	1	0.0052	0.3276	0.5777	
B^2	0.1868	1	0.1868	11.67	0.0051	
C^2	0.1155	1	0.1155	7.22	0.0198	
D^2	1.01	1	1.01	62.90	< 0.0001	
Residual	0.1920	12	0.0160			
Lack of Fit	0.1845	10	0.0184	4.91	0.1808	not significant
Pure Error	0.0075	2	0.0038			
Cor Total	8.46	26				

The RSM result showing higher values R^2 (0.9773), Adjusted R^2 (0.9508) and Predicted R^2 (0.923) confirmed a good fitting of experimental data to model.

Figure 6.11(a) through Figure 6.11 (e) presents 3D surface plots showing various interactive effect of pH, contact time, initial fluoride concentration and adsorbent dose for percent removal efficiency of fluoride by using AMFSB.. Two independent variables were varied simultaneously to evaluate interactive effects of various parameters. The 3D plot can be interrelated as red color indicating high % removal and moving towards blue % removal decreases. It was found that % removal of fluoride was range between 50 and 91 %.

For fluoride removal using AMFB optimal conditions of parameters was predicted using Desirability ramp solutions. The RSM analysis predicted maximum % removal efficiency to be 85% at optimum pH of 7.1, contact time of 165.885 min, initial fluoride concentration of 5.26912 mg/L. and adsorbent dose of 6.21 mg/L. The results obtained by RSM were verified by batch adsorption experiments at obtained optimum conditions. Maximum 83.6 % removal of fluoride was obtained in batch study conducted with optimum variable conditions. The batch study revealed that actual % removal of fluoride was very near to the results of RSM analysis. It confirmed that RSM with BBD a design approach can be effectively employed to optimize input parameters for fluoride removal by Acid modified biochar.

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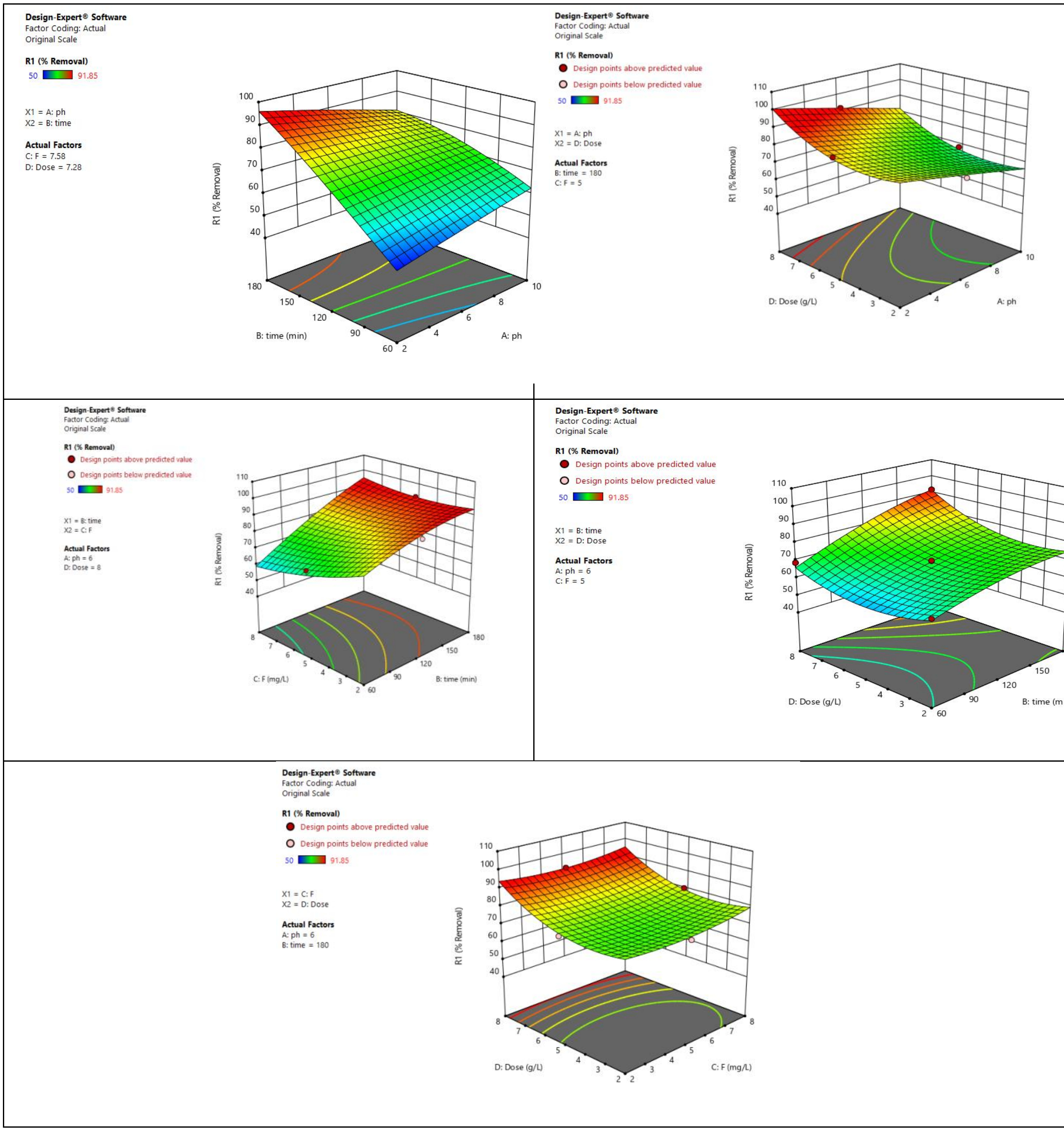

Figure 6.11: Response surface plot for effects of various parameters on %removal of fluoride

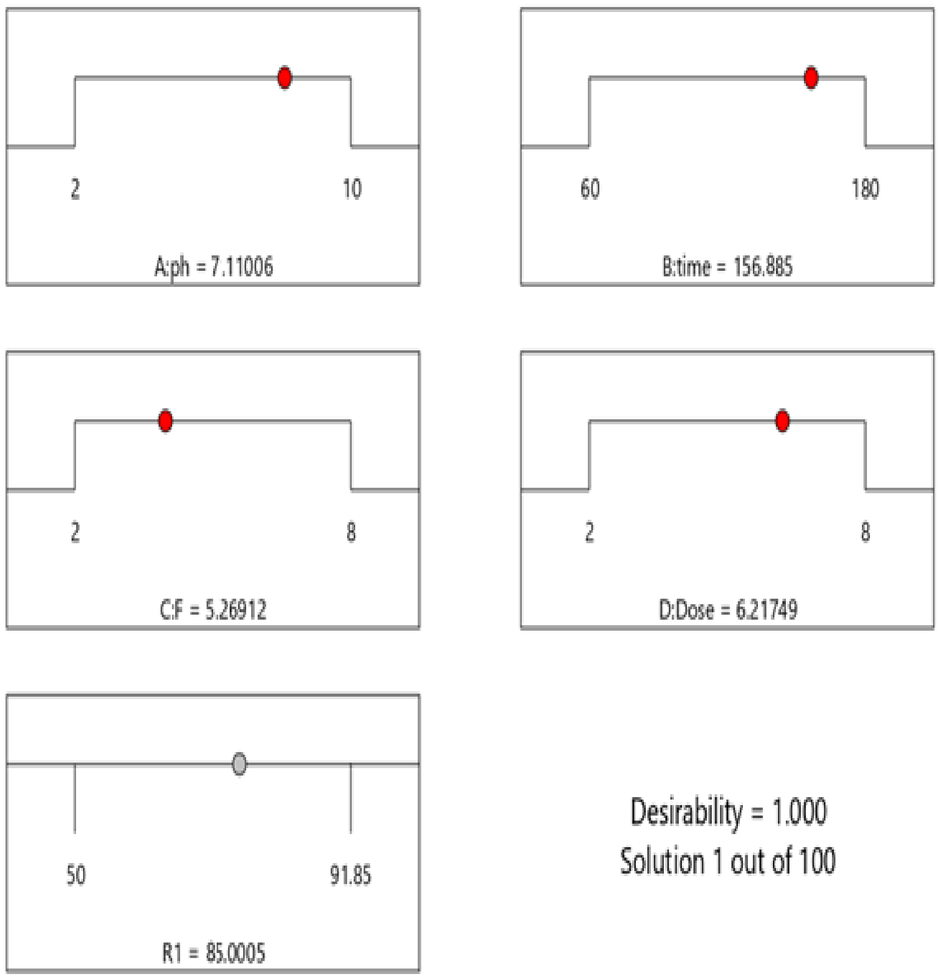

Figure 6.12: Desirability ramp for numerical optimization of process parameters

6.7 *Comparison of fluoride removal using AMFSB with other adsorbent*

Many adsorbents have been explored and proved to be efficient in fluoride removal from water environment as a result of endeavor put by different research through the ages. **Table 6.8** demonstrates comparative results some of the previously reported adsorbents with Fish Scale biochar (FSB) and Acid modified fish scale biochar (AMFSB). The FSB and AMFSB showed relatively good adsorption capacity for fluoride as compared adsorbent listed in **Table 6.8**

Table 6.8 Comparison of fluoride removal capacity of different adsorbent

Adsorbent	**Adsorption capacity (mg/g)**	**Reference**
Used tea leaves	0.51	Methodis et al.,
Rice straw activated carbon	15.90	Daifullah et al
Baggasee carbon	1.15	Yadav et al
Activated Eicbornia crassipes	0.027	Haldar et al
Granular ceramic	0.941	Chen et al., 2010
Carbon slurry	4.66	Gupta et al., 2007
Hydroxyaptite	3.12	Mourabet et al., 2015
Egg shell powder	1.09	Bhaumik et al. 2012
Fish scale dust	4.89	Bhaumik et al., 2017
Fish scale biochar	2.12	Present study
Acid modified biochar	5.15	Present study

Chapter 7

Conclusion

7.1 Conclusions

In this present investigation a waste based Fish scale biochar and its composites was studied for its potential to remove fluoride from water environment. The following conclusions are derived after detailed investigation of novel adsorbents prepared for efficient fluoride removal.

The present work has demonstrated that the abundantly available fish scale in fish market has successfully converted into an excellent and feasible adsorbents for removal of fluoride from water environment. It will a unveil some of the existing of solid waste management problem in the municipal market which rreduces the burden of environmental pollution due to fishery waste

In terms of the magnitude of fluoride contamination problem, exploring the novel and environment friendly Fish scale biochar(FSB) and Acid modified fish scale biochar (AMFSB) seems to be a promising solution for fluoride decontamination of drinking water.

7.2 Future Scope of the study

- Temperature dependent Temkin isotherm and kinetic parameters to be studied in detail.
- Hybrid process for the treatment of fluoride to be developed for further efficient removal of fluoride
- Desorption and regeneration studies to be undertaken to maximise the material usage. This aspect could not be done in present study due to some problems imposed due to Covid-19 pandemic.
- Real life sample would be also used for exploring the efficiency fluoride removal
- The experiment should be done taking the detailed investigation for effect of Iron , hardness causing salts etc. for multispecies effect on fluoride removal..

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Fish scale waste: Potential low-cost adsorbent for fluoride removal

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Wastes generated at fish industry are considered as an important pollutant having a serious impact on the environment. Fish waste generally has high biological oxygen demand (BOD) and typically possesses strong offensive smell. Fish scales constitute major part of fishery waste and usually be disposed as a waste with no commercial value. The feasibility of using fish scale derived biochar is investigated as a low-cost adsorbent for defluoridation. A batch removal and kinetic study was performed to examine the efficiency of fluoride removal from simulated spiked water sample. Some influencing parameters such as adsorbent dose contact time, agitation speed etc. on the fluoride removal kinetics are also evaluated. Experimental outcome reveals that fish scale biochar (FSB) can successfully be used as an effective adsorbent in water environment for fluoride removal.

Keywords: Fishery waste, fish scales, adsorption, biochar, fluoride removal.

Introduction

Consumption of fish and shrimp worldwide is increased over the last decade. As an outcome of these activities a huge production of fish scale is salvaged globally. In India, this waste is discarded as garbage and indiscriminately disposed without recovery of any useful product[1]. About 18–30 million tons of fish wastes is generated at fish processing industry of which 4% are fish scales[2]. Depending on the fish species, the yield of scales from fish is around 4–10%[3]. In last few decades, variety of low-cost adsorbents were derived from different types of waste/by-products of agricultural, municipal and industrial sources which were reported as effective pollutant removal from water and wastewaters[4]. Many conventional methods like membrane filtration, precipitation, ion-exchange, electro-coagulation, reverse osmosis, nanofiltration and adsorption are widely used for defluoridation. These methods so far are either not sustainable or economical for various unfavorable factors.

In past few decades, many biosorbents from various trees and animal sources have been tried as defluoridation agents. leaf powder[5–7], activated rice husk[8,9], barks[10,11], tamarind seeds[12], seed extracts of *Moringa oleifera*[13], tea ash[14,15], egg shell powder[16], treated powdered corn cob[17], chitin, chitosan[18] are few among them. In recent times, adsorbent produced from industrial waste have attracted many researchers for using as relatively less costly, renewable and abundantly available materials. Similarly, many studies have reported biochar as a universal sorbent for the removal of pollutants from soil and water environment. Biochar possesses relatively large specific surface area, high porosity and stable carbon matrix structure which make it a material of choice as an adsorbent[19]. A few studies have shown fish scales are used as effective biosorbent for removal of lead, chromium, arsenic and many such heavy metals. Table 1 shows recent studies made on fish scale as an adsorbent for removal of heavy metals from water environment.

This study is conducted to examine the use of Rohu Fish (Labeo Rohita) scales (FS) waste collected from fish market as a raw material to produce fish scale biochar (FSB) as a novel inexpensive adsorbent for defluoridation of drinking water and industrial wastewater. The primary emphasis of this present investigation was to reduce the high amount environmental burden related to fish waste disposal. This will also result in value addition of usages of waste materials. Few researchers have evaluated the potential of fish scale to remove heavy metals from water environment as listed in Table 1. The existing literature reveals that, no previous study has been done to explore the potential of fish scale biochar (FSB) for fluoride removal from water environment which

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Comparative assessment of commercial activated carbon and fish scale derived activated carbon for adsorptive removal of fluoride from drinking water

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Excessive fluoride concentration above WHO (2011) standard (> 1.5 mg/L) is observed worldwide in groundwater. Considering its serious concern a laboratory based investigation was undertaken to find the fluoride elimination potential by the Commercial Activated Carbon (CAC) and indigenously developed Fish Scale Activated Carbon (FSAC) from water solution. Batch sorption studies were carried out to observe some important process parameters such as adsorbent dose, contact time, pH etc. on removal kinetics. At pH 2, CAC could remove upto 75% of fluoride wheras FSAC could remove up to 92.68% of fluoride at pH 6. The percent removal of fluoride enhanced with the increase in sorbent mass. The equilibration state was found to be achieved within 2 and 3 h for CAC and FSAC respectively. Both CAC and FSAC exhibit reasonably well fluoride uptake capacity for initial fluoride level of 7 and 5 mg/L respectively. The equilibrium data fitted well into Freundlich as well as Langmuir isotherms models. The experimental investigations suggest that both Commercially Available Activated Carbon (CAC) and Fish Scale Derived Activated Carbon (FSAC) can be adopted as adsorbent for defluridation purpose in the treatment of drinking water. Fish scale derived activated carbon (FSAC) showed more fluoride uptake capacity than commercially available activated carbon (CAC).

Keywords: Adsorption, fluoride, commercial and fish scale carbon, removal kinetics.

Introduction

Water is elixir of all forms of life. Presence of undesirable element in excess in water makes the water unfit for consumptive use. Fluoride is one such kind of pollutant of concern. Excessive fluoride concentration above WHO standard (i.e. > 1.5 mg/L) is observed in groundwater throughout the globe. Prolonged consumption of water with excess fluoride (> 1.5 mg/L) is responsible for fluorosis in human beings. Prolonged exposure of fluoride through drinking water is being contributed to a serious health hazard of dental and skeletal fluorosis. The fluorine-containing rocks are main natural geological sources of elevated fluoride levels in groundwater. Besides this, anthropogenic sources like discharges from aluminium smelters, ceramic production units, and coal fired power stations, electroplating processes, fertilizer manufacturing industries, glass manufacturing and processing industries, and semiconductor manufacturing industries are contributing to fluoride contamination of water environment[1]. Numerous endeavours are attempted earlier to establish a sustainable engineering method of fluoride removal under different constraints in developing countries. A surge of conventional engineering methods are used and practiced for defluoridation of water with various physico-chemical unit operation[2]. Membrane filtration techniques are broadly comprised of electro-dialysis, nano-filtration and reverse osmosis[3]. The challenges in adopting most of these methods are their limited fluoride removal capacities, high operational and maintenance cost, post-treatment alterations of water quality, generation of toxic sludge and its disposal into the environment[4].

Among these techniques of defloration, adsorption method is most favoured method due to its ease of operation, greater accessibility to variety of adsorbents, lower cost of treatment. In water purification and industrial wastewater treatment, activated carbons are widely used an important and efficient commercial adsorbents[5]. In recent years, many defluoridation studies have foucused on preparion and use of carbons derived from naturally available materials. The

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Fixed bed column adsorption study for removal of fluoride by Acid modified Fish Scale Biochar.

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Abstract:
Fluoride (F^-) is well known geogenic water contaminant and found in many parts of the world in subsurface water. It is element of concern due to its harmful effects on human health. In the present use of study a waste based biochar i.e. acid modified fish scale biochar was investigated for its potential to remove fluoride from water through a modified fish scale biochar packed continuous column adsorption. The influence of some salient effect of process parameter such as bed height, flow rate and initial F^- ion concentration was investigated through breakthrough curves and the relevant well known breakthrough models were examined. For bed height of 1, 2 and 3 cm the breakthrough time was observed as 283.64, 441 and 673.53 min respectively. The highest breakthrough adsorption capacity (q_b) was found to 1.91 mg/gm at 5mg/L initial fluoride concentration and 1 cm bed height. To further analyze the breakthrough curves, i.e. Bed Depth Service Time (BDST), Thomas and Yoon–Nelson were applied on experimental data. From the experimental data it is evident that the BDST model significantly demonstrates the fixed bed adsorption with high R^2 values as compared to other mathematical models. The breakthrough service time was observed as 283.64, 441 and 673.53 min for bed height 1, 2 and 3cm respectively. The breakthrough curves were also successfully analyzed and described by both Thomas and Yoon–Nelson models.

Keywords: Fluoride removal, Biochar, Fixed bed column, Breakthrough modeling

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A Review of Metal oxide Nanomaterials for Fluoride decontamination from Water Environment

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Abstract

Fluoride pollution in water emerges a challenging problem to environmental researchers especially in regions where people depend on groundwater for drinking. Natural water bodies are experienced Fluoride impurities from geogenic and anthropogenic sources. Fluoride contamination in drinking water sources has been recognized as a major problem in many countries worldwide especially in several parts of India, China, Sri Lanka, South Africa, Tanzania, Argentina, East Africa, part of South Africa, Turkey and some part of South America. Intrusion of Fluoride with drinking water manifests several health effects such as dental caries and teeth mottling besides skeletal fluorosis. Due to clinical manifestations caused by drinking Fluoride contaminated water, the World Health Organization (WHO) has recommended 1.5 mg L-1. Hence, it is very much needed to supply water with safe F^-. Various physico-chemical methods are available for defluoridation of water, out of which adsorption method is common and widely be used .to remove fluoride from water. Till date, activated alumina is most conventional adsorbing material that are conveniently being used for this purpose. However, activated alumina performed well in acidic environment and regeneration issue poses a complex problem. Other traditional adsorbents though are able to uptake Fluoride from water environment the low sorption capacities and efficiencies restricted their wide application. A major breakthrough took place in recent years due to application of nanomaterial in water purification. As compared with traditional materials used, nanostructure based adsorbents exhibited much higher

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Adsorptive Removal of Fluoride from Water Using Non-conventional Adsorbents

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Abstract The rapid industrialization and ever-growing population have led to degradation of water quality and reduction in availability safe drinking water. Presence of priority and secondary pollutants in underground water is posing serious health concerns. Fluoride in drinking water is referred as a two-edge sword for its beneficial (up to 1 mg/L) and detrimental effects (>1.5 mg/L). In the present study, an attempt is made to assess the fluoride removal efficiencies of some waste material as well as the naturally occurring substances. In the present study, fly ash, modified neem bark powder and fish scale biochar were investigated for their feasible use as adsorbent for fluoride removal from water environment. Batch sorption experiments were employed to examine the effect of influencing parameters like adsorbent dose, contact time, pH, initial fluoride concentration and agitation speed, etc. The batch sorption data showed non-conventional adsorbents can be used effectively in fluoride removal and simultaneously also renders to reduce refuse disposal problem of human settlement.

Keywords Adsorption · Non-conventional adsorbent · Fluoride removal · Batch studies

1 Introduction

The presence of fluoride contamination of drinking water source is a serious concern worldwide. Many countries like Sri Lanka, parts of South Africa, China, Turkey

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Fish Scale Waste- a potential sustainable material for water pollution remediation

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ABSTRACT *An enormous quantity of non-edible by-products of fishery waste including fish scales are generated at fish markets and fish-processing industries. At the end of the day this fish waste is generally dumped in-land or hauled into water bodies haphazardly without any commercial recovery and valorization of product. Though some components of fish waste are utilized as animal feed, fish silage, fish-meal and in production of surgical products, biodiesel, biogas, fertilizers, natural pigments, ornaments, cosmetics and in pharmaceutical industries still the main bulk as scale is discarded as waste leading major concern of environmental pollution. A fish yields scales around 4-10 % of its biomass depending on its species, which constitute major part of fishery waste. Non utilization of industrial by-products like fishery waste has great impact on the environmental pollution and economy of the country. In recent years use of waste based adsorbents is gaining lot of attention in water and wastewater treatment. Use fish scales as an adsorbents for removal of dyes, heavy metals and other inorganic pollutants from water and wastewaters is a very recent innovation and a value added sustainable material can be used for waste management. Fish scale based adsorbents have shown excellent adsorbent capacities in removal of heavy metals, industrial dyes and various inorganic pollutants. Researchers have mainly studied effect of influencing process parameters, optimization, equilibrium, kinetics and thermodynamics of adsorption. The present review aims to provide succinct information regarding use of Fish scale as an adsorbent for water remediation, furthermore identifying limitations and future scope of its application. Utilization of fish scale waste for removal of pollutants from water environment can be innovative waste minimization option for Fishery waste management.*

Keywords: *Fish scale, adsorption, pollutants remediation, sustainable waste management*

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