Optimization of fluoride biosorption by using microbial biomass

Abstract

In this study microbial biosorbent was used for fluoride removal from aqueous solutions. Batch and column studies were employed for the biosorbent (dead biomass). The biosorbent used was autoclaved biomass and these biosorbent was used to study the optimum conditions that favours fluoride removal. In batch mode maximum fluoride removal of 95% was observed after 8 hours of treatment under optimum conditions. In this case, pseudo second order kinetics was best fitted than pseudo first order kinetics and Freundlich isotherm model is best in describing the fluoride adsorption. For column study, 67% was the maximum fluoride removal obtained using immobilized biosorbent. For optimizing the conditions for fluoride sorption Response surface methodology (RSM) was used and a maximum fluoride removal of 90% was obtained. To characterize and elucidate the fluoride adsorption Fourier transform infrared spectroscopy (FTIR) and Scanning electron microscopy (SEM) along with Energy dispersive X-ray spectroscopy techniques were used. This work suggests that the biosorbent used could be efficient for fluoride removal in aqueous solution.

Keywords: Fluoride; biosorbent; adsorption; optimization; aqueous solution.

Chapter 1

Introduction

1.1 Fluoride:

Fluoride is widely distributed in nature, and it is the 13th most abundant element on the planet [1]. Fluoride is the most electronegative of other chemical elements. Therefore, it combines with other elements and does not occur in the elemental state [2]. It is the lightest halogen and can exist as a diatomic gas. Fluorine is distributed universally in soils, plants and animals including humans. It is an essential element in humans for the formation of tooth enamel but when it exceeds the permissible limit it is harmful to the humans [3]. Fluorine is considered as one of the significant ground water contaminants and consuming fluorine contaminated water can cause both long-term and short-term effects on human health. So, developing a highly efficient and cost-effective technique for fluorine removal in drinking water is a serious concern in the society and it has an impact on the overall development in growing nations.

1.2 Chemical nature of fluoride:

Fluoride is an element of the halogen group which is placed at VIIA in the periodic table. Fluoride exists as yellow green pungent gas with the atomic number 9 and with the molecular weight of 18.999 g/mol. It is univalent and the stereochemistry of fluorine resembles that of OH because of their similarity in ionic radii [4]. It is the most electronegative element in the periodic table [5] and the inorganic form of fluorine can either exists freely or it is bound to the mineral matrix. The electronic configuration of fluorine is $1s^2\,2s^2\,2p^5$. It needs to gain only one electron in its outer shell to attain the stable electronic configuration. This property of fluorine makes it a highly electronegative species. The high reactivity of fluorine results from its high electronegativity, low dissociation energy and greater

bond strength of the compounds it forms. So, fluorine generally exists in combined form with other elements.

1.3 Fluoride sources:

1.3.1 Natural sources:

Fluoride is naturally found in the earth's crust in the rocks, clay, and coals [6]. Fluoride is incredibly reactive, so it exists as fluoride ions in the minerals such as fluorspar or fluorite, fluorapatite, and cryolite. Fluorite or fluorspar (CaF_2) is usually associated with quartz, calcite, dolomite, or barite [7]. The largest amount of fluoride exists as fluorapatite [$Ca_5(OH, F)(PO_4)_3$] [8]. Besides fluorspar (49%), fluorapatite (4%), and cryolite (54%), several other silicates, such as topaz, oxides, carbonates, sulfates, phosphates, sellaite and sodium fluoride, contains minimum amount of inorganic fluoride [9]. Host minerals, such as mica (layer silicates), amphiboles (chain silicates), apatite, and tourmaline, and clays, such as montmorillonite, kaolinite, and bentonite, also contain inorganic fluoride. A part of the fluorine may be present in clay material and limestone [10].

1.3.2 Anthropogenic sources:

In the developing countries the native fluoride content in the soil is widely affected by the application of fertilizers and from industrial pollutants. The fluorine content in the soil is enriched from different sources and the main sources include coal burning, oil refining, steel production, chemical production, clay production, Aluminum smelting, glass and enamel manufacture, brick and ceramic manufacturing, distribution of fluoride-containing fertilizers and pesticides, wastes from sewage and sludges, production of uranium hexafluoride (UF6), and uranium trifluoride (UF3) from the nuclear industry. Phosphatic fertilizers are the most important sources of fluoride contamination to agricultural lands, and it may elevate the soil fluoride content by 5-10 ppm. The main source of fluorine contamination in water is from the industries and leaching from the minerals [5,9,10].

1.4 Fluorine adsorption in human body:

In human the main route of fluoride adsorption is via the gastrointestinal tract. The fluoride ions are released from the soluble compounds such as sodium fluoride, hydrogen fluoride, fluor silicic acid and sodium monofluorophosphate and are completely absorbed. Fluoride is adsorbed by passive diffusion. Fluoride is released into the blood stream by absorption from both stomach and intestine. It is absorbed in the form weak acid hydrogen fluoride (HF) which employs that the fluoride in the acidic environment of the stomach lumen is readily converted into HF [11]. Once, it is adsorbed into the blood circulation fluorine highly retains in the Ca rich areas like bones and teeth.

1.5 Advantages of fluorine intake:

Studies suggest that the sufficient intake of fluorine can prevent tooth decay and helps in the strengthening of bones. Fluorine protects the tooth decay by remineralization and demineralization [12]. Less than 1.5 ppm has benefits such as

- Prevents dental carries

- Provides resistance to acid attack in teeth

- Rebuilds the weakened tooth enamel

- Slows down the loss of minerals from tooth enamel

- Prevents the growth of harmful oral bacteria

- Supports mineralization of bones

- Improves gum health

1.6 Health impacts of consuming fluorinated water:

The permissible limit of fluorine in drinking water is less than 1.5 ppm which is standardized by the WHO. So, intake of fluorine in excess amounts can cause serious health issues. Dental fluorosis is characterized by the appearance of yellowish stains on the tooth, and this may occur when a developing tooth is exposed to high concentration of fluoride [13]. Skeletal fluorosis results in weakening of bones and malformation of skeleton. The possible ion exchange reactions between hydroxide and fluoride in the calcium hydroxy phosphate. This result in the pain in bones and joints. The bones will become hardened and less elastic increasing the risk of bone fracture [14]. Fluorine exposure can damage the parathyroid gland. This results in hyperparathyroidism which causes increase in secretion of thyroid hormones. It causes depletion of Ca in bones and excess concentration of Ca in blood [15]. It leads to health problems such as fluorosis, neurological damage, thyroid disorder, Alzheimer's disease, infertility as well as liver and kidney damages [16].

1.7 Removal of fluoride in drinking water:

Groundwater contamination by various pollutants is considered as a major threat for the environment and society in the developing countries. Fluoride is highly reactive and one of the pollutants of groundwater contamination [17]. The World Health Organization (WHO) recommended a permissible limit of 1.5 ppm of fluoride in drinking water [18]. More than 20 developed and developing countries has been reported for excessive fluoride concentration such as Mexico, central and western China, South Africa, and India . Excessive fluoride concentration in water is consumed by 200 million people, worldwide. In India more than 15 states have rich fluoride concentration in groundwater [19] and 25 million people are affected by fluoride contamination [20].

Fluoride contamination in water mainly happens through industrial effluents with high fluoride concentration from semiconductors manufacturing, electroplating, glass and ceramic production,

aluminum smelters and coal fired power plants [21]. It is also released into the water naturally by weathering of fluoride containing rocks [22]. So, technologies such as nanofiltration [23], membrane separation [24], electro-coagulation [25], reverse osmosis [26], adsorption [27], ion exchange process [28], Nalgonda technology [29], have been adapted for defluorination of water. However, there are various disadvantages such as high cost, energy consumption and production of secondary contaminants after treatment in these methods [30]. Among these techniques, adsorption has many advantages in water treatment because of its cost effectiveness, regeneration of adsorbents, easy implementation, and maintenance [31]. So, there is a need for development of potential biosorbents because they are naturally abundant, and they have less harmful effects on environment. Biosorbents can be prepared either from plant sources [32] or microbial sources such as bacteria, fungi, algae [33, 34]. So, in this study bacterial isolates from fluorine contaminated region are used as the source for preparation of biosorbents.

The present study focusses on optimizing the process parameters such as biosorbent dosage, initial fluoride concentration, pH, temperature, contact time for effective fluoride removal. Batch and column mode of study was performed for fluoride removal. In addition to that adsorption kinetics and isotherms was constructed for studying the fluoride sorption onto the biosorbents. Finally, characterization using FTIR, SEM along with EDX was performed for further elucidation of fluoride sorption.

Chapter 2

Review of literature

2.1 Conventional methods available for defluoridation:

The conventional methods available for defluoridation are precipitation, membrane separation, ion exchange process and adsorption. In precipitation alum salts and lime were the most used coagulants. One of the most common precipitation techniques is the Nalgonda technique, in which fluoride removal is dependent on the flocculation, sedimentation, and filtration of the fluoride from the aqueous solution. It can treat water in large quantities, and it is cost effective but after treatment there is high sludge formation [37]. Membrane separation involves a semi-permeable membrane which acts as a barrier for separation of contaminants [38]. Reverse osmosis, nanofiltration, dialysis, and electrodialysis are examples of membrane separation. These methods are effective; however, it is costly. Ion exchange process is a technique which utilizes the various cationic and anionic resins for the purification, but resins are expensive and produces high fluoride loaded wastes [39]. Among these techniques adsorption is cost effective, and adsorbents are readily available [40].
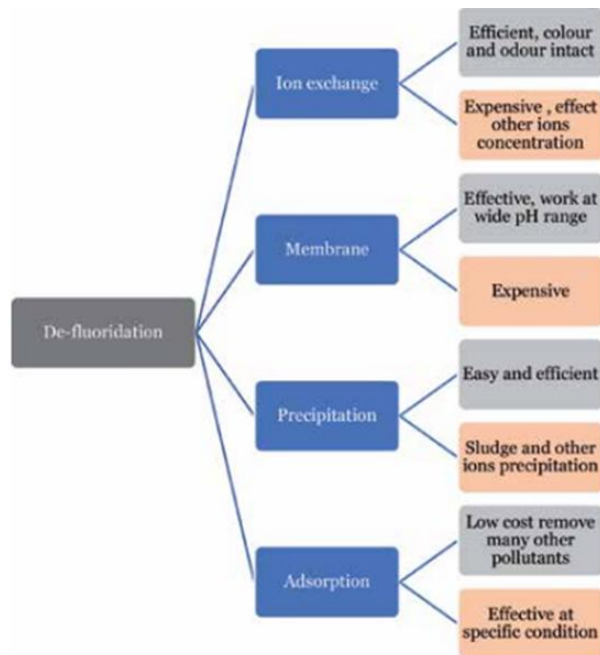
Figure 1: Advantages and disadvantages associated with conventional methods for defluoridation [41]

2.2 Adsorption:

Adsorption is a surface phenomenon which causes the transfer of molecules from the bulk fluid to the solid surface. Compared with other methods adsorption is a cheap method which is reusable. Generally, there are two types of adsorptions which is physical adsorption and chemical adsorption. Physical adsorption is caused by intermolecular forces like van der Waals and the adsorption is weak. Chemical adsorption is caused by the formation of chemical bonds, and it is more stable and firmer than physical adsorption. In adsorption, chemical adsorption and physical adsorption takes place simultaneously [42].

2.2.1 Biosorption:

Biosorption process is known as an attractive biotechnological process which employs naturally abundant or waste biomass for removing contaminants from aqueous solutions [43]. The biosorption

is a bioremediation emerging tool for wastewater treatment that has gained attention in the scientific community over the past three decades.

Biosorption is the property of certain biomaterials to bind and concentrate selected ions or other molecules from aqueous solutions on its surface. Both live and dead biomass can be used for biosorption.

2.2.2 Advantages of using biosorption in water treatment:

The overall incentives of biosorption for wastewater treatment [44] are:

- Low cost of biosorbents.

- Great selectivity and efficiency for metal removal at low concentration.

- Potential for biosorbent regeneration

- High velocity of sorption and desorption

- Limited generation of secondary residues

- More environment friendly life cycle of the material.

So far, an industrially relevant method for removal of toxic metals has not been achieved yet. Biosorbents with different degrees of metal adsorption capacities, availability, and selectivity have been shown to be promising for water treatment.

2.3 Fluoride removal by various adsorbents:

2.3.1 Activated carbon:

Activated charcoal has a good adsorption property because of its high porosity, surface area and catalytic activity. However activated charcoal has a low affinity and adsorption capacity for inorganic pollutants like Fluoride. So, to overcome this problem the activated charcoal which was modified with different chemical species used. Vences-Alvarez et al. [45] used granular activated carbon (GAC)

anchored with lanthanum oxyhydroxides to remove fluoride from solution. The adsorption capacity of GAC-La was 5 times higher than commercially available activated carbon. The adsorption process followed Langmuir isotherm and pseudo second order kinetics with an adsorption capacity of 9.98 mg/g. In addition to that, a removal efficiency of 92.6 % was obtained in the first hour. Roy et al. [46] used calcium-impregnated activated charcoal for fluoride removal and a removal efficiency of 99.68 % was obtained with a contact time of 40 min. The adsorption process followed Langmuir isotherm and best fitted with pseudo second order kinetics with adsorption capacity of 46.32 mg/g.

2.3.2 Biochar and bone char:

Biochar is a carbon rich material which is produced by the pyrolysis of biomass with the absence of oxygen. Biochar for fluoride removal is a widely used method because of its availability, low cost, and easy production. Li et al. [47] used polypyrrole-grafted peanut shell biological carbon for fluoride removal and a fluoride removal efficiency of 91.2 % was obtained. The maximum adsorption capacity of 17.15 mg/g was obtained and best fitted with Langmuir isotherm and pseudo second order kinetics. Wang et al. [48] studied fluoride removal by lanthanum-loaded pomelo peel biochar (PPBC-La). After 9 h of treatment 82% of fluoride removal was obtained. The adsorption was well described by pseudo second order kinetics and Freundlich isotherm models.

2.3.3 Chitosan and modified chitosan:

Chitosan, poly-β (1-4)-2-amino-2-deoxy-D-glucopyranose is a polysaccharide of chitin poly-β (1-4)-2-acetamide-2-deoxy-D-glucopyranose obtained by N-deacetylation. Zhang et al. [49] used Fe-impregnated chitosan (Fe-CTS) granular adsorbent for the adsorption of fluoride from aqueous solutions with an adsorption capacity of 1.97 mg/g at an initial fluoride concentration of 10 mg/L. Prabhu and Meenakshi [50] prepared polyamidoamine grafted chitosan beads (PAAGCB) and protonated PAAGCB (H+ -PAAGCB). Different metal ions, including Al^{3+}, Ce^{3+}, La^{3+} and Zr^{3+} were

loaded on PAAGCB. Compared with other metal ions, Zr-PAAGCB showed maximum defluoridation capacity of 17.47 mg/g.

2.3.4 Polymers:

Surface properties of polymers are modified to improve the adsorption affinity of fluoride because of its changeable surface properties, high surface activity, relatively low cost, and useful properties for adsorbent synthesis. Valdez-Alegria et al. [51] synthesized four biopolymers based on chitosan-polyvinyl alcohol (Ch-PVA) cross-linked with, ethylene glycol diglycidyl ether (EGDE) for fluoride removal from water. From the results obtained, Ch-PVA-NaOH-TPP performed best in defluoridation. The adsorption equilibrium data followed Freundlich adsorption isotherm, showing a maximum fluoride adsorption capacity of 12.64 mg/g.

2.3.5 Metal organic frameworks:

Metal Organic Frameworks (MOFs) are a coordination network with organic ligands containing potential voids [52]. It exhibits excellent adsorption properties because of the alignment of organic ligands and metal ions or clusters in MOFs which can form different framework pore structures [53]. MOFs materials are porous and have large specific surface area with structural and functional diversity. In recent years, MOFs are used to absorb excessive fluoride ions. Karmakar et al. [54] synthesized Aluminium fumarate (AlFu) MOFs under hydrothermal conditions and it was found to be micro-porous with surface area of 1156 m2 /g and average pore size of 17 Å. The adsorption capacity was around 100% in the pH range 2-7 and it decreased slightly after pH 8. Experimental data was best fitted with Freundlich isotherm at all the temperatures and a maximum adsorption capacity of 600 mg/g at 293 K was obtained.

2.3.6 Layered double hydroxides:

Layered double hydroxides (LDHs) are supramolecular materials which has a positively charged main laminates and interlayer anions through the interaction of non-covalent bonds. LDHs enable interlayer anions to exchange with various anions and have been widely used to remove anions from polluted water. including fluoride. Huang et al. [55] synthesized three-dimensional layered flower-like Mg-Al LDHs by a solvothermal. When applied to remove fluoride ion from polluted water, Mg-Al LDHs showed maximum adsorption capacity of 28.60 mg/g.

2.3.7 Clay:

Defluoridation by adsorption onto cost-effective natural materials like clay was the most utilized method. Ben Amor et al. [56] used raw Tunisian clays in the defluoridation of natural water. The percentage of fluoride removal was 73% for kaolinite and 46% for smectite was obtained. Mobarak et al. [57] used modified natural clay which is modified with decyltrimethylammonium bromide and a combination of hydrogen peroxide with decyltrimethylammonium bromide. The experimental data were fitted well with Langmuir model and pseudo-second-order model with a maximum adsorption capacity of 53.66 mg/g.

2.3.8 Biosorbents:

Biosorbents are materials of natural origin like agricultural wastes and microbial biomasses such as algal, bacterial, fungi and yeast. The advantage of using biosorbents is that it is readily available, cost effective and no harmful effects on ecosystem. These biosorbents are effective in treating water because of the availability of surface functional groups like carboxyl, hydroxyl, sulfuryl groups etc. on their surfaces. Various chemical and physical treatment like acid and alkali treatment, carbonization, pyrolysis, or grounding is performed to increase its adsorptive capacity [58,59]. The adsorptive capacities and characteristics of various biosorbents are given in the Table 1 below.

Table1: Adsorptive capacities and characteristics of various biosorbents in fluoride removal

S.No	Biosorbent	Adsorption capacity (mg/g)	Isotherm	Kinetic	References
1	Activated rice husk ash	0.402	Langmuir	Pseudo 2nd order	Mondal et al., 2012 [60]
2	Magnetic corn stover biochar	6.42	Redlich-Peterson	Pseudo 1st order	Mohan et al., 2014 [61]
3	Zr-impregnated coconut shell carbon	7.51	Langmuir	Pseudo 2nd order	Sathish et al., 2007 [62]
4	Ragi seed powder	7.8	Freundlich	Pseudo 2nd order	Gandhi et al., 2012 [63]
5	Activated carbon of *Cynodon dactylon*	4.702	Redlich-Peterson & Langmuir	Pseudo 2nd order	Alagumuth u et al., 2011 [64]
6	Pineapple (Ananas comosus) peel powder	1.753	Temkin	Pseudo 2nd order	Gandhi et al., 2016 [65]
7	Orange (Citrus	2.722	Temkin	Elovich	Gandhi et al., 2016 [65]

	sinensis) peel powder				
8	Mangrove plant leaf powder	2.183	Langmuir, Freundlich & Temkin	Pseudo 1st order	Patil et al., 2013 [66]
9	*Spirogyra* sp. IO1	1.27	Langmuir	Pseudo 2nd order	Mohan et al., 2007 [67]
10	Ca^{2+}-treated live *Nostoc* sp. (BTA 394)	4.72	Langmuir	Pseudo 2nd order	Mukherjee et al., 2017 [68]
11	*Pleurotus ostreatus* 1804	1.272	Langmuir	Intra-particle diffusion	Ramanaiah et al., 2007 [69]
12	Acid treated banana peel	1.340	Langmuir	Pseudo 2nd order	Mohamma d and Majumder, 2014 [70]
13	Natural apple pulp	1.38	Langmuir	Pseudo 2nd order	Zarrabi et al., 2014 [71]
14	*Citrus documana* peel	0.391	Elovich & Pore diffusion	Pseudo 2nd order	Chakrapani et al., 2010 [72]
15	Pyrolysed *Cocos*	18.5	Freundlich	-	Ajisha and Rajagopal, 2014 [73]

	nucifera midribs				

Chapter 3

Materials and methods

3.1 Bacterial culture:

The isolates were obtained from Microbiology laboratory, Department of Biotechnology, Mepco Schlenk Engineering College, Tamil Nadu, India. These strains were grown in NB broth and stored in -80°C. Overnight cultures were prepared from the stock cultures. The biomasses obtained from the overnight cultures (NB broth) were used in the preparation of biosorbents.

3.2 Fluoride measurement in aqueous solution:

(Modified protocol of spectrometric determination of the fluoride)

The fluoride was measured by using zirconium-alizarin reagent method. About 0.03 g of Zirconium oxychloride and 0.035 g of alizarin red was dissolved in 25 ml of double distilled water to which 2 ml of concentrated H_2SO_4 and 6 ml of concentrated HCl was added. It was then diluted to 50 ml by double distilled water. The fluoride solutions were prepared in the range of 2 to 10 ppm standard fluoride stock solution. From the five various concentrations of the standard fluoride stock solution, 5ml of sample was taken and 0.5 ml of prepared reagent was added and incubated in dark for about 5 minutes and absorbance was measured at 525 nm using spectrophotometer. A graph of fluoride concentration versus absorbance was plotted and used for the determination of concentration of fluoride in the aqueous solution [74].

3.3 Preparation of biosorbents:

Overnight cultures (NB broth) of the bacterial isolates were prepared, and it was used as the inoculum for producing high amount of biomass. After 24 hours of incubation at 37°C, the cultures

were centrifuged at 10,000 rpm for 10 minutes. Then their pellet was collected and dried in the hot air oven for 12 hours. These dried biomasses were autoclaved at 15 lbs. for 20 minutes and used in the selection of efficient biosorbent for fluoride removal.

3.4 Selection of isolate for biosorbent:

From the isolated cultures, one efficient isolate was chosen based on the % removal of fluoride by the biosorbent. From the prepared biosorbents 5 mg of each were taken and kept for adsorption in separate flasks containing 5 ppm of NaF solution, which was allowed to agitate in shaker at 160 rpm for about 24 hours. The solutions were centrifuged at 10,000 rpm for 10 minutes, and the supernatants were taken as sample. To 5 ml of samples, 0.5 ml of prepared reagent was added and incubated for 5 minutes in dark. Then, their absorbance was measured at 525 nm and % removal of fluoride was calculated. The bar graph for % removal of fluoride was shown in the Fig.2 and isolate 1 showed highest % removal of fluoride, so it was chosen as the biosorbent for further experiments.
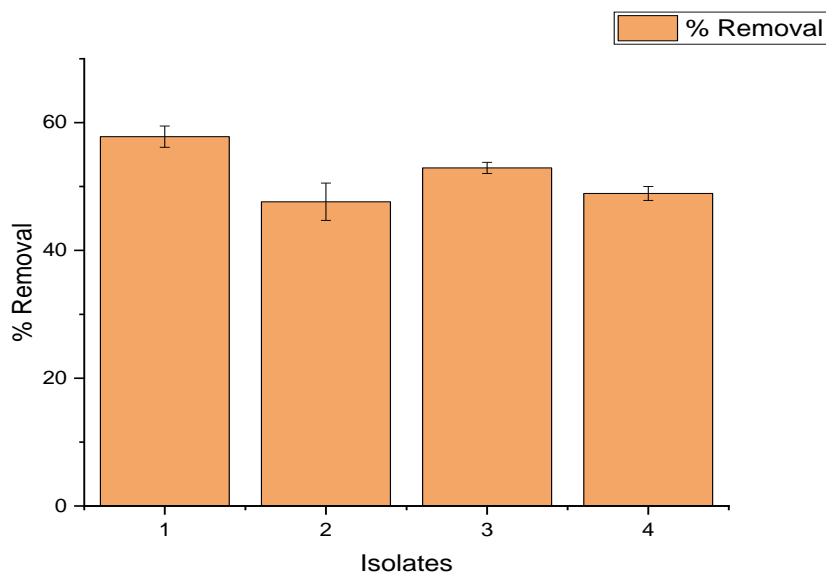
Figure 2: Percentage removal of fluoride by isolates for isolate selection

3.5 Preparation of immobilized biosorbents:

2% (W/V) Sodium Alginate solution was prepared for 100ml. Then the alginate solution was mixed with 0.5% (W/V) of biosorbent and kept undisturbed for 12 hours. Then the beads were formed by dripping the solution with syringe from a height of 20cm approximately into 200ml of 0.2 M $CaCl_2$ solution [75]. Then the beads prepared were stored for further experiments.

3.6 Batch mode of adsorption using biosorbents:

The adsorption studies for batch mode were carried out in 100 mL conical flasks containing 50 ml of NaF solution with different initial fluoride concentration of 0.5,2.5,5,7.5 mg/L. The reaction mixture was kept in shaker for agitation at 160 rpm with other conditions constant (biosorbent dosage:100 mg/L; temperature:37°C; pH:7; contact time:8 hours) and The influence of biosorbent dosage on fluoride removal was studied for 200, 400, 600, 800, 1000 mg/L doses by keeping other parameters constants (initial fluoride concentration:5 ppm; temperature: 37°C; pH:7; contact time: 8 hours). The influence of contact time on fluoride removal was observed by collecting samples at 1 hour interval from the reaction mixture (biosorbent dosage:100mg/L; initial fluoride concentration:5 mg/L; pH:7; temperature 37°C). Adsorption kinetics was done for biosorbent dosage of 100mg/L with initial fluoride concentration 5 mg/L, pH 7 and temperature 37°C. Adsorption isotherm was also constructed for understanding the adsorption of fluoride to biosorbent (biosorbent dosage:100 mg/L; temperature:37°C; pH:7; contact time:8 hours). The influence of pH on fluoride removal was also studied by varying the pH between the range of pH 2-9 (biosorbent dosage:5 mg/L; initial fluoride concentration: 5 mg/L; temperature: 37°C; contact time: 8 hours). The reaction mixture was maintained at different temperatures (25, 30, 35, 40, 45, 50°C) for studying its influence on fluoride removal (biosorbent dosage:100 mg/L; initial fluoride concentration:5 mg/L; pH:7; contact time: 8 hours). The residual fluoride concentration in the aqueous solution can be estimated by zirconium oxychloride

method using spectrophotometer at 525 nm. The adsorption capacity of fluoride to biosorbent was calculated by the equation given below:

$$q_e = \frac{(C_e - C_0) \text{ x } V}{w} \quad (\text{Eq. 1})$$

where q_e is the fluoride adsorbed at equilibrium (mgg^{-1}), C_e is the fluoride concentration at equilibrium (mgL^{-1}), C_0 is the initial concentration of fluoride in the solution (mgL^{-1}), V is the volume of solution (mL), and w is the weight of the biosorbent (mg). The % removal of fluoride was calculated by the following equation:

$$\% \text{ Removal} = \frac{(C_0 - C_f)}{C_0} \text{ x } 100 \quad (\text{Eq. 2})$$

where C_0 is the initial concentration of fluoride in the solution (mgL^{-1}) and C_f is the final concentration of fluoride (mgL^{-1}).

3.7 Column study for fluoride removal using biosorbent:

Packed bed column was used in the column study for fluoride removal using immobilized biosorbent. Immobilized beads were loaded in the column and 5 mg/L of fluoride solution with pH 7 and temperature 37°C was topped up to the column at the flow rate 100ml/hour [75]. The outlets were collected at the end of every hour and the residual fluoride concentration in the aqueous solution can be estimated by zirconium oxychloride method using spectrophotometer at 525 nm. Fluoride removal was calculated from the formula given above.

3.8 Characterization of fluoride adsorbed biosorbent with FTIR, SEM and EDX:

The adsorption of biosorbent was analysed using FTIR to study the functional groups at their surface. The FTIR spectrum allows us to classify the groups that are present in the biosorbent which are

responsible for binding fluoride from the solution onto biosorbent. The morphology and porosity of biosorbent before and after adsorption can be analysed using Scanning electron microscopy. The surface images of biosorbent were produced by scanning it with a focused beam of electrons (25kV,100X magnification). The signals produced contains information about the surface topography and composition of biosorbent. Energy Dispersive X-ray Spectrometry was used for elemental analysis of the biosorbents before and after fluoride adsorption. This was done to confirm the fluoride adsorption [76].

3.9 Design of experiments using Response surface methodology:

Response surface methodology (RSM) composes of various mathematical and statistical techniques, which is used for analysing the effects of several independent variables [77]. It uses quantitative data obtained from the designed experiments to get the optimum operating conditions [78,79]. The response model can be expressed the following equation [80]:

$$Y = f(X_1, X_2, X_3, \dots \dots X_n) \pm e \quad (\text{Eq. 3})$$

where Y is the response, f is the response function, X_i are the independent variables and e is the experimental error. RSM approximates f by a suitable polynomial for independent process variables. The quadratic model for RSM may be expressed as the following equation [81]:

$$Y = \beta_0 + \sum_{i=1}^{n} \beta_i X_i + \sum_{i=1}^{n} \beta_{ii} X_i^2 + \sum_{i=1}^{n} \sum_{j=1}^{n} \beta_{ij} X_i X_j + e \quad (\text{Eq. 4})$$

where Y is the predicted response, β_0 is the constant coefficient, β_i is the linear coefficient, β_{ii} is the quadratic coefficients, X_i and X_j are the values of independent process variables and e is the residual error.

The experimental design and statistical significance were done using Design expert trial 13 software. Central composite design was used to investigate the response function for four independent variables.

The independent variables were initial fluoride concentration (A; X_1), biosorbent dosage (B; X_2), pH (C; X_3), temperature (D; X_4) and the response was % removal of fluoride.

Chapter 4

Results and discussion

3 Effect of initial concentration of fluoride on fluoride removal:

Adsorption for various initial fluoride concentration (0.5, 2.5, 5, 7.5 ppm) was studied after 8 hours of treatment with the biosorbent. From Fig.4, maximum fluoride removal was observed at 0.5 mg/L initial fluoride concentration with maximum adsorption of 99.49% of fluoride. This is due to the high availability of adsorption sites for adsorption. Further, there is a decrease in percentage removal as fluoride concentration is increased in the solution. The availability of adsorption sites was limited in a fixed dose of biosorbent as the fluoride concentration was increased. So, subsequently the rate of adsorption was reduced [82]. There was an increase in adsorption capacity with an increase in fluoride concentration. Maximum adsorption capacity (2.4487 mg/g) was observed at 5 mg/L, and it is taken as the optimum initial concentration for fluoride removal. Similar trend has been reported in previous studies conducted using Neem charcoal [83], wheat straw, sawdust and activated bagasse carbon of sugarcane [84].

Table 2: Adsorption capacity and % removal for effect of initial fluoride concentration

S.No	Initial fluoride concentration (mg/L)	q_e (mg/g)	% Removal
1	0.5	0.49	99.49
2	2.5	1.91	76.67
3	5	2.44	48.97

4	7.5	2.21	29.55
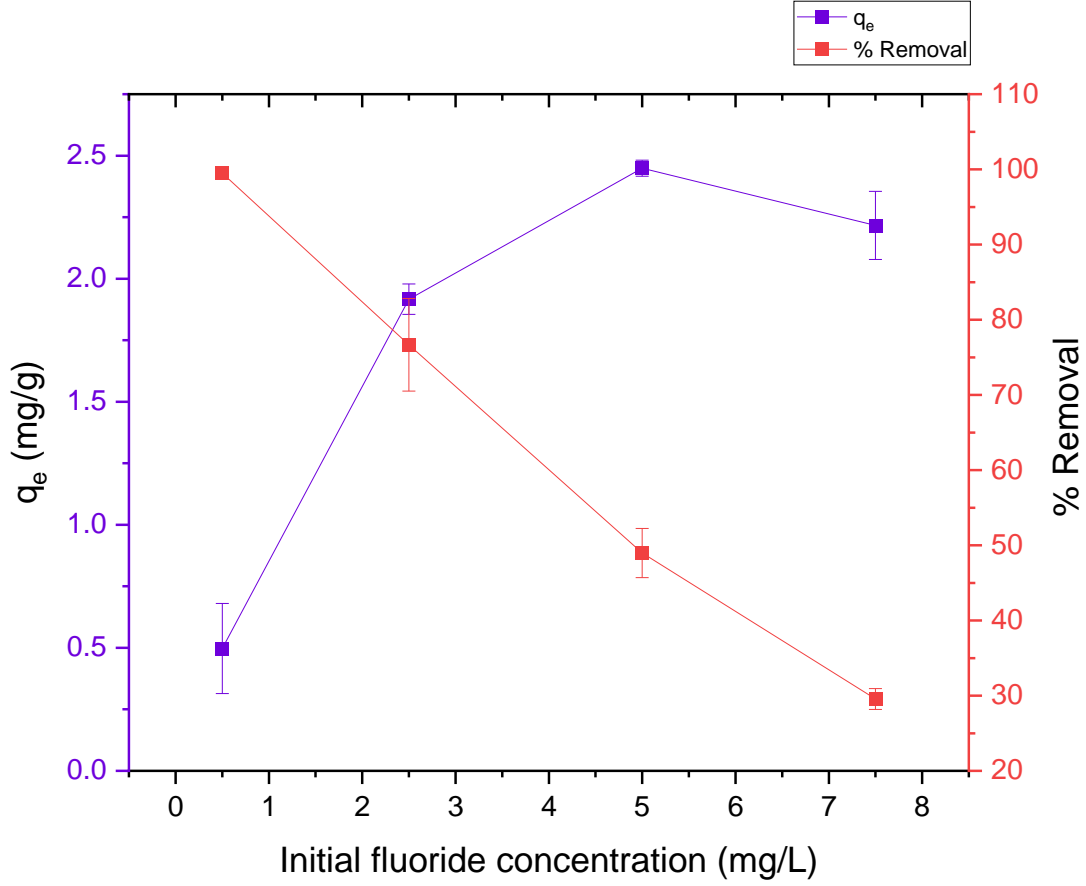
Figure 4: Effect of initial concentration of fluoride on fluoride removal

3.2 Adsorption isotherms:

Langmuir and Freundlich isotherm models were used for describing the adsorption mechanism. Langmuir isotherm model assumes a monolayer adsorption with no lateral interaction of adsorbate molecules on adsorbent surface. The linear form of Langmuir isotherm can be expressed as follows:

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{C_e}{q_m} \quad (\text{Eq. } 5)$$

where C_e is the fluoride concentration at equilibrium (mg L^{-1}), q_e is the fluoride adsorbed at equilibrium (mg g^{-1}), q_m is the maximum adsorption capacity (mg g^{-1}), b is the Langmuir constant (L mg^{-1}). The R^2 (0.7688) obtained explains the unsuitability of Langmuir model for fluoride adsorption in this case. The affinity between the adsorbent and adsorbate can be calculated by a dimensionless factor R_L, which can be determined from the following equation:

$$R_L = \frac{1}{(1 + bC_0)} \quad (Eq. 6)$$

where b is the Langmuir constant (L mg^{-1}) and C_0 is the initial concentration of fluoride in the solution (mg L^{-1}). The R_L value (0.1678) obtained for this reaction is within the range (0< R_L< 1) and this shows adsorption is favorable.

Freundlich isotherm model is applied on a heterogeneous surface and the linear form of Freundlich isotherm model is given as:

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \quad (Eq. 7)$$

where q_e is the fluoride adsorbed at equilibrium (mgg^{-1}), C_e is the fluoride concentration at equilibrium (mgL^{-1}), K_f is the adsorption capacity (Lmg^{-1}) and 1/n is the adsorption intensity (gmg^{-1}). The best was observed in Freundlich with regression coefficient value of 0.9589 and the value of 1/n (0.402; 1/n <0.5) indicated good adsorption [85].

Langmuir and Freundlich isotherm constants for the removal of fluoride from aqueous solution using biosorbent was calculated and shown in the table 3.
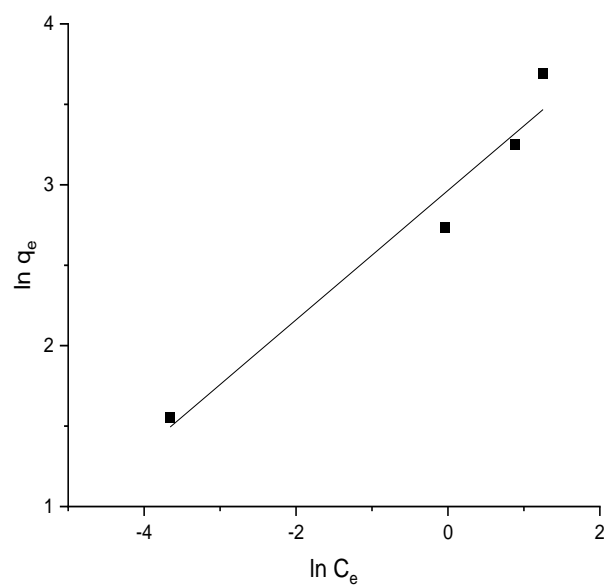
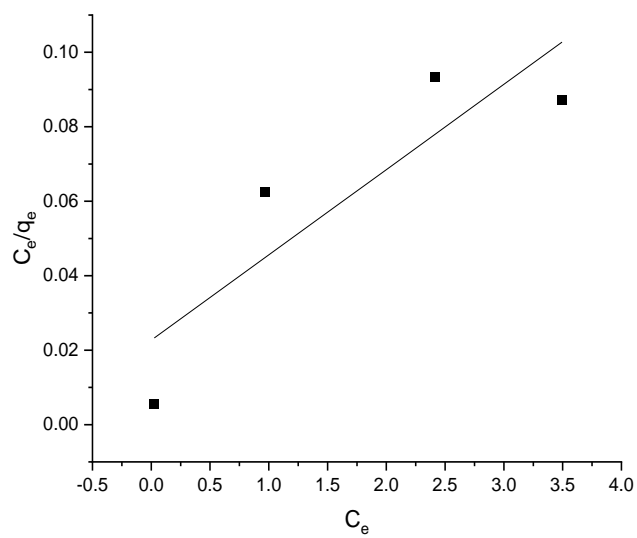**Figure5: Langmuir isotherm model for fluoride biosorption**

Figure 6: Freundlich adsorption isotherm for fluoride biosorption

Table 3: Isothermal model fitting parameters for fluoride adsorption on biosorbent

Langmuir				Freundlich		
b (Lmg^{-1})	q_m (mgg^{-1})	R_L	R^2	K_f (Lmg^{-1})	n (mgg^{-1})	R^2
0.9912	4.405	0.1678	0.7688	1.9392	2.9649	0.9589

3.1 Effect of biosorbent dosage on fluoride removal:

The effect of various dosage of biosorbent (200, 400, 600, 800, 1000 mg/L) on fluoride removal was studied. The defluorination efficiency by the biosorbent dosage of 400 mg/L with adsorption capacity 4.614 (mgg^{-1}), showed highest fluoride removal and further increase in the biosorbent dosage resulted in a decrease in fluoride removal. At higher doses of biosorbent, aggregation of particles happens, and the adsorption sites are not exposed for further adsorption of fluoride [86,85]. In 5 mg/L of fluoride solution at the dosage 400 mg/L of biosorbent there is 90% of the fluoride adsorption after 8 hours of treatment.

Table 4: Adsorption capacity and % removal for effect of biosorbent dosage

S.No	Biosorbent dosage	q_e	% Removal

	(mg/L)	(mg/g)	
1	200	2.40	48.16
2	400	4.61	92.28
3	600	3.50	70.02
4	800	3.39	67.98
5	1000	3.26	65.26
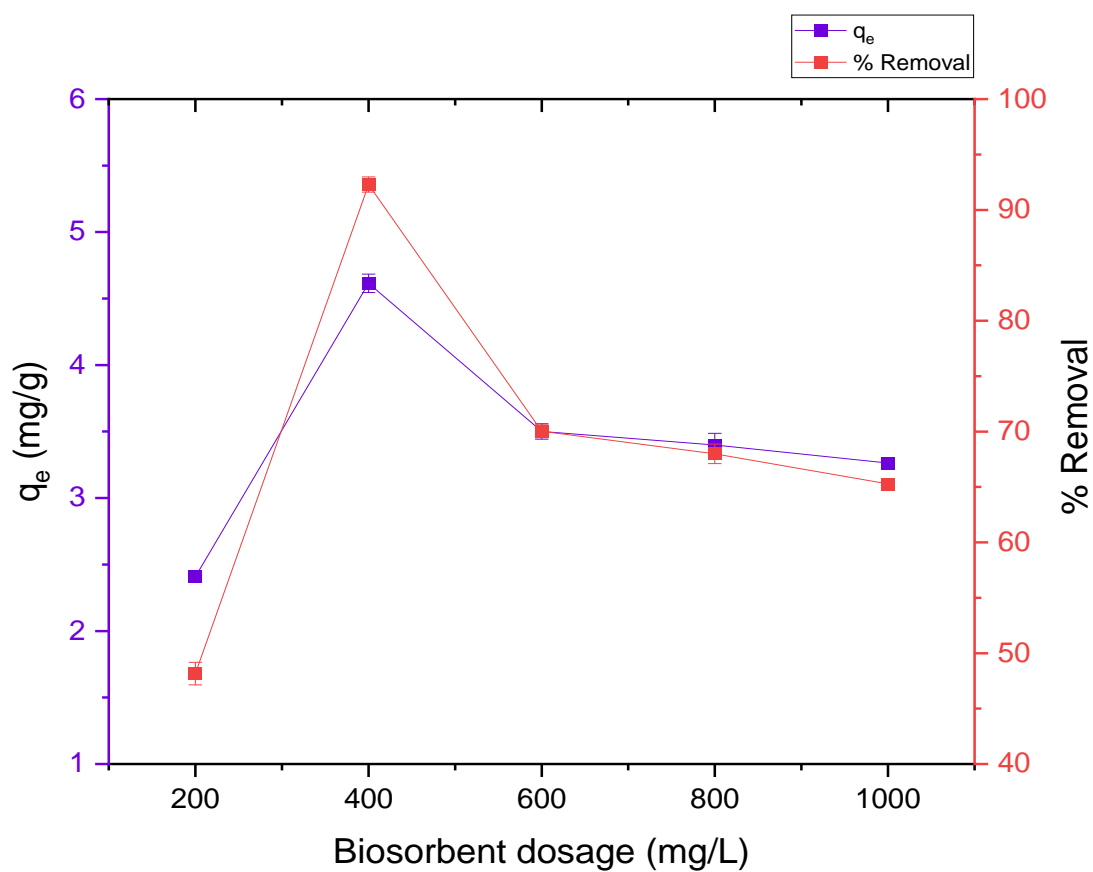
Figure 7: Effect of biosorbent dosage on fluoride removal

3.4 Effect of contact time on fluoride removal:

The effect of contact time on fluoride adsorption by the biosorbent was studied. In this study it was found that the extent of sorption and adsorption capacity increased with increase in time up to 8 hours and a maximum removal of 95% was observed. After this time interval there is no significant increase in the sorption because of the achievement of sorption equilibrium. At first the increase in sorption is due to the availability of adsorption sites on the adsorbent surface and after few hours there is no vacant adsorption sites for fluoride adsorption and therefore the sorption was almost constant.

Table 5: Adsorption capacity and % removal for effect of contact time

S.No	Time h	q_e (mg/g)	% Removal
1	1	2.5	51.35
2	2	3.23	64.76
3	3	3.47	69.53
4	4	3.71	74.32
5	5	3.90	78.15
6	6	4.16	83.35
7	7	4.52	90.45
8	8	4.76	95.23
9	12	4.81	96.28
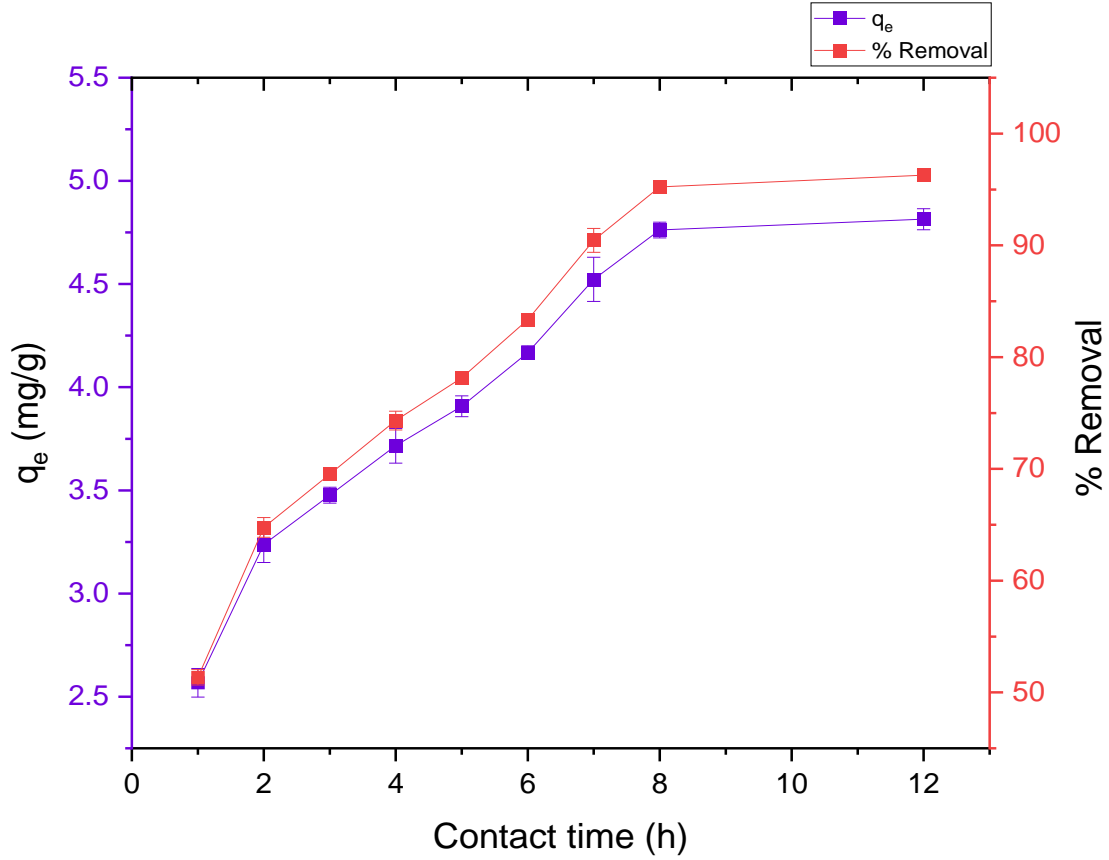
Figure 8: Effect of contact time on fluoride removal

3.4 Sorption kinetics:

Sorption kinetics was used in finding the rate of the reaction which helps in understanding the fluoride adsorption to biosorbent. The pseudo first order and pseudo second order models were used to elucidate the adsorption. The suitability of kinetic models can be determined by the proximity of R^2 value to 1. The equation for pseudo first order kinetics is as follows [88]:

$$\ln(q_e - q_t) = \ln q_e - k_1 \text{ x t} \quad (Eq. 8)$$

where q_e is the fluoride adsorbed at equilibrium (mg g^{-1}), q_t is the fluoride adsorbed at the time t, t is the time required for fluoride removal (hours) and k_1 is the equilibrium rate (min^{-1}). The pseudo second order equation [89] is as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e{}^2} + \left(\frac{1}{q_e}\right) x\, t \quad (Eq.\, 9)$$

where t is the time required for fluoride removal (hours), q_e is the fluoride adsorbed at equilibrium

(mg g^{-1}), q_t is the fluoride adsorbed at the time t and k_2 is the second order kinetic constant (g

mg^{-1}min^{-1}). The regression coefficient obtained for pseudo first order and pseudo second order

kinetic equation is 0.4448 and 0.9825 respectively. From the regression coefficient it was concluded

that pseudo second order equation is more suitable than pseudo first order equation. From the results

obtained it was concluded the adsorption was dominated by chemisorption [90]. Pseudo first and

second order kinetic model parameters was calculated and given in the table 2.
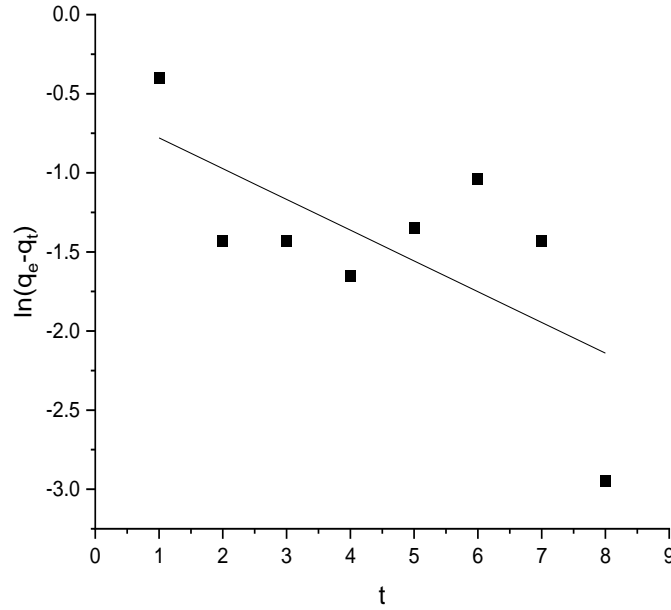
Figure 9: Pseudo first order kinetic model for fluoride biosorption
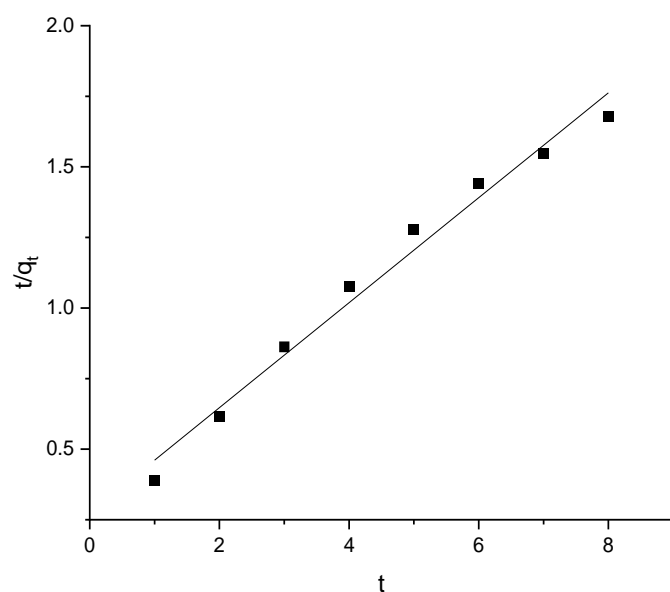
Figure 10: Pseudo second order kinetic model for fluoride biosorption

Table 6: Kinetic model fitting parameters for fluoride adsorption on biosorbent

Pseudo first order kinetic model q_e (mgg^{-1})	k_1 (min^{-1})	R^2	Pseudo second order kinetic model q_e (mgg^{-1})	h $(mgg^{-1}min^{-1})$	k_2 $(gmg^{-1}min^{-1})$	R^2
1.7939	0.1945	0.4448	5.3792	3.6363	0.1256	0.9825

3.5 Effect of pH on fluoride removal:

The pH of an aqueous solution is an important parameter that influence sorption because it can affect the surface charges of biosorbents. The biosorbent was effective in the pH 4 with maximum sorption of 80% and there is a significant decrease in sorption and adsorption capacity above and below the pH 4. At acidic pH, the presence of functional groups such as hydroxyl and carboxyl impart positive charge on the adsorbent surface [91], and fluoride is highly electronegative, and their electrostatic interaction with adsorbent surface favors adsorption [92]. At alkaline pH, there is an increase in hydroxyl ion concentration that interferes in fluoride adsorption [93]. So, there is a decrease in fluoride removal at alkaline pH.

Table 7: Adsorption capacity and % removal for effect of pH

S.No	pH	q_e (mg/g)	% Removal
1	2	2.18	43.76
2	3	3.48	69.76
3	4	4.28	85.67
4	5	3.28	65.79
5	6	3.00	60.13
6	7	2.39	47.80
7	8	3.23	64.68
8	9	2.86	57.35
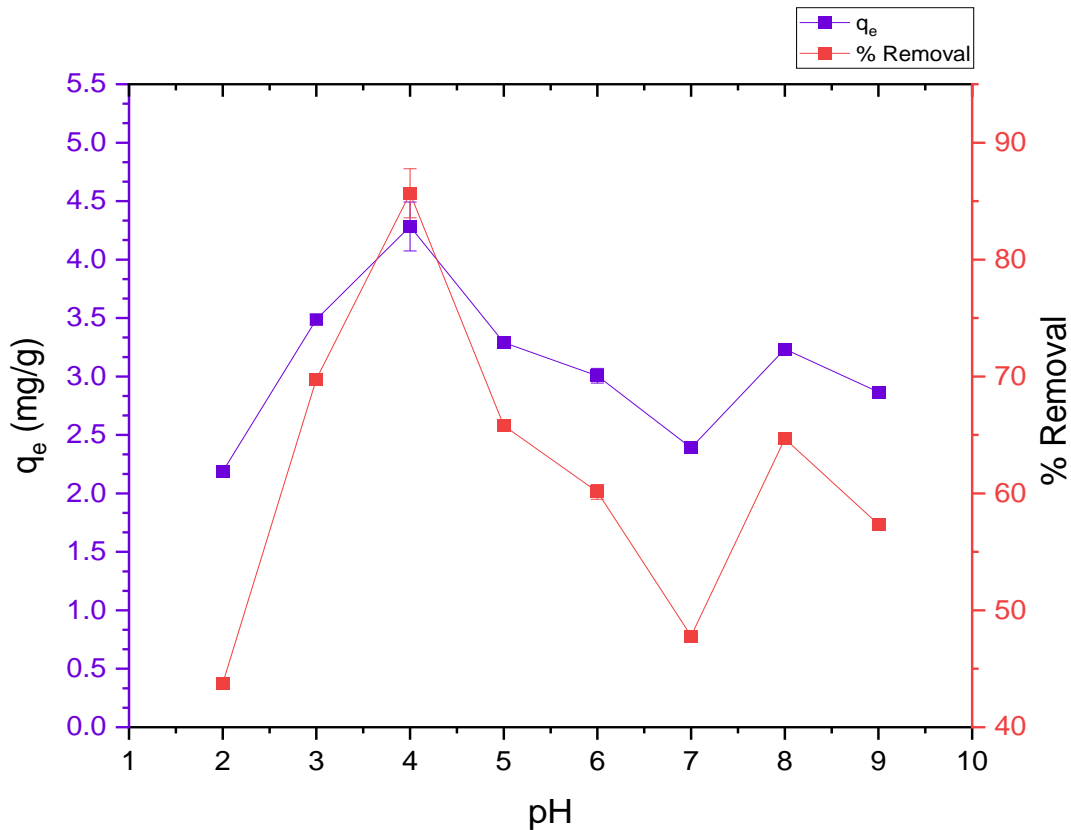
Figure 11: Effect of pH on fluoride removal

3. Effect of temperature on fluoride removal:

The effect of various temperatures (25, 30, 35, 40, 45, 50°C) on fluoride removal was studied. The maximum fluoride removal was observed at 45°C with 93% fluoride removal with maximum adsorption capacity of 4.68 (mgg^{-1}). At first, sorption of fluoride increases with the increase in temperature until it reaches 45°C because in chemisorption increase in temperature favors adsorption and increases adsorption capacity [94], until it reaches an equilibrium point and there is a decrease in sorption after the optimum temperature. Because at higher temperature there is structural modification on the surface of biosorbents. The reaction is endothermic as increasing the temperature results in favorable adsorption [95].

Table 8: Adsorption capacity and % removal for effect of pH

S.No	Temperature °C	q_e (mg/g)	% Removal
1	25	2.31	46.39
2	30	2.78	55.76
3	35	3.97	79.46
4	40	4.17	83.46
5	45	4.68	93.78
6	50	4.15	83.05
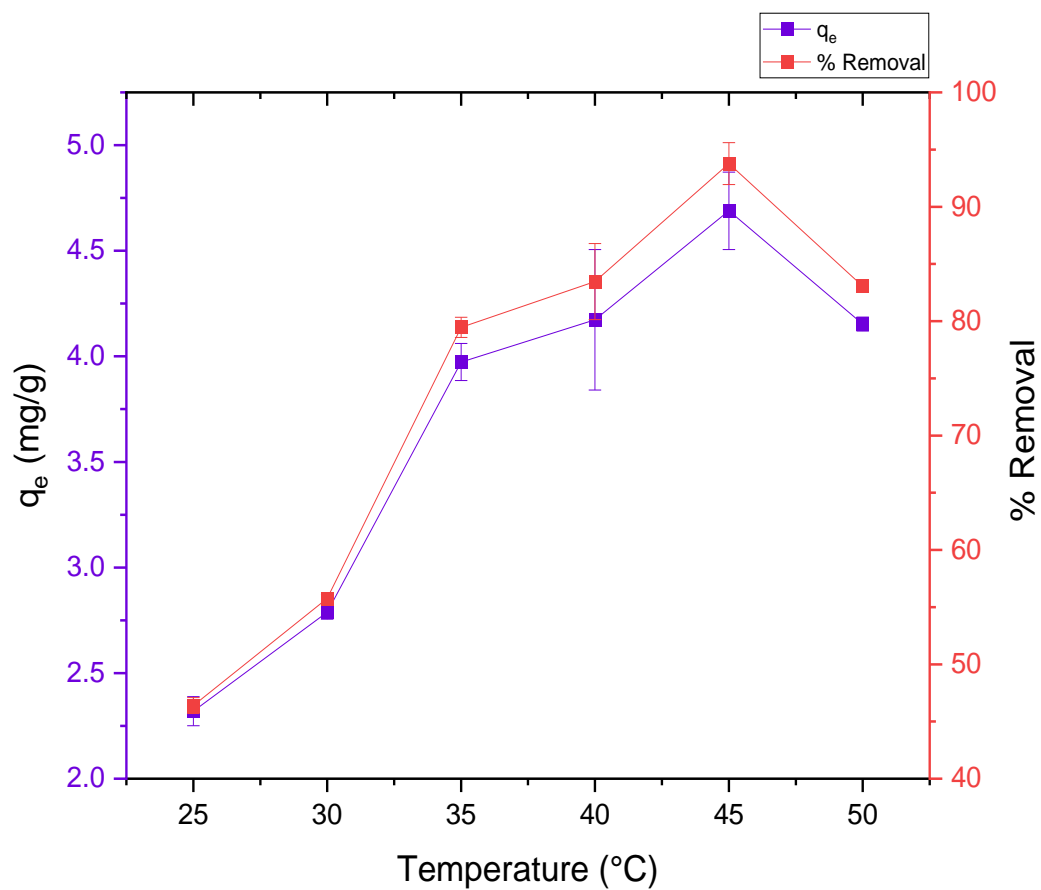
Figure 12: Effect of temperature on fluoride removal

3.7 Optimization of fluoride biosorption using Response surface methodology:

The design consists of 30 sets of experimental conditions and their response was in terms of % removal of fluoride. The percentage of fluoride removal using biosorbent was between the range 45.55 to 96.52%. The design suggested a quadratic polynomial model for the responses which was shown in the Table 9. The model was justified based on the proximity of R^2 value to 1.

The ANOVA results for the responses are given in Table 11. The model F-value of 12.65 implies the model is significant. P-values less than 0.0500 indicate model terms are significant. In this case A, B, C, D, B², C² are significant model terms [96,97]. The plot between the actual and predicted values was displayed in the Fig.13 and the plot for independent variables A, B, C, D were shown in the Fig.14. For optimizing the independent variables for adsorption, a perturbation graph was plotted and shown in the Fig.15. From which it is concluded that initial fluoride concentration 5.5 mg/L, biosorbent dosage 550 mg/L, pH 7, temperature 45°C is optimum for fluoride adsorption.

Table 9: Fit Summary for fluoride biosorption

Source	Sequential p-value	Lack of Fit p-value	Adjusted R²	Predicted R²	
Linear	0.0483	0.0013	0.1978	0.0119	
2FI	0.9875	0.0005	-0.0087	-0.4738	

Quadratic	< 0.0001	0.0865	0.8491	0.5616	Suggested
Cubic	0.0865		0.9345		Aliased

Table 10: Fit Statistics for fluoride biosorption

Std. Dev.	5.34	R²	0.9219
Mean	74.99	Adjusted R²	0.8491
C.V. %	7.12	Predicted R²	0.5616
		Adeq Precision	13.7261

Table 11: ANOVA for Quadratic model for fluoride biosorption

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	5050.65	14	360.76	12.65	< 0.0001	Significant
A-Initial fluoride concentration	569.53	1	569.53	19.98	0.0004	
B-Biosorbent dosage	241.49	1	241.49	8.47	0.0108	
C-pH	610.07	1	610.07	21.40	0.0003	
D-Temperature	144.64	1	144.64	5.07	0.0397	
AB	16.98	1	16.98	0.5958	0.4522	
AC	0.0931	1	0.0931	0.0033	0.9552	
AD	96.31	1	96.31	3.38	0.0860	
BC	14.63	1	14.63	0.5132	0.4848	
BD	36.42	1	36.42	1.28	0.2761	
CD	0.5337	1	0.5337	0.0187	0.8930	

A²	10.49	1	10.49	0.3680	0.5531	
B²	1287.13	1	1287.13	45.15	< 0.0001	
C²	2179.56	1	2179.56	76.45	< 0.0001	
D²	44.51	1	44.51	1.56	0.2306	
Residual	427.63	15	28.51			
Lack of Fit	353.44	9	39.27	3.18	0.0865	not significant
Pure Error	74.20	6	12.37			
Cor Total	5478.29	29				
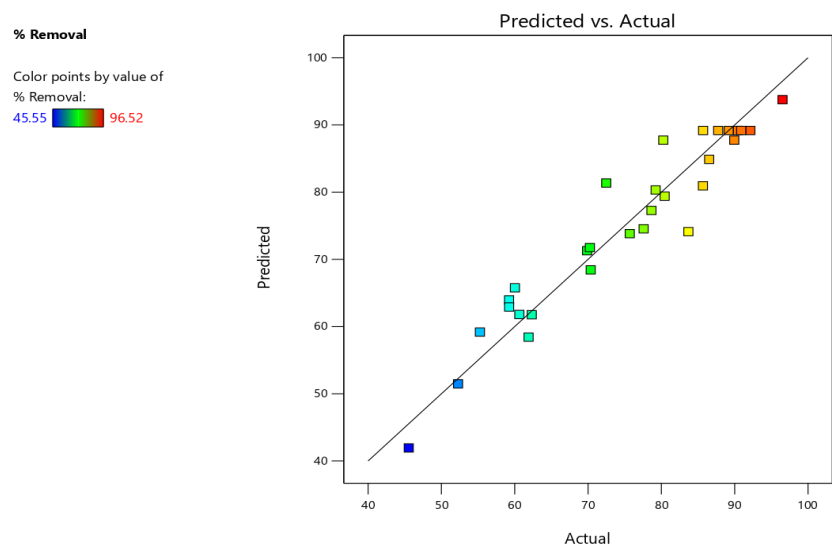
Figure 14: Comparison between the actual values and the predicted values of RSM model for fluoride adsorption onto biosorbent.
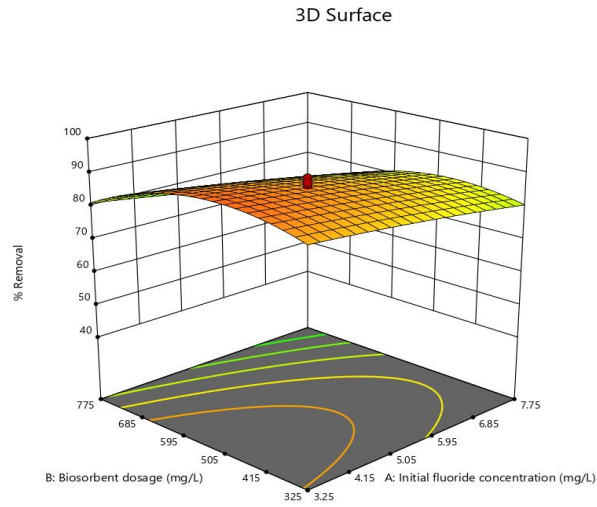
Figure 15a: The effects of experimental parameters A (Initial fluoride concentration) and B (Biosorbent dosage) on the fluoride adsorption onto biosorbent.
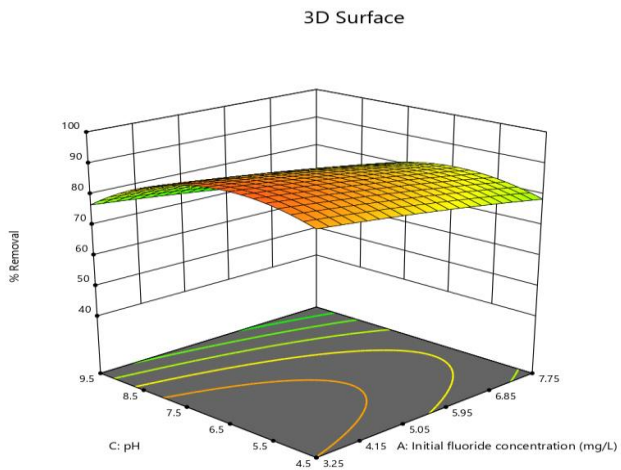
Figure 15b: The effects of experimental parameters A (Initial fluoride concentration) and C (pH) on the fluoride adsorption onto biosorbent.
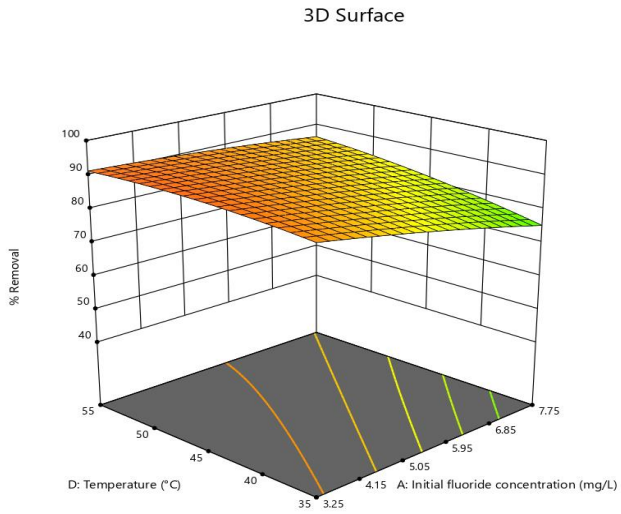
Figure 15c: The effects of experimental parameters A (Initial fluoride concentration) and D (Temperature) on the fluoride adsorption onto biosorbent.

,
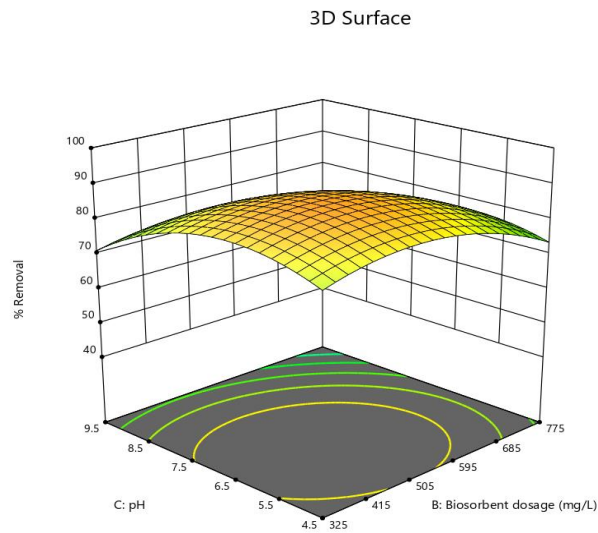
Figure 15d: The effects of experimental parameters B (Biosorbent dosage) and C (pH) on the fluoride adsorption onto biosorbent.
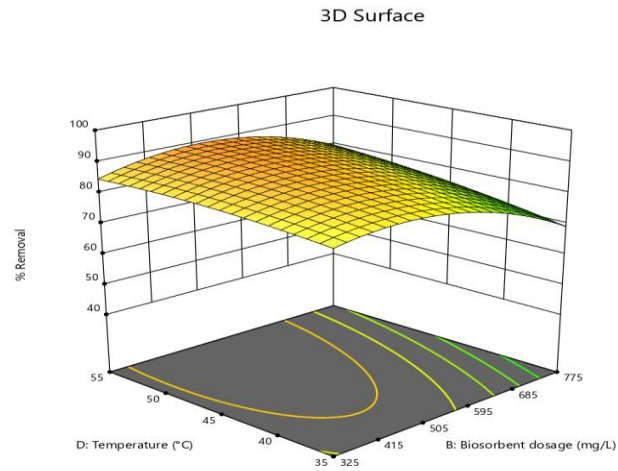
Figure 15e: The effects of experimental parameters B (Biosorbent dosage) and D (Temperature) on the fluoride adsorption onto biosorbent.
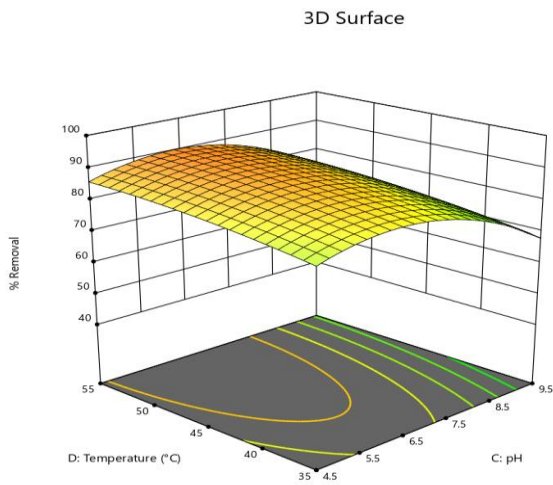
Figure 15f: The effects of experimental parameters C (pH) and D (Temperature) on the fluoride adsorption onto biosorbent.
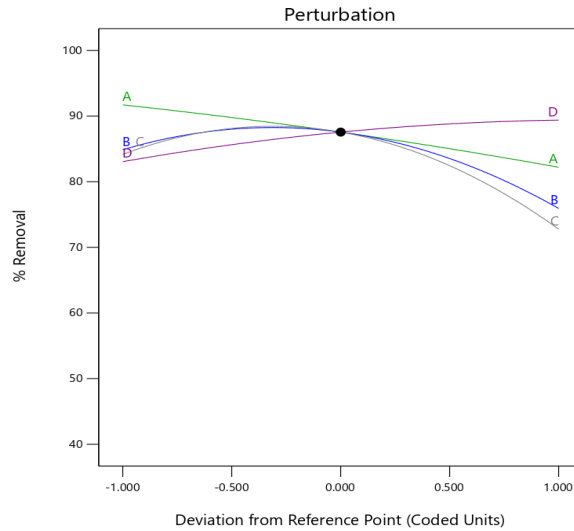
Figure 16: Perturbation plot of fluoride biosorption at optimal condition.

Initial fluoride concentration (A): 5.5 mg/L

Biosorbent dosage (B):550 mg/L

pH (C): 7

Temperature: 45 °C

3.8 Immobilization of biosorbent using packed bed column:

The immobilized biosorbent was packed in the column and aqueous solution with 5 mg/L fluoride concentration was fed into the column. Fluoride removal was observed at the end of each hour. As the time increases fluoride removal was decreased because of the unavailability of adsorption sites for fluoride in the aqueous solution. This may be attributed because of the preoccupied adsorption sites by fluoride. So, when time increases there is no availability of vacant adsorption sites.
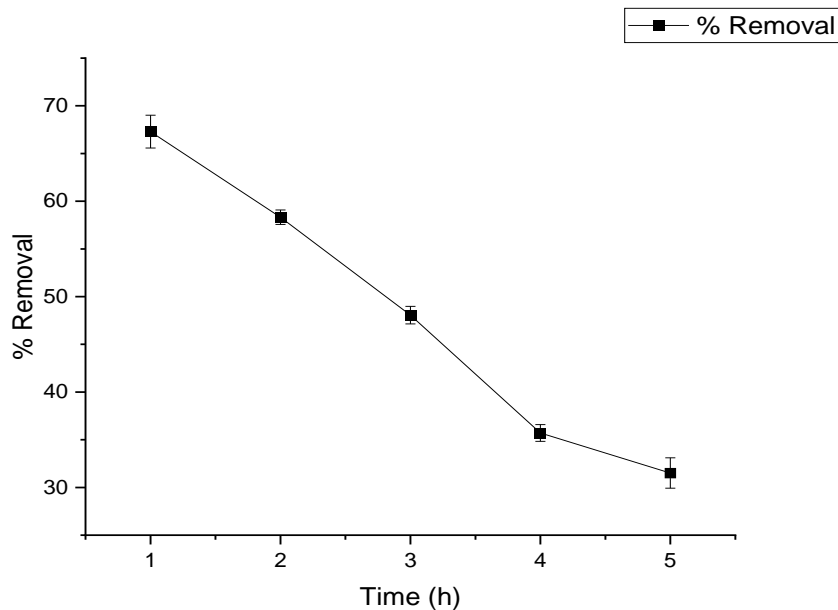
Figure 17: Percentage removal of fluoride using immobilized biosorbent

3.9 Characterization of biosorbent using FTIR, SEM and EDX analysis:

FTIR analysis of biosorbent:

FTIR analysis is used for understanding the functional groups present on the biosorbent surface which plays an important role in fluoride adsorption. The FTIR spectrum of biosorbent before sorption shows distinct peak at 3421.72, 2106.27, 1643.35, 1402.25, 1332.81, 1224.80, 1074.35 and 536.21 cm^{-1}. The band at 3421.72 cm^{-1} represents the presence of O-H stretching vibrations of alcoholic hydroxyl group [98]. The bands at 1643 cm^{-1} and 1402.25 cm^{-1} may be attributed to the asymmetric and asymmetric vibration of carboxyl group respectively [99]. The band at 1074.35 cm^{-1} was due to the C-O-C

vibration. After fluoride sorption there was a shift in the bands from 3421.72, 1643.35, 1402.25, 1224.80, 1074.35 and 536.21 cm^{-1} to 3427.51, 1521.84, 1400.32, 1230.58, 1033.85 and 414.70 cm^{-1}. These shifts in the bands after sorption indicates their involvement in fluoride adsorption. There is an appearance of distinct peak at 1116.78 cm^{-1} after fluoride adsorption because of C-F interactions which confirms the interaction of fluoride with the functional groups of biosorbent [100]. The result obtained implies that the fluoride interacts with functional groups of biosorbent.
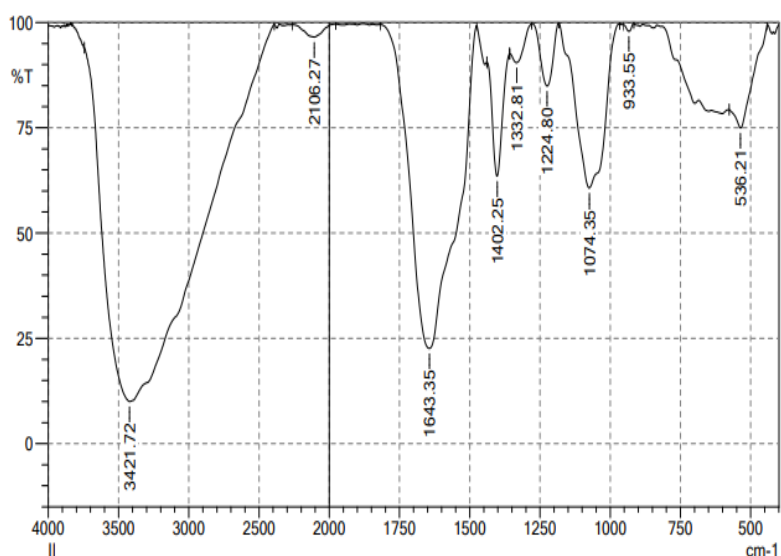

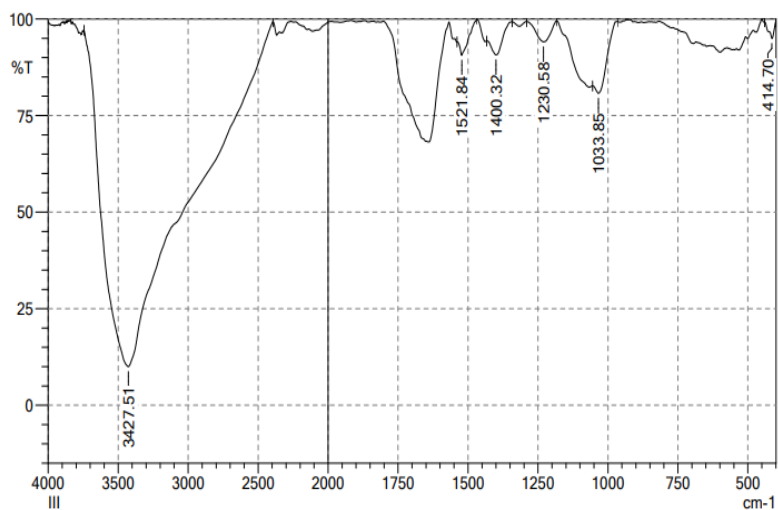**Figure 18a: FTIR spectrum of biosorbent before adsorption**

Figure 18b: FTIR spectrum of biosorbent after adsorption

3.10 SEM and EDX analysis of biosorbents:

The scanning electron micrographs obtained before and after sorption are shown in figure 1 and 2. From the figure 1 before fluoride sorption we can see the microporous structure which is responsible for sorption. But after fluoride sorption there was a structural modification due to deposition of fluoride on the biosorbent. For further confirmation of fluoride sorption EDX analysis was performed. The EDX analysis before and after fluoride sorption shows the fluoride deposition after sorption which can be depicted from the figures 3 and 4. So this study confirms fluoride sorption by the biosorbent [101].
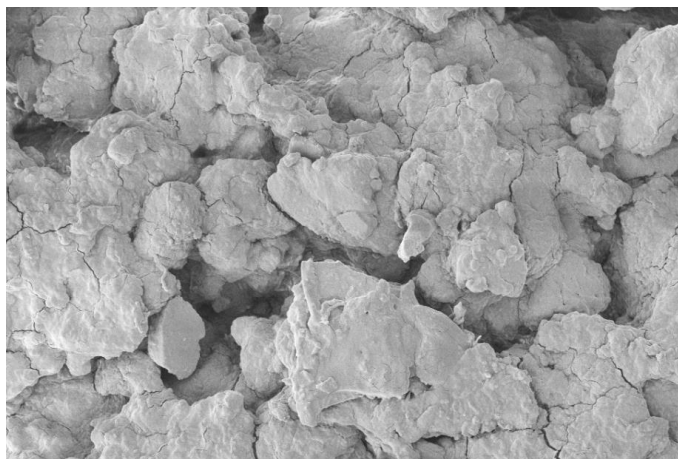
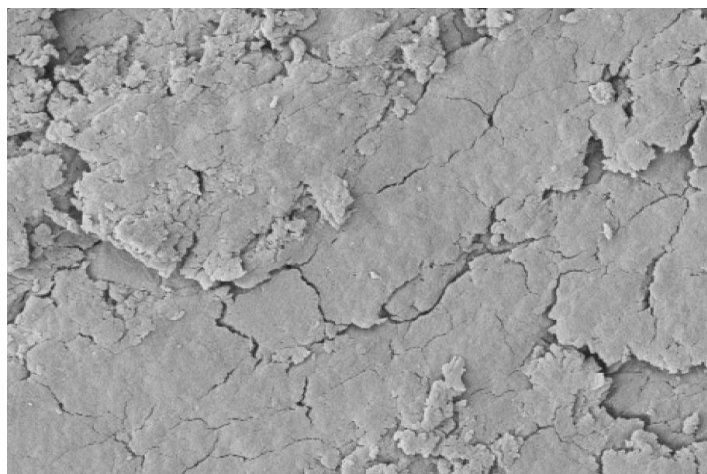

Figure 19a- SEM images biosorbent before adsorption

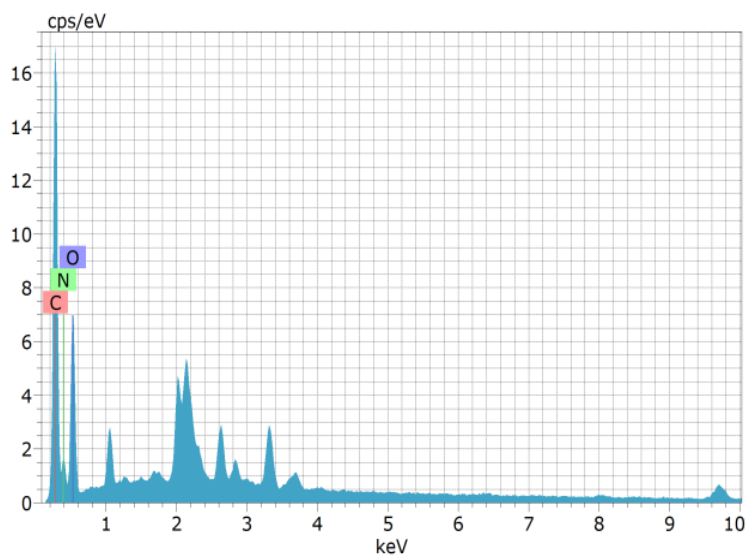**Figure 19b- SEM images biosorbent after adsorption**

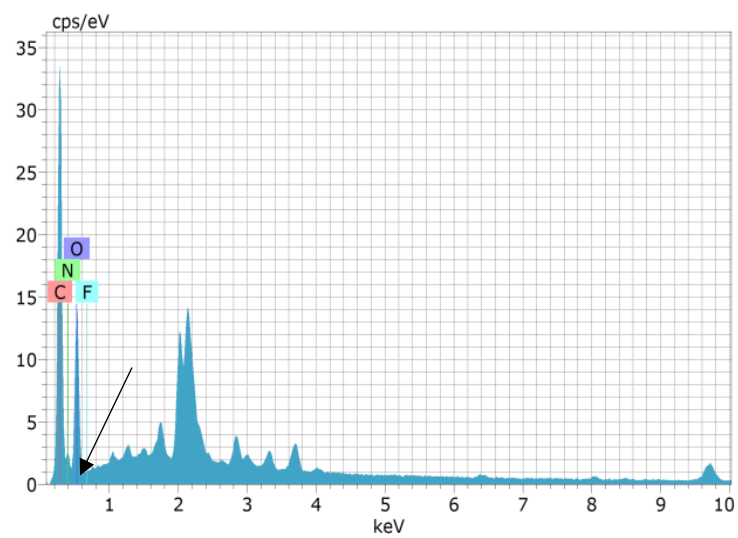**Figure 20a- EDX analysis of biosorbent before fluoride adsorption**

Figure 20a- EDX analysis of biosorbent after fluoride adsorption

Chapter 5

Conclusion

The phenomenon that drives fluoride removal by biosorbent is adsorption. The biosorbent was prepared from isolate1 because of its high fluoride removal compared to other isolates. The process parameters that influence fluoride sorption such as initial fluoride concentration (5 mg/L), biosorbent dosage (400 mg/L), contact time (8 hours), pH (4) and temperature (45°C) were studied and maximum % removal obtained for each parameter is set as optimum. In batch and column studies there is fluoride removal of 95% and 67% respectively. The conditions for fluoride sorption were optimized using Response surface methodology (RSM) and maximum fluoride removal of 90% was obtained for the optimum condition (Factor 1- pH: 7; Factor 2-temperature:45°C, Factor 3-biosorbent dosage: 550 mg/L and Factor 4-initial fluoride concentration:10 mg/L). The biosorbents before and after fluoride sorption was characterized using FTIR, SEM and EDX analysis to elucidate the fluoride sorption onto the biosorbent.

Chapter 6

Reference

[1] Mason B and Moore C (1982), Principles of geochemistry. Wiley, New York, NY, p 350.

[2] Wedephol Handbook of geochemistry, vol 2, Part 4. Springer, New York, NY, 9 (1974) K-1 pp.

[3] WHO (1996), Guidelines for drinking water quality. Recommendations, vol 1. World Health Organisation, Geneva, 188 pp.

[4] O'Donnell (1975), TA Fluorine, Comprehensive inorganic chemistry, vol II. Pergamon Press, Oxford, UK.

[5] Neumuller OA (1981), Rommps Chemie Lexicon, vol. 2, 8th edn, Franck'sche Verlagshandlung, Stuttgart (German).

[6] Kirk-Othmer (1980) Encyclopedia of chemical technology, vol. 10, 3rd edn. Wiley, New York, NY.

[7] Prud'homme M (1990) Fluorspar. In: Canadian mineral yearbook, 1989 energy, mines, and resources. Ottawa, ON.

[8] Fuge R (1988) Sources of halogens in the environment, influences on human and animal health. Environ Geochem Health 10(20):51–61.

[9] Reimann C, Decaritat P (eds) (1998) In: Chemical elements in environment. Fact sheets for the geochemist and environmental scientist. Springer, New York, NY.

[10] Fuge R, Andrews MJ (1988) Fluorine in U.K. environment. Environ Geochem Health 10(3–4): 96–104.

[11] Whitford MG, Pashley DH (1984) Fluoride absorption: the influence of gastric acidity. Calcif Tissue Int 36(1):302–307.

[12] WHO (1997) Guideline for drinking water quality health criteria and other supporting information, vol 2, 2nd edn. World Health Organization, Geneva.

[13] Choubisa SL, Sompura K, Bhatt SK, Choubisa DK, Pandya H, Joshi SC, Choubisa L (1996) Prevalence of fluorosis in some villages of Dungarpur district of Rajasthan. Ind J Environ Health 38:119–126.

[14] S. Kumar, A. Gupta, J.P. Yadav, Removal of fluoride by thermally activated 427 carbon prepared from neem (Azadirachta indica) and kikar (Acacia arabica) 428 leaves, J. Environ. Biol. 29 (2) (2008) 227–232.

[15] S. Kumar, A. Gupta, J.P. Yadav, Removal of fluoride by thermally activated carbon prepared from neem (Azadirachta indica) and kikar (Acacia arabica) 428 leaves, J. Environ. Biol. 29 (2) (2008) 227–232.

[16] E.M. Nigri, A. Bhatnagar, S. D. F. Rocha, Thermal regeneration process of bone char used in the fluoride removal from aqueous solution, J. Clean. Product. 142 (2017) 3558-3570.

[17] J. Hussain, I. Hussain, K.C. Sharma, Fluoride, and health hazards: community perception in a fluorotic area of central Rajasthan (India): An arid environment, Environ. Monit. Assess. 162 (2010) 1-14.

[18] WHO, Fluorine and fluorides, Environmental Health Criteria 36, World Health Organization, Geneva, 1984.

[19] Meenakshi, R. C., Maheshwari, 2006. Fluoride in drinking water and its removal, J.Hazard. Mater. 137, 456-463.

[20] He, J. S., Siah, T. S., Chen, J. P., 2014. Performance of an optimized Zr-based nanoparticle-embedded 480 PSF blend hollow fiber membrane in treatment of fluoride contaminated water,Water Res. 56, 88-97.

[21] S. Gupta, S. Banerjee, R. Saha, J. K. Datta, N. Mondal, Fluoride geochemistry of groundwater in Nalhati-1 block of the Birbhum district, West Bengal, India, Research report Fluoride 39 (2006) 318-320.

[22] Arlappa, N., Qureshi, A., Srinivas, R., 2013. Fluorosis in India: an overview. Int J Res Dev Health, 1(2), pp97-102.

[23] Bhatnagar, A., Kumar, E., Sillanpää, M., 2011. Fluoride removal from water by adsorption-a review. Chem. Eng. J. 171, 811-840.

[24] L. Ma, X. Wanga, J. Tao, X. Feng, X. Liu, W. Qin, Differential fluoride tolerance between sulfur- and ferrous iron-grown Acidithiobacillus ferrooxidans and its mechanism analysis, Biochem. Eng. J. 119 (2017) 59–66.

[25] S.V. Jadhav, K.V. Marathe, V.K. Rathod, A pilot scale concurrent removal of fluoride, arsenic, sulfate, and nitrate byusing nanofiltration: competing ion interaction and modellingapproach, J. Water Process Eng. 13 (2016) 153–167.

[26] P.I. Ndiaye, P. Moulin, L. Dominguez, J.C. Millet, F. Charbit, Removal of fluoride from electronic industrial effluentby RO membrane separation, Desalination 173 (1) (2005) 25–32.

[27] M.A. Sandoval, R. Fuentes, J.L. Nava, I. Rodríguez, Fluoride removal from drinking water by electrocoagulation in a continuous filter press reactor coupled to a flocculator and clarifier, Sep. Purif. Technol. 134 (2014) 163–170.

[28] V. Colla, T.A. Branca, F. Rosito, C. Lucca, B.P. Vivas, V.M. Delmiro, Sustainable reverse osmosis application for wastewater treatment in the steel industry, J. Clean. Prod. 130 (2016) 103–115.

[29] I. Ali, Water treatment by adsorption columns: evaluation at ground level, Sep. Purif. Rev. 43 (3) (2014) 175–205.

[30] J. Markovski, J. Garcia, K.D. Hristovski, P. Westerhoff, Nano-enabling of strong-base ion-exchange media via a room temperature aluminum hydroxide synthesis method to simultaneously remove nitrate and fluoride, Sci. Total Environ. 599–600 (2016) 1848–1855.

[31] P. Tirkey, T. Bhattacharya, S. Chakraborty, Optimization of fluoride removal from aqueous solution using Jamun (Syzygium cumini) leaf ash, Process Saf. Environ. Prot. 115 (2018) 125–138.

[32] F.G. Gentili, J. Fick, Algal cultivation in urban wastewater: an efficient way to reduce pharmaceutical pollutants, J. Appl. Phycol. (2016).

[33] Chen, N., Zhang, Z., Feng, C., Li, M., Zhu, D., Chen, R., Sugiura, N., 2010. An excellent fluoride sorption behavior of ceramic adsorbent, J. Hazard. Mater. 183, 460-465.

[34] S. Singh, B. Kumar Singh, Removal of fluoride from groundwater by carbonised Punica granatum carbon ("CPGC") bio-adsorbent, J. Geosci. Environ. Protec. 3 (2015) 1-9.

[35] N.K. Mondal, A. Samanta, S. Dutta, S. Chattoraj, Optimization of Cr (VI) biosorption onto Aspergillus niger using 3-level Box-Behnken design: Equilibrium, kinetic, thermodynamic and regeneration studies, J. Genet. Eng. Biotechnol. 15 (2017) 151-160.

[36] M.A. Grace, E. Clifford, M.G. Healy, The potential for the use of waste products from a variety of sectors in water treatment processes, J. Clean. Prod. 137 (2016) 788-802.

[37] Barnard WR, Nordstrom DK (1982) Fluoride in precipitation, Methodology with fluoride-selective electrode. Atmospheric Environment, 16:99.

[38] Suneetha, M., Sundar, B.S., Ravindhranath, K., 2015. Studies on defluoridation techniques: a critical review. Int. J. Chem Tech Res. 8, 295–309.

[39] Jadhav, S.V., Bringas, E., Yadav, G.D., Rathod, V.K., Ortiz, I., Marathe, K.V., 2015. Arsenic and fluoride contaminated groundwaters: a review of current technologies for contaminants removal. J. Environ. Manag. 162, 306–325.

[40] Mohapatra, M., Anand, S., Mishra, B.K., Giles, D.E., Singh, P., 2009. Review of fluoride removal from drinking water. J. Environ. Manag. 91, 67–77.

[41] Sutar, S., Otari, S., Jadhav, J., 2022. Biochar based photocatalyst for degradation of organic aqueous waste: A review. Chemosphere 287, 132200.

[42] George Wypych, in Handbook of Adhesion Promoters, 2018.

[43] Zaharia.C, Application of Waste Materials as 'Low Cost' Sorbents for Industrial Effluent Treatment. A Comparative Overview. Int. J. Mater. Prod. Technol. 2015, 50, 196–220.

[44] Torres, E. Biosorption: A Review of the Latest Advances. Processes 2020, 8, 1584.

[45] Vences-Alvarez, E.; Velazquez-Jimenez, L. H.; Chazaro-Ruiz, L. F.; Diaz-Flores, P. E.; Rangel-Mendez, J. R., Fluoride removal in water by a hybrid adsorbent lanthanum carbon. Journal of Colloid and Interface Science 2015, 455, 194-202.

[46] Roy, S.; Das, P.; Sengupta, S.; Manna, S., Calcium impregnated activated charcoal: Optimization and efficiency for the treatment of fluoride containing solution in batch and fixed bed reactor. Process Safety and Environmental Protection 2017, 109, 18-29.

[47] Li, C. L.; Chen, N.; Zhao, Y. A.; Li, R.; Feng, C. P., Polypyrrole-grafted peanut shell biological carbon as a potential sorbent for fluoride removal: Sorption capability and mechanism. Chemosphere 2016, 163, 81-89.

[48] Wang, J. G.; Chen, N.; Feng, C. P.; Li, M., Performance and mechanism of fluoride adsorption from groundwater by lanthanum-modified pomelo peel biochar. Environmental Science and Pollution Research 2018, 25 (16), 15326-15335.

[49] Zhang, J.; Chen, N.; Tang, Z.; Yu, Y.; Hu, Q. L.; Feng, C. P., A study of the mechanism of fluoride adsorption from aqueous solutions onto Fe-impregnated chitosan. Physical Chemistry Chemical Physics 2015, 17 (18), 12041-12050.

[50] Prabhu, S. M.; Meenakshi, S., A dendrimer-like hyper branched chitosan beads toward fluoride adsorption from water. International Journal of Biological Macromolecules 2015, 78, 280-286.

[51] Valdez-Alegria, C. J.; Fuentes-Rivas, R. M.; Garcia-Rivas, J. L.; Arce, R. E. Z.; Nunez, M. D. J.; Garcia-Gaitan, B., Synthesis of Chitosan-Polyvinyl Alcohol Biopolymers to Eliminate Fluorides from Water. Biomolecules 2020, 10 (1), 1-15.

[52] Batten, S. R.; Champness, N. R.; Chen, X.-M.; Garcia-Martinez, J.; Kitagawa, S.; Ohrstrom, L.; O'Keeffe, M.; Suh, M. P.; Reedijk, J., Terminology of metal-organic frameworks and coordination polymers (IUPAC Recommendations 2013). Pure and Applied Chemistry 2013, 85 (8), 1715-1724.

[53] Banerjee, D.; Cairns, A. J.; Liu, J.; Motkuri, R. K.; Nune, S. K.; Fernandez, C. A.; Krishna, R.; Strachan, D. M.; Thallapally, P. K., Potential of Metal-Organic Frameworks for Separation of Xenon and Krypton. Accounts of Chemical Research 2015, 48 (2), 211-219.

[54] Karmakar, S.; Dechnik, J.; Janiak, C.; De, S., Aluminium fumarate metal-organic framework: A super adsorbent for fluoride from water. Journal of Hazardous Materials 2016, 303, 10-20.

[55] Huang, P. P.; Cao, C. Y.; Wei, F.; Sun, Y. B.; Song, W. G., MgAl layered double hydroxides with chloride and carbonate ions as interlayer anions for removal of arsenic and fluoride ions in water. Rsc Advances 2015, 5 (14), 10412-10417.

[56] Ben Amor, T.; Kassem, M.; Hajjaji, W.; Jamoussi, F.; Ben Amor, M.; Hafiane, A., Study of defluoridation of water using natural clay minerals. Clays and Clay Minerals 2018, 66 (6), 493-499.

[57] Mobarak, M.; Selim, A. Q.; Mohamed, E. A.; Seliem, M. K., Modification of organic matter-rich clay by a solution of cationic surfactant/H2O2: A new product for fluoride adsorption from solutions. Journal of Cleaner Production 2018, 192, 712-721.

[58] Torres, E. Biosorption: A Review of the Latest Advances. Processes 2020, 8, 1584.

[59] Mahato, N.; Sharma, K.; Sinha, M.; Baral, E.R.; Koteswararao, R.; Dhyani, A.; Cho, M.H.; Cho, S. Bio-sorbents, industrially important chemicals and novel materials from citrus processing waste as a sustainable and renewable bioresource: A review. J. Adv. Res. 2020, 23, 61–82.

[60] Mondal, N.K., Bhaumik, R., Banerjee, A., Datta, J.K., Baur, T. A comparative study on the batch performance of fluoride adsorption by activated silica gel and activated rice husk ash, Int. J. Environ. Sci. 2(3) (2012) 1643-1661.

[61] Mohan, D., Kumar, S., Srivastava, A. Fluoride removal from ground water using magnetic and nonmagnetic corn stover biochars, Ecol. Eng. 73 (2014) 798-808.

[62] Sathish, R.S., Raju, N.S.R., Raju, G.S., Rao, G.N., Kumar, K.A., Janardhana, C. Equilibrium and kinetic studies for fluoride adsorption from water on zirconium impregnated coconut shell carbon, Sep. Sci. Technol. 42(4) (2007) 769-788.

[63] Gandhi, N., Sirisha, D., Chandra Shekar, K.B., Asthana, S. Removal of fluoride from water and wastewater by using low cost adsorbents, Int. J. ChemTech Res. 4(4) (2012) 1646-1653.

[64] Alagumuthu, G., Veeraputhiran, V., Venkataraman, R. Fluoride sorption using Cynodon dactylon based activated carbon, Hem. Ind. 65(1) (2011) 23-35.

[65] Gandhi, N., Sirisha, D., Chandra Shekar, K.B. Adsorption of fluoride (F-) from aqueous solution by using pineapple (Ananas comosus) peel and orange (Citrus sinensis) peel powders, Int. J. Environ. Bioremed. Biodegrade. 4(2) (2016) 55-67.

[66] Patil, S., Renukdas, S., Patel, N. Defluoridation of water using biosorbents: kinetic and thermodynamic studies, Int. J. Res. Chem. Environ. 3(1) (2013) 125-135.

[67] Mohan, S.V., Ramanaiah, S.V., Rajkumar, B., Sarma, P.N. Biosorption of fluoride from aqueous phase onto algal Spirogyra IO1 and evaluation of adsorption kinetics, Bioresour. Technol. 98 (5) (2007) 1006-1011.

[68] Mukherjee, S., Mondal, M., Banerjee, S., Halder, G. Elucidation of the sorptive uptake of fluoride by Ca2+ - treated and untreated algal biomass of Nostoc sp. (BTA 394): isotherm, kinetics, thermodynamics and safe disposal, Process Saf. Environ. Protect. 107 (2017) 334-345.

[69] Ramanaiah, S.V., Mohan, S.V., Sarma, P.N. Adsorptive removal of fluoride from aqueous phase using waste fungus (Pleurotus ostreatus 1804) biosorbent: kinetics evaluation, Ecol. Eng. 31(1) (2007) 47-56.

[70] Mohammad, A., Majumder, C.B. Removal of fluoride from synthetic waste water by using bio-adsorbents, Int. J. Res. Eng. Technol. 3(4) (2014) 776-785.

[71] Zarrabi, M., Sepehr, M.N., Amrollahi, M., Taghavi, M. Biosorption of fluoride by apple pulp from aqueous solution, Winter 16(2) (2014) 213-219.

[72] Chakrapani, C.H., Babu, C.H.S., Vani, K.N.K., Rao, K.S. Adsorption kinetics for the removal of fluoride from aqueous solution by activated carbon adsorbents derived from the peels of selected Citrus fruits, European J. Chem. 7(1) (2010) 419-427.

[73] Ajisha, M.A.T., Rajagopal, K. Characterization and adsorption study using Cocos nucifera midribs for fluoride removal, J. Inst. Eng. India Ser. A. 94(4) (2014) 209-217.

[74] H.E Bumsted and J.C Wells, Spectrophotometric method for determination of the fluoride ion, Analytical chemistry, volume 24, No. 10 (1952).

[75] Poornima G. Hiremath and Thomas Theodore, Biosorption of Fluoride from Synthetic and Ground Water Using Chlorella vulgaris Immobilized in Calcium Alginate Beads in an Upflow Packed Bed Column (2017).

[76] D. Thakre, S. Rayalu, R. Kawade, S. Meshram, J. Subrt, N. Labhsetwar, Magnesium incorporated bentonite clay for defluoridation of drinking water, J. Hazard. Mater. 180 (2010) 122-130.

[77] Myers, R.H., Montgomery, D.C., (2002), Response Surface 1 Methodology, Process and Product Optimization Using Designed Experiments, 2nd ed. John Wiley & Sons, New York, NY.

[78] Alam ZM, Muyibi SA, Toramae J (2007) Statistical optimization of adsorption processes for removal of 2,4-dichlorophenol by activated carbon derived from oil palm empty fruit bunches. J Environ Sci 6:674–677.

[79] Tan AW, Ahmad AL, Hameed BH (2008) Adsorption of basic dye on high-surface-area activated carbon prepared from coconut husk: equilibrium, kinetic and thermodynamic studies. J Hazard Mater 154:337–346.

[80] Sahu JN, Acharya J, Meikp BC (2009) Response surface modeling and optimization of chromium (VI) removal from aqueous solution using tamarind wood activated carbon in batch process. J Hazard Mater 172(2–3):818–825.

[81] Can MY, Kaya Y, Algur OF (2006) Response surface optimization of removal of nickel from aqueous solution by cone biomass of Pinus sylvestris. Bioresour Technol 97:1761–1765.

[82] Chakrabarty, S., Sarma, H.P., 2012. Defluoridation of contaminated drinking water using neem charcoal adsorbent: kinetics and equilibrium studies. Int. J. Chem. Tech. Res. 4, 511–516.

[83] Asheesh Kumar Yadava, b, Rouzbeh Abbassi a, Asha Guptac, Mohammad Dadashzadehd, Removal of fluoride from aqueous solution and groundwater by wheat straw, sawdust and activated bagasse carbon of sugarcane, Ecological Engineering, 52 (2013) 211–218.

[84] Chiban, M., Carja, G., Lehutu, G., Sinan, F., 2016. Equilibrium and thermodynamic studies for the removal of as(V) ions from aqueous solution using dried plants as adsorbents, Arabian Journal of Chemistry, 9, S988–S999.

[85] M. Karthikeyan, K.K.S. Kumar, K.P. Elango, Batch sorption studies on the removal 501 of fluoride ions from water using eco-friendly conducting polymer/bio- 502 polymer composites, Desalination 267 (1) (2011) 49–56.

[86] Kebede B, Beyene A, Fufa F, Megersa M, Behm M (2016). Experimental evaluation of sorptive removal of fluoride from drinking water using iron ore. Appl. Water. Sci. 6:57-65.

[87] Seid Tiku Mereta, Biosorption of fluoride ion from water using the seeds of the cabbage tree (Moringa stenopetala), African Journal of Environmental Science and Technology, 11(1), pp. 1-10, (2017).

[88] Y.S. Ho, G. McKay, A comparison of chemisorption kinetic models applied to 479 pollutant removal on various sorbents, Process Saf. Environ. Protect. 76 (4) 480 (1998) 332–340.

[89] Y.S. Ho, G. McKay, Pseudo-second order model for sorption processes, Proc. 481 Biochem.

[90] Duran, C., Ozdes, D., Gundogdu, A., Senturk, H.B., 2011. Kinetics and isotherm of basic dyes adsorption onto almond shell (Prunus dulcis) as a low cost adsorbent. J. Chem. Eng. Data 56, 2136–2147.

[91] Mohan, S. V., Karthikeyan, J., 2000. Removal of diazo dye from aqueous phase by algae Spirogyra species, Toxicol. Environ. Chem. 74, 147-154.

[92] Ilhami, T., Gulay, B., Emine, Y., Gokben, B., 2005. Equilibrium and kinetic studies on biosorption of Hg (II), Cd (II) and Pb (II) ions onto micro algae Chlamydomonas reinhardtii. J. Environ. Manag. 77, 85-92.

[93] Mohan, S. V., Bhaskar, Y. V., Karthikeyan, J., 2003. Biological decolorization of simulated azo dye in aqueous phase by algae Spirogyra species, Int. J. Environ Pollut. 21 (3), 211-222.

[94] A.K. Meena, G.K. Mishra, P.K. Rai, C. Rajagopal, P.N. Nagar, J. Hazard. Mater. 122 (2005) 161–170.

[95] U.R. Lakshmi, V.C. Srivastav, I.D. Mall., D.H. Lataye, J. Env. Mangm. 85 (2008) 757-773.

[96] Ria Bhaumik and Naba Kumar Mondal, optimizing adsorption of fluoride from water by modified banana peel dust using response surface modelling approach, Appl Water Sci (2016) 6:115–135.

[97] Soumya Bikash Ghosh, Ria Bhaumik, Naba Kumar Mondal, Optimization study of adsorption parameters for removal of fluoride using aluminium-impregnated potato plant ash by response surface methodology, Clean Techn Environ Policy (2016).

[98] H. Y, K. Medikondu, R. Kunta, Characterization and defluoridation studies of 533 active carbon derived from Typha angustata Plants, JAST 3 (2) (2012) 167–181, 534.

[99] S. Mustapha, D. T. Shuaib, M. M. Ndamitso, M. B. Etsuyankpa, A. Sumaila1, U. M. Mohammed5 and M. B. Nasirudeen, Adsorption isotherm, kinetic and thermodynamic studies for the removal of Pb (II), Cd (II), Zn (II) and Cu (II) ions from aqueous solutions using Albizia lebbeck pods, Applied Water Science (2019) 9:142

[100] Annadurai Sakthi Thesai, Arivalagan Pugazhendhi, Sundaram Rajakumar, Mariappan Rajan, Pudukadu Munusamy Ayyasamy, Batch and column approach on biosorption of fluoride from aqueous

medium using live, dead and various pretreated Aspergillus niger (FS18) biomass, Surfaces and Interfaces (2019)

[101] D. Mohan, R. Sharma, V. K. Singh, P. Steele, Charles. U, Pittman. J, Fluoride removal from water using biochar, a green waste, low-cost adsorbent: equilibrium uptake and sorption dynamics modeling. Ind. Eng. Chem. Res. 51 (2012) 900-914.