Current Trends in Biotechnology and Pharmacy
Vol. 15 (1) 70-78 January 2021, ISSN 0973-8916 (Print), 2230-7303 (Online)
DOI: 10.5530/ctbp.2021.1.8

Zirconium alginate beads: A renewable source for the biosorption of fluoride from contaminated ground water

Aruna Jyothi Kora [1, 2*]
[1]National Centre for Compositional Characterisation of Materials (NCCCM)
Bhabha Atomic Research Centre (BARC), ECIL PO, Hyderabad-500062, India
[2]Homi Bhabha National Institute (HBNI), Anushakti Nagar, Mumbai-400 094, India
*Corresponding author: koramaganti@gmail.com

Abstract

In view of the fluoride induced toxic effects on human health; an effective and simple biosorption method was developed for fluoride laden groundwater using zirconium alginate beads. The various parameters affecting the batch adsorption in fluoride spiked groundwater such as initial fluoride concentration (2.5-10 mg/L), residence time (10-120 min) and pH (5, 7, 9) were studied. The fluoride concentration in the solutions was measured by spectrophotometry at 550 nm using in-house developed zirconyl-xylenol orange complex reagent. The biosorbent was characterized with techniques such as X-ray diffraction (XRD), Fourier transform infrared Spectroscopy (FTIR), scanning electron microscopy (SEM) and energy dispersive X-ray fluorescence (EDX). At pH 5, 7 and 9; fluoride removal of 90.5, 46.6 and 88.8% by the biosorbent was noted in groundwater spiked with 10 mg/L of fluoride, within 30 min. Thus, the zirconium alginate beads were found to be potential biosorbents for remediation of groundwater contaminated with fluoride. Further studies are going on to find out the reusability of the developed biosorbent at field conditions. The biosorption mechanism was derived from sorption studies, FTIR, SEM and EDXRF techniques.

Key words: alginate, bioremediation, biosorption, fluoride, groundwater, zirconium

Introduction

The fluoride ion has been classified as one of the major contaminants in drinking water and its pollution in groundwater has been recognized as a severe problem worldwide. It enters into the water resources via dissolution of geogenic minerals and anthropogenic discharge of effluents from metal plating, semiconductor, glass and ceramic manufacturing; coal, uranium and aluminium mining; and fertilizer industries. The World Health Organization (WHO) has lay down a maximum permissible limit of 1.5 mg/L for fluoride in drinking water. Though minute level of fluoride is beneficial for humans in the range of 0.5-1.0 mg/L, the excess intake is detrimental leading to dental and skeletal fluorosis. More than 70 countries of the world including India, Sri Lanka, China, Thailand, Turkey, Iraq, Iran, Afghanistan, Japan, South Arica, USA, Mexico, Argentina, Jordan, Egypt, Libya, Algeria, Sudan and Kenya have drinking water supplies naturally contaminated with fluoride. An elevated fluoride concentration in ground and drinking waters has been reported in nearly 20 states of India such as Rajasthan, Telangana, Andhra Pradesh, Karnataka, Maharashtra, Gujarat, Madhya Pradesh, Bihar, Jharkhand, West Bengal, Haryana, Tamil Nadu, Assam, Punjab, Chhattisgarh, Kerala, Uttar Pradesh, Odisha, Delhi, Jammu and Kashmir. Numerous techniques such as ion exchange, precipitation, membrane

Vol. 15 (1) 70-78 January 2021, ISSN 0973-8916 (Print), 2230-7303 (Online)
DOI: 10.5530/ctbp.2021.1.8

separation are generally used for the elimination of fluoride from water. However, the precipitation method is limited by the requirement of additional treatment, sludge generation, high cost and presence of residual aluminium. The ion exchange and membrane separation techniques are energy intensive and expensive (Paudyal et al., 2013; Velazquez-Jimenez et al., 2015). As an alternative, adsorption of fluoride from groundwater using a natural, renewable, functional group enriched biopolymer, alginate was attempted, as a simple and cost effective methodology.

The biopolymer alginate is a naturally occurring anionic polysaccharide produced by a variety of brown algae and the bacteria *Pseudomonas aeruginosa* and *Azotobacter*. The important characteristics of the alginate are its (i) renewability, (ii) biodegradability, (iii) non toxicity (iv) gelation, (v) generally recognized as safe (GRAS) status and (vi) low cost. It is widely used as a thickening agent in textile printing, emulsifier, stabilizer, thickener and gelling agent in food and disintegrating agent in pharmaceutical industries. It is also used as a micro-encapsulation agent for the production of insoluble artificial seeds in plant tissue culture, entrapping/immobilizing agent for enzymes, as a haemostatic agent in skin wound dressings, an impression-making material in prosthetics and dentistry, as a hydrogel in bioengineering research, fish feed binder and as a sustained drug delivery system (Hitoshi et al., 2002; Lee and Mooney, 2012).

In view of the fluoride induced toxic effects on human health; an effective and simple biosorption method was developed for the fluoride laden groundwater using zirconium alginate beads. The effect of initial fluoride concentration, residence time and pH on batch adsorption of fluoride in spiked groundwater was investigated. The fluoride concentration in the solutions was measured by spectrophotometry at 550 nm using in-house developed zirconyl-xylenol orange complex reagent. The biosorbent was characterized with X-ray diffraction, Fourier transform infrared spectroscopy, scanning electron microscope and energy dispersive X-ray fluorescence techniques.

Materials and methods

Zirconium oxychloride octahydrate (Loba Chemie, Mumbai, India), sodium alginate (Sigma, Bengaluru, India), calcium chloride dihydrate, hydrochloric acid and xylenol orange (SD Fine, Mumbai, India) of AR grade were used. A 100 mg/mL certified fluoride calibration standard solution (Thermo Scientific Orion 940907) traceable to National Institute of Standards and Technology (NIST) reference material was used for working standard solution preparation. The u*ltrapure water with a* resistivity of *18.2 MOhm*-cm obtained from Elga Purelab Flex 3 ultrapure water polishing unit (High Wycombe, England) was used for all the experiments.

Preparation of zirconium alginate beads: The zirconium alginate beads were prepared according to the reported method with minor modifications (Huo Yakun et al., 2011). A 3% (w/v) of homogenous sodium alginate polymer solution was prepared in ultrapure water by continuous overnight stirring at room temperature. A 10 mL of sodium alginate solution was dropped into 30 mL of 200 mM zirconium oxychloride solution, using a 5 mL micropipette tip under continuous stirring. The drops were turned out into beads of 4-5 mm diameter in zirconium oxychloride solution and the beads were further soaked in the same solution for 24 h for completion of gelation process. Then, the beads were washed thoroughly with ultrapure water for removal of unreacted zirconium ions (Fig. 1).

Characterization of groundwater: The ground water samples were collected from the bore well of National Centre for Compositional characterization of Materials (NCCCM), Hyderabad, India. The collected water was analyzed for physicochemical parameters including pH, conductivity and total dissolved solids using Elico water quality analyzer PE 138 (Hyderabad, India). The fluoride content in the groundwater samples was measured by

Vol. 15 (1) 70-78 January 2021, ISSN 0973-8916 (Print), 2230-7303 (Online)
DOI: 10.5530/ctbp.2021.1.8

spectrophotometric method, based on zirconyl-xylenol orange complex reagent. The metal indicator dye, xylenol orange forms an orange coloured complex with zirconium ions (Zr^{4+}), which is decolourized via the dissociation of the complex by the fluoride ions leading to the formation of colourless zirconium fluoride. The reagent zirconyl-xylenol orange was prepared by mixing 0.01% (w/v) of the dye with 0.04% (w/v) of depolymerized zirconium solution in 20% (v/v) of HCl. The reagent and the sample was added in 1:4 volume ratio, i.e. 1 mL of the reagent was mixed with 4 mL of the sample solution and the resulting colour of the mixture was determined by recording the absorbance at 550 nm (Cabello-Tomas and West, 1969; Rù•ièka et al., 1966; S. V. Rao et al., 2002). The fluoride concentration in the sample solutions were estimated based on the calibration plots obtained with aqueous standards (Fig. 2). The concentration of various metals such as calcium, magnesium, zinc, barium, iron; manganese, copper, lead and cadmium in groundwater was determined using Jobin Yvon Horiba JY-2000 inductively coupled plasma-optical emission spectrometer (ICP-OES) (Longjumeau, France) and Analytik Jena AG Contra AA 700 continuum source-electro thermal atomic absorption spectrometer (CS-ETAAS) (Jena, Germany), respectively. The concentration of anions such as sulphate, chloride and phosphate in groundwater was analyzed with Dionex ICS-3000 ion chromatography system (Sunnyvale, USA) employing IonPac AG20 guard and IonPac AS20 analytical columns. The total heterotrophic bacteria in groundwater were enumerated using nutrient agar medium. The total coliforms and *Escherichia coli* were concurrently determined with HiCrome coliform selective agar medium (Table 1).

Biosorption studies: The fluoride uptake studies were carried out in batch mode by equilibrating 0.3 g of the zirconium alginate beads with 10 mL of groundwater spiked with different fluoride concentrations (2.5-10 mg/L) at various pH (5, 7 and 9) conditions under continuous mixing. A control experiment was also done by equilibrating 0.3 g of zirconium alginate beads with 10 mL of groundwater, with no fluoride addition. The samples were collected at specific intervals (10-120 min) and the supernatants were collected after centrifugation. The centrifugates were analyzed

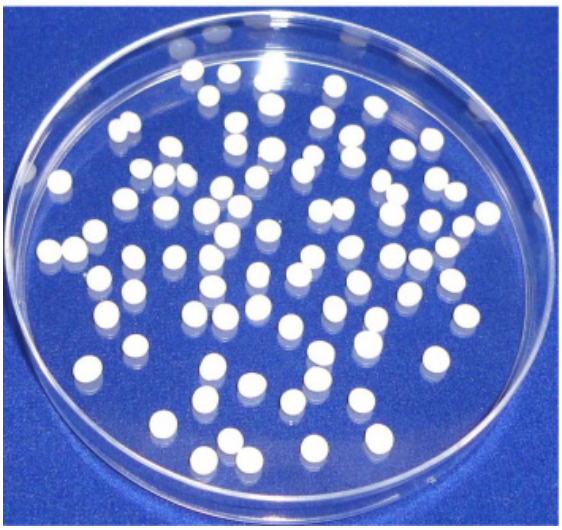

Fig. 1 The digital photograph of zirconium alginate biosorbent beads.

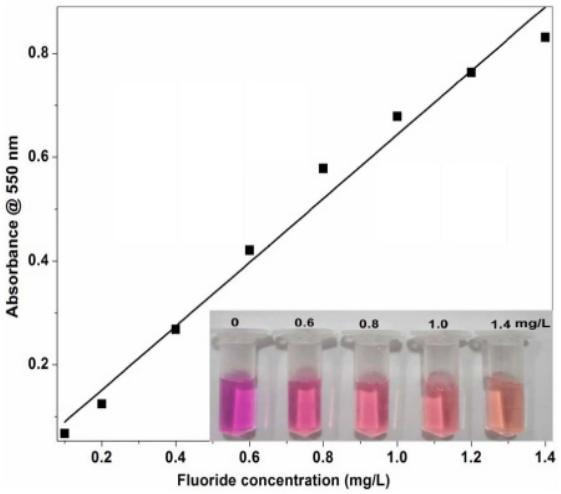

Fig. 2 The calibration plot showing the absorbance at 550 nm *vs.* fluoride concentration. Inset: Solution colour at various fluoride levels.

Vol. 15 (1) 70-78 January 2021, ISSN 0973-8916 (Print), 2230-7303 (Online)
DOI: 10.5530/ctbp.2021.1.8

for fluoride levels using an Analytic Jena AG Specord 200 Plus UV-visible spectrophotometer (Jena, Germany). The amount of adsorbed fluoride per unit weight of the zirconium alginate biosorbent was quantified with the following equation

$$q = \frac{(C_0 - C_e)V}{m} \quad (1)$$

Where, q = Amount of fluoride adsorbed per unit weight of biosorbent (mg/g)

C_0 = Initial fluoride concentration (mg/L)

Ce = Equilibrium fluoride concentration (mg/L)

V = Solution volume (L)

m = Dry weight of the biosorbent (g)

In triplicate the biosorption experiments were done and the data were represented as mean (±) standard deviation (SD).

Characterization of biosorbent: The Labconco Freezone 4.5L Plus benchtop cascade freezedry system (Kansas City, USA) was used for lyophilization of native and fluoride sorbed biosorbents. The Bruker Optics TENSOR 27 FTIR spectrometer (Ettlingen, Germany) was employed for recording the IR spectra of the lyophilized powders at 1000-4000 cm^{-1}. The Rigaku, Ultima IV diffractometer (Tokyo, Japan) was utilized for X-ray diffraction analysis at 40 kV and 30 mA using monochromatic Cu Ká radiation (ë = 1.5406 Å). The intensity data was recorded for the powdered biosorbents at a 2θ range of 35-70º and scan rate of 1º/min. The lyophilized powders of native and fluoride sorbed adsorbent were carbon sputter coated and visualized under Zeiss EVO 18 Research scanning electron microscope (Carl Zeiss Microscopy Ltd., Cambridge, UK) at an accelerating voltage of 20 kV. The energy dispersive X-ray fluorescence spectra of the biosorbents were collected with x-act (Oxford Instruments Analytical Ltd., High Wycombe, UK) spectrometer fitted with silicon drift detector, running at 20 kV.

Results and discussion

The adsorption method is preferred for the removal of fluoride ions from groundwater due to its low cost, design simplicity, flexibility, selectivity and efficiency. It can be exploited in a developing country like India, where renewable, cheap and locally available adsorptive resources are abundant in comparison with expensive, synthetic adsorption media used in industrialized countries (Velazquez-Jimenez et al., 2015). In literature, alginate beads doped with Fe (III) (Velazquez-Jimenez et al., 2015), Al (Zhou et al., 2014), hydrous ferric oxide (Sujana et al., 2013) and La (Huo Yakun et al., 2011) were used as adsorptive materials for fluoride removal from water. In this context, zirconium alginate beads were prepared from renewable, natural biopolymer alginate for the removal of fluoride from groundwater.

Fluoride uptake studies : The obtained zirconium alginate beads were spherical in shape and size ranged from 4-5 mm. 1). The spherical shape of the beads also favours its application in continuous flow fixed bed columns (Li et al., 2013). The capability of zirconium alginate beads towards fluoride uptake in ground water was studied at varying fluoride ion concentration (2.5-10 mg/L), solution pH (5, 7 and 9) and residence time (10-120 min) in batch mode. The critical parameter in determining the fluoride adsorption is the solution pH. The pH effect on fluoride uptake at an initial fluoride concentration of 2.5 mg/L at varying reaction time of 10-120 min is shown in Fig. 3. The fluoride uptake of 75.7 and 72.5% was noted at pH 5 and 9, respectively in comparison with 47.5% at pH 7, within 10 min. At pH 5 and 9 and 30 min of reaction, the uptakes were 87.7 and 95.8%, respectively indicating the near saturation of adsorption. While at pH 7, the uptake is linear and increased with an increase in reaction time and showed an uptake of 63.1% only at 30 min. Thus, the data suggests that fluoride ion adsorption is rapid at pH 5 and 9, in comparison with neutral pH of 7. Similar trend was observed at a concentration of 5 mg/L, with corresponding uptake of 87.3, 88.7 and 63.1% at pH 5, 9 and 7,

Vol. 15 (1) 70-78 January 2021, ISSN 0973-8916 (Print), 2230-7303 (Online)
DOI: 10.5530/ctbp.2021.1.8

respectively (Fig. 4). The uptakes of 90.4, 92.5 and 50.6% were noted at 7.5 mg/L of fluoride, at pH 5, 9 and 7, respectively (Fig. 4). At an elevated concentration of 10 mg/L of fluoride, the respective uptakes were 90.5, 88.8 and 46.6% at pH 5, 9 and 7 (Fig. 5). The pH dependent biosorption is in concurrence with earlier fluoride removal study with lanthanum alginate bead (Huo Yakun et al., 2011). At 120 min, the removal values were found be 98, 98 and 93% at pH 5, 9 and 7, respectively at 10 mg/L of fluoride. At these conditions, the fluoride uptake values were 5.1, 5.1 and 4.8 mg/g, respectively. These values are comparable with earlier fluoride biosorption study carried out using hydrous ferric oxide doped alginate beads (8.9 mg/g) (Sujana et al., 2013) and alginate bioencapsulated nano-hydroxyapatite composite (3.8 mg/g) (Pandi and Viswanathan, 2014). In the current report, it is significant to note that the fluoride removal was achieved at variable

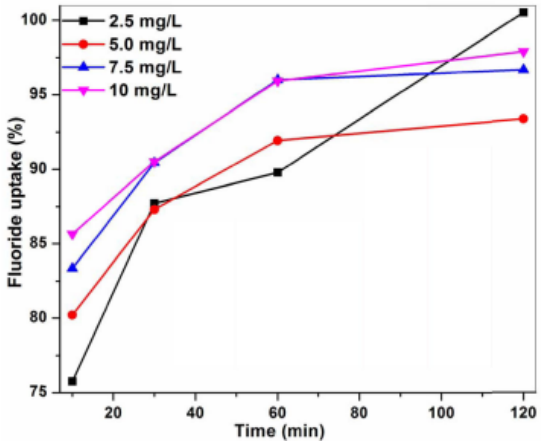

Fig. 3 The time dependent fluoride uptake by the biosorbent at pH 5 and varying initial fluoride concentration.

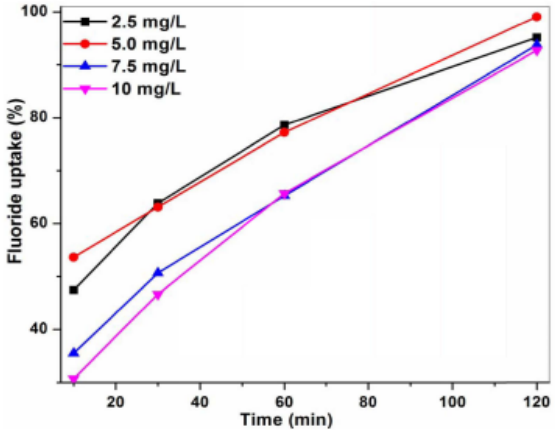

Fig. 4 The time dependent fluoride uptake by the biosorbent at pH 7 and varying initial fluoride concentration.

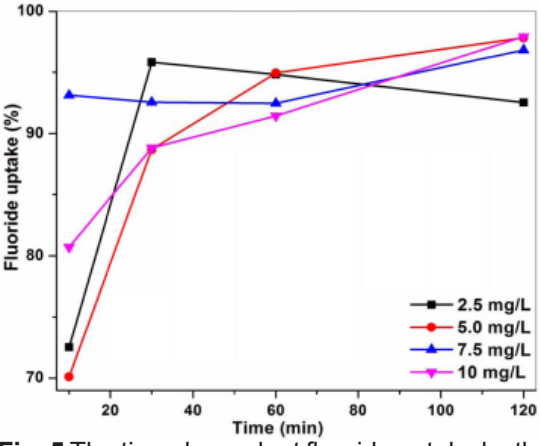

Fig. 5 The time dependent fluoride uptake by the biosorbent at pH 9 and varying initial fluoride concentration.

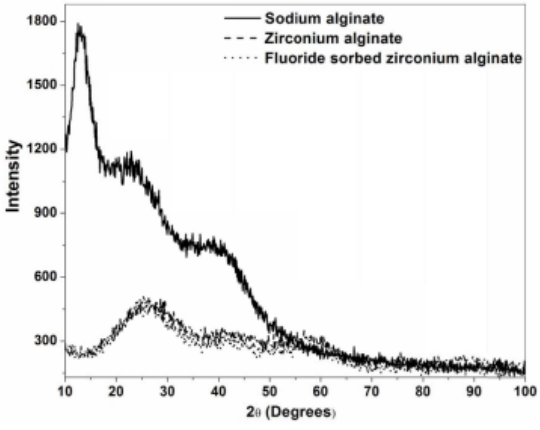

Fig. 6 The XRD pattern of biosorbents sodium alginate, zirconium alginate and fluoride sorbed zirconium alginate.

Vol. 15 (1) 70-78 January 2021, ISSN 0973-8916 (Print), 2230-7303 (Online)
DOI: 10.5530/ctbp.2021.1.8

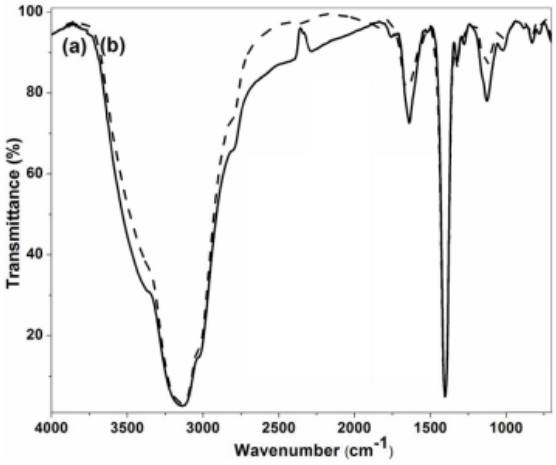

Fig. 7 The FTIR spectra of zirconium alginate biosorbent (a) before and (b) after fluoride uptake.

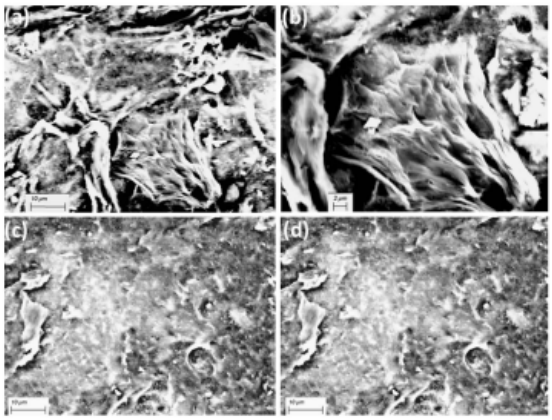

Fig. 8 The scanning electron micrographs of zirconium alginate biosorbent before fluoride uptake, at (a) 10 µm and (b) 2 µm; after fluoride uptake, at (c) 10 µm and (d) 2 µm scale.

groundwater pH. In addition, the biosorption was successful at physicochemical conditions of groundwater such as total dissolved solids (750 mg/L) and in the presence of cations including Ca (143 mg/L), Mg (23.4 mg/L), Mn (293.8 µg/L), Cu (130.1 µg/L); and anions such as Cl^- (108 mg/L), SO_4^{2-} (100 mg/L) and NO_3^- (14.8 mg/L).

Biosorbent characterization and mechanism: The biosorbent zirconium alginate was characterized by an array of techniques before and after uptake of fluoride from groundwater.

X-ray diffraction (XRD): The XRD pattern of sodium alginate, zirconium alginate and fluoride sorbed zirconium alginate is shown in Fig. 6. For sodium alginate, the three characteristic peaks were noted at 13.5 º, 22.9 º and 39 º indicating the semi crystalline structure (Fontes et al., 2013; Helmiyati and Aprilliza, 2017; Huo Yakun et al., 2011). But in the case of zirconium alginate and fluoride sorbed zirconium alginate, the one of the peaks disappeared and the other became less intense, implying a change in the crystal structure. The amorphous nature of the zirconium alginate sorbent facilitates a better access to fluoride and zirconium is known for its affinity towards fluoride (Huo Yakun et al., 2011).

Fourier transform infrared spectroscopy (FTIR): The IR spectra of zirconium alginate before and after fluoride adsorption are indicated in Fig. 7. The zirconium alginate exhibits characteristic absorbance peaks at 3135, 1751, 1639, 1402, 1319, 1276, 1127, 1027, 827 and 778 cm^{-1}. The broad peak at 3135 corresponds to OH functional groups of the biopolymer. The peak at 1751 cm^{-1} could be accounted to carbonyl stretch of carboxylic acids. The dominant peaks at 1639 and 1402 cm^{-1} could be ascribed to symmetric and asymmetrical stretches of carboxylate groups, respectively. The peaks observed at 1276 and 1127; 1027 and 827 cm^{-1} attribute to C-O stretches of polyols, uronic and mannuronic acids, respectively.

While, after fluoride uptake the zirconium alginate shows peaks at 3136, 1827, 1657, 1402, 1319, 1276, 1124, 1011, 827 and 778 cm^{-1}. After adsorption, a major shift in the absorbance peaks of carboxylate and C-O-C groups was noted from 1751 to 1827, 1639 to 1657; and 1027 to 1011

Vol. 15 (1) 70-78 January 2021, ISSN 0973-8916 (Print), 2230-7303 (Online)
DOI: 10.5530/ctbp.2021.1.8

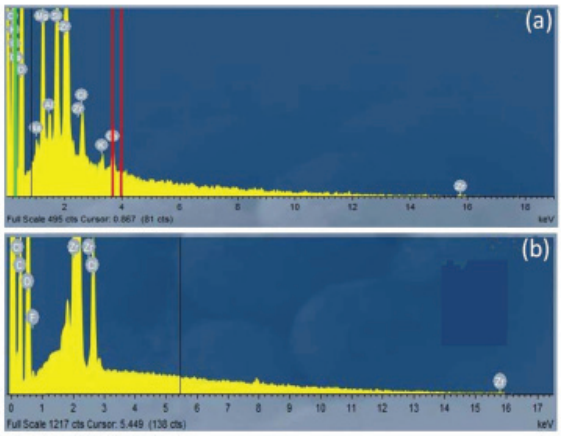

Fig. 9 The EDX spectra of (a) native and (b) fluoride sorbed zirconium alginate biosorbent.

cm^{-1}, respectively. Thus, it indicates a coordination interaction between Zr^{4+} and F^-, based on hard soft acid-base theory. The inductive electronic attraction effect of halogen atom with metal ions brings a shift in the peaks of carboxylate and C-O-C groups (Zhou et al., 2014). It is known that the positively charged Zr^{4+} ions at the surface of alginate attracts the negatively charged fluoride ions via electrostatic interaction (Vijaya et al., 2011). Thus, the results confirm the electrostatic and coordination interaction mechanism in defluoridation of groundwater (Sujana et al., 2013; Vijaya et al., 2011; Zhou et al., 2014).

Scanning electron microscopy (SEM)* and *Energy dispersive X-ray fluorescence (EDX) :
The surface and morphological characteristics of zirconium alginate before and after fluoride uptake was visualized using SEM (Fig. 8). Before fluoride adsorption, the biosorbent was porous, flaky and fibrillar in nature, which aid in efficient diffusion of fluoride ions into the matrix and adsorption rate. Upon fluoride uptake, significant morphological and structural changes such as shrinkage, enhanced roughness and compactness of biosorbent were noticed, indicating that the fluoride adsorption is indeed a surface phenomenon (Helmiyati and Aprilliza, 2017; Huo Yakun et al., 2011; Kora et al., 2016; Li et al., 2013; Qiusheng et al., 2015; Vijaya et al., 2011; Zhou et al., 2014). The energy dispersive X-ray fluorescence (EDX) spectra of native and fluoride sorbed zirconium alginate are shown in Fig 9. The presence of fluoride in the biosorbent was confirmed from the shown peak in the spectra, along with other elements such as Zr, Cl, C, O, Na, K, Ca etc after fluoride uptake (Pandi and Viswanathan, 2014; Sujana et al., 2013; Swain et al., 2013).

Conclusions

A simple biosorbent based method for the fluoride removal from groundwater was developed using zirconium alginate beads. At pH 5, 9 and 7; 98, 98 and 93% removal was noted in 10 mg/L fluoride spiked groundwater within 120 min. The zirconium alginate beads could be used as a potential biosorbent for the remediation of fluoride contaminated groundwater. Further detailed

Tab. 1 The compositional analysis of collected groundwater.

Parameter	Value ± SD
pH	7.0 ± 0.05
Conductivity (mS/cm)	1.07 ± 0.02
Total dissolved solids (mg/L)	750 ± 10.4
Calcium (mg/L)	143 ± 5
Magnesium (mg/L)	23.4 ± 1.3
Zinc (mg/L)	0.13 ± 0.02
Barium (mg/L)	< 0.05
Iron (mg/L)	< 0.01
Manganese (µg/L)	293.87 ± 6.4
Copper (µg/L)	130.1 ± 15.2
Lead (µg/L)	< 0.7
Cadmium (µg/L)	< 0.06
Chloride (mg/L)	108 ± 5.7
Fluoride (mg/L)	1.14 ± 0.07
Sulphate (mg/L)	100 ± 1.5
Nitrate (mg/L)	14.86 ± 0.9
Total heterotrophic bacteria (CFU/mL)	8.5×10^2
Total coliforms (CFU/100 mL)	0
Escherichia coli (CFU/100 mL)	0

Vol. 15 (1) 70-78 January 2021, ISSN 0973-8916 (Print), 2230-7303 (Online)
DOI: 10.5530/ctbp.2021.1.8

studies are envisaged on fluoride sorption characteristics of the biosorbent in column mode to find out its suitability and reusability at field conditions.

Acknowledgement

The author would like to thank Dr. Athyala Christian Sahayam, Head, Bulk Analysis Section (BAS) and Dr. Sunil Jai Kumar, Former Head, NCCCM/BARC for their constant encouragement and support throughout the study.

References

1. Cabello-Tomas, M.L., West, T.S., 1969. Kinetochromic spectrophotometry-I: Determination of fluoride by catalysis of the zirconium-xylenol orange reaction. Talanta 16, 781-788.
2. Fontes, G.C., Calado, V.M.A., Rossi, A.M., Rocha-Leão, M.H.M.d., 2013. Characterization of antibiotic-loaded alginate-Osa starch microbeads produced by ionotropic pregelation. BioMed Research International 2013, 1-11.
3. Helmiyati, Aprilliza, M., 2017. Characterization and properties of sodium alginate from brown algae used as an ecofriendly superabsorbent. IOP Conference Series: Materials Science and Engineering 188, 012019.
4. Hitoshi, M., Ohta, H., Akiba, K., Onodera, Y., 2002. Uptake and recovery of ruthenium by alginate gel polymers. Anglais 39, 655-660.
5. Huo Yakun, Ding Wenming, Huang Xia, Xu Jingnian, Menghua, Z., 2011. Fluoride removal by lanthanum alginate bead: Adsorbent characterization and adsorption mechanism. Separation Science and Engineering, Chinese Journal of Chemical Engineering 19, 365-370.
6. Kora, A.J., Bhaskarapillai, A., Toleti, S.R., 2016. Exopolymer produced by *Pseudomonas aeruginosa*: A super sorbent for ruthenium. Separation Science and Technology, 1-6.
7. Lee, K.Y., Mooney, D.J., 2012. Alginate: properties and biomedical applications. Progress in polymer science 37, 106-126.
8. Li, X., Qi, Y., Li, Y., Zhang, Y., He, X., Wang, Y., 2013. Novel magnetic beads based on sodium alginate gel crosslinked by zirconium(IV) and their effective removal for Pb(2)(+) in aqueous solutions by using a batch and continuous systems. Bioresour Technol 142, 611-619.
9. Pandi, K., Viswanathan, N., 2014. Synthesis of alginate bioencapsulated nano-hydroxyapatite composite for selective fluoride sorption. Carbohydrate polymers 112, 662-667.
10. Paudyal, H., Pangeni, B., Inoue, K., Kawakita, H., Ohto, K., Ghimire, K.N., Alam, S., 2013. Preparation of novel alginate based anion exchanger from *Ulva japonica* and its application for the removal of trace concentrations of fluoride from water. Bioresource Technology 148, 221-227.
11. Qiusheng, Z., Xiaoyan, L., Jin, Q., Jing, W., Xuegang, L., 2015. Porous zirconium alginate beads adsorbent for fluoride adsorption from aqueous solutions. RSC Advances 5, 2100-2112.
12. Rù•ièka, J.A., Jakschová, H., Mrklas, L., 1966. Determination of fluorine in bones and teeth with xylenol orange. Talanta 13, 1341-1344.
13. S. V. Rao, Singh, R., Chaurasia, S.C., 2002. A simple field method for the estimation of fluoride in ground water for common man's use. Bhabha Atomic Research Centre (BARC) News letter, Mumbai, India 219, 6-10.
14. Sujana, M.G., Mishra, A., Acharya, B.C., 2013. Hydrous ferric oxide doped alginate beads for fluoride removal: Adsorption

Vol. 15 (1) 70-78 January 2021, ISSN 0973-8916 (Print), 2230-7303 (Online)
DOI: 10.5530/ctbp.2021.1.8

kinetics and equilibrium studies. Applied Surface Science 270, 767-776.

15. Swain, S.K., Patnaik, T., Patnaik, P.C., Jha, U., Dey, R.K., 2013. Development of new alginate entrapped Fe(III)–Zr(IV) binary mixed oxide for removal of fluoride from water bodies. Chemical Engineering Journal 215-216, 763-771.

16. Velazquez-Jimenez, L.H., Vences-Alvarez, E., Flores-Arciniega, J.L., Flores-Zuñiga, H., Rangel-Mendez, J.R., 2015. Water defluoridation with special emphasis on adsorbents-containing metal oxides and/or hydroxides: A review. Separation and Purification Technology 150, 292-307.

17. Vijaya, Y., Popuri, S.R., Reddy, A.S., Krishnaiah, A., 2011. Synthesis and characterization of glutaraldehyde-crosslinked calcium alginate for fluoride removal from aqueous solutions. Journal of Applied Polymer Science 120, 3443-3452.

18. Zhou, Q., Lin, X., Li, B., Luo, X., 2014. Fluoride adsorption from aqueous solution by aluminum alginate particles prepared via electrostatic spinning device. Chemical Engineering Journal 256, 306-315.