



Fluoride removal using simple protonated and xanthate modified protonated *Ficus religiosa* branch powder in a fixed-bed column

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ABSTRACT

Fluoride anion (F^-) is considered as micronutrient. It is essential for the maintenance of bone skeleton and prevent dental decay. The excess amounts present in water pose toxicity to the consumers. In the present study, comparative sorption behavior of protonated and xanthate modified powdered branches of *Ficus religiosa* was investigated for their defluoridation potential in an industrially viable continuous flow mode. The protonated and the chemically modified materials were characterized by SEM, FTIR, and other analytical techniques. The appearance of the band around $1,030\text{ cm}^{-1}$ indicated the incorporation of C=S into the modified material. After protonation, amines (NH_2) peak was shifted to acidic site (NH_3^+) to bind with anions (F^-). The efficiency of defluoridation was observed on various bed heights (5–30 cm) and initial concentration (25–100 mg/L) at a constant flow rate of 2 mL/min. The maximum sorption capacity for protonated biomass was found to be 9.03 mg/g, and for xanthate modified biomass 19.72 mg/g at 50 mg/L inlet concentration and 30 cm bed height. Breakthrough curves were obtained and the model (Bed depth service time and Yoon-Nelson) parameters were calculated from respective breakthrough curves. The results indicated that xanthate modified biomass was better for defluoridation of contaminated water than simply protonated one. The study concluded that this material could be efficiently used for the removal of fluoride ions from polluted waters in a continuous flow mode.

Keywords: *Ficus religiosa*; Fluoride; Breakthrough curves; Continuous flow process, Xanthate modified

1. Introduction

Fluoride (F^-), a monovalent anion, is an essential micronutrient for skeleton and teeth mineralization in human beings. The permissible limit for fluoride reported by WHO and EPA is 1.5 and 1.0 mg/L for drinking and irrigation water respectively [1]. When in excess, fluoride ion is known to be absorbed into human tissues due to consumption of fluoride contaminated water and thus reacts with calcium present in bones and teeth (fluorapatite). This dental and skeletal fluorosis is caused when F^- is present above safe limits [2]. Surface and ground water is contaminated with F^- by two different means

i.e. anthropogenic and natural sources. Industrial discharge (glass manufacture, pesticides, semiconductors etc.) and weathering of fluoride ores such as cryolite, fluorapatite, and fluorite are main sources of fluoride ion in water bodies [3].

Different widely used defluoridation techniques include ion exchange, precipitation, and adsorption [4–6]. The use of agricultural materials, as an alternative to activating carbon, has emerged as a relatively cost-effective method of defluoridation of contaminated waters. Several studies have been reported on biosorption of fluoride using *Tamarindus indica* [7], *Polyalthia longifolia* [8], *Colocasia esculenta* [9] *Aegle marmelos* [10] *Tinospora cordifolia* [11] *Citrus limetta* [12] *Delonix regia* [13] *Sargassum sp.* [14], and sugarcane bagasse [15] in batch mode.

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The batch mode has advantages like the insight into the uptake mechanism and feasibility of the process [16]. It also shows that the modification of biomass usually increases the removal capacity. It is not suitable when larger volumes of contaminated waters are required to be treated [17]. The continuous flow mode in a fixed-bed column is more industrially viable.

Ficus religiosa, a widely distributed tree in Indian sub-continent, is available easily in Pakistan. Being semi-evergreen, the branches are easily available at almost no cost throughout the year as waste material. The present comparative sorption studies are based on the defluoridation potential of protonated *Ficus religiosa* (PFR) and xanthate modified protonated *Ficus religiosa* (XPFR) in fixed bed column. The lignin, cellulose, hemicelluloses, and pectin are the main components of *Ficus religiosa* (Peepal tree); these groups contain active sites for potential binding of fluoride ion. The branches of *Ficus religiosa* have been reported for removal of heavy metals (lead and cadmium) and the leaves for adsorptive removal of F^- in the batch mode [18,19]. To the best of our knowledge, no studies have been reported for the use of powdered branches of *Ficus religiosa* in a fixed bed column for the removal of F^- from its aqueous solutions.

The effects of variation in bed height and the concentration of fluoride ions were studied at a constant flow rate. The data was used for the construction of respective breakthrough curves. Various parameters were calculated using breakthrough curves on a different condition such as a change in bed height and initial concentration of fluoride ion [20]. These curves were used to evaluate the mathematical models BDST and Yoon Nelson model.

2. Materials and methods

2.1. Reagents and chemicals

Reagents/chemicals used in the present studies including sodium fluoride and carbon disulfide were of analytical grade, obtained directly from Merck. Stock solution (1,000 mg/L) of fluoride was prepared using sodium fluoride. The dilution of the stock solution was required for the desired concentration of working solutions (25–100 mg/L).

2.2. Preparation of biomass

Dried branches (excluding leaves, flowers and fruits) of Peepal tree (*Ficus religiosa*) were collected from Dharampura, Lahore (31.582°N, 74.329°E). The clean and dust free branches were washed with water and then allowed to oven dry until constant mass. These branches of *Ficus religiosa* were crushed in a blender (Kenwood) and sieved for a specific fraction of $<177 \mu\text{m}$ for continuous flow studies. The separated fraction of powdered biomass was thoroughly washed with sufficient deionized water to remove all water-soluble impurities and pigments; washed biomass was dried in an oven and preserved in the airtight plastic recipient.

2.3. Xanthate modification and protonation

The powdered branches were chemically functionalized with xanthate. The xanthatation process was accomplished using the method reported elsewhere [21]. Briefly, 20 g of

dried biomass *Ficus religiosa* (FR) were taken in an Erlenmeyer flask, added 125 mL of sodium hydroxide solution (17%, w/v) and mixed with continuous stirring on a rotatory shaker (N.S Engineering concern) for 2 h. Then 5 mL of CS_2 was added in the mixture and kept shaking for 24 h and filtered. The obtained xanthate product was excessively washed with distilled water to remove alkali. The material was dried and stored in the recipient. For protonation, simple and xanthate modified biomasses were soaked separately in concentrated hydrochloric acid (HCl) for half an hour and filtered. The protonated biomasses were extensively washed with distilled water to remove excess of HCl, dried in the oven till constant mass, preserved in containers and labeled as protonated *Ficus religiosa* (PFR) and protonated xanthate modified *Ficus religiosa* (PXFR) respectively.

2.4. Immobilization of biomass

Protonated simple and protonated xanthate modified *Ficus religiosa* were silica-immobilized to enhance the density of biomass to assist column packing by the method described elsewhere [22]. Immobilized protonated biomass of both types was washed, dried, and saved in the airtight recipient. Distinctly, labeled immobilized protonated *Ficus religiosa* (IPFR) and immobilized protonated xanthate modified *Ficus religiosa* (IPXFR) were used for breakthrough analysis and characterization studies.

2.5. Characterization of PFR and PXFR

Surface morphology of biosorbent PFR and PXFR was characterized by the point of zero charge (pH_{pzc}), Fourier transform infrared spectroscopy (FTIR), scanning electron microscope (SEM) and energy dispersive spectroscopy (EDS) using the standard procedures [23,24]. Zero surface charge of biomass was determined as described elsewhere [25].

2.6. Fluoride analysis

The concentration of fluoride ions in the column effluent was determined by fluoride combination ion selective electrode (ISE-HI 4110). Fluoride electrode acted as a potentiometric sensor for free fluoride ion from aqueous solution. The instrument was calibrated with fluoride standards after adding total ionic strength adjustment buffer solution (TISAB II) in recommended ratio 1:10.

2.7. Column biosorption studies

Fixed bed column biosorption studies were conducted in a glass column of 20 mm inside diameter and 600 mm height. It was packed with a measured quantity of adsorbent to gain required bed height (5, 15 and/or 30 cm). Glass wool was fixed at the bottom and top of required bed height for a steady flow of fluoride solution (25, 50 and 100 mg/L) through the column and to prevent any interruption.

The removal efficiency of fluoride ion in fixed bed column on IPFR and IPXFR were investigated on different column design parameters i.e. the initial concentration of fluoride (25–100 mg/L), bed heights of 5–30 cm at a flow rate of 2 mL/min (linear velocity $v_l \sim 1.13 \text{ cm/min}$). The constant flow rate of the fixed column was attained by peristaltic (Fisher medium flow) pump.

The effluent was collected after regular intervals of time to measure the fluoride concentration (C_e , mg/L) in effluent via ion selective electrode (ISE-HI 4110). The difference of initial and effluent fluoride concentration was considered as adsorbed concentration (C_d , mg/L) by the column at a given instance. Dimensionless ratio (C_e/C_o) of effluent concentration (C_e) to influent concentration (C_o) was used to plot breakthrough curves (C_e/C_o vs ' t '). Breakthrough time (t_b), exhaust time (t_e), and volume of treated fluoride solution (V_{eff}) were calculated from the breakthrough curves for various parameters like bed height and the concentration of fluoride solution at constant the flow rate.

2.8. Breakthrough parameters

Breakthrough curves (S-shaped) were used to evaluate the performance of the column. The breakthrough time was selected when the C_e/C_o became equal to 0.1 and the exhaust time was selected at C_e/C_o of 0.9. The column became saturated and required regeneration when effluent fluoride concentration became almost equal to influent concentration. Mass of fluoride ion adsorbed on biomass q_{total} (mg) was computed by mathematical Eq. (1).

$$q_{\text{total}} = \frac{v_1}{1000} \int_{t=0}^{t=t_{\text{total}}} C_d dt \quad (1)$$

The capacity of fluoride adsorption (q_e) for a given amount of material (m) was determined as given in Eq. (2).

$$q_e = \frac{q_{\text{total}}}{m} \quad (2)$$

The removal efficiency of fluoride ion ' $R\%$ ' was calculated by using Eq. (3).

$$R\% = \frac{q_{\text{total}}}{m_{\text{total}}} \times 100 \quad (3)$$

where m_{total} is the amount of fluoride ions fed into the column under the given conditions.

2.9. Modeling of breakthrough curves

Breakthrough curves were used to evaluate the efficiency of the continuous flow process and to provide data for mathematical model studies. Different mathematical models have been developed for fixed bed column biosorption process. In present studies, bed depth service time (BDST) and Yoon-Nelson (Y-N) models were applied to the breakthrough curves data; equations of both models are given in Table 1.

Bohart and Adams derived BDST model equation [26], to evaluate the biosorption rate of fluoride on the surface of biomass. The plot of service time vs. bed height explains the linear relationship according to the BDST model. The Y-N model explains that the decreasing probability in biosorption capacity is proportional to sorbate biosorption probability and sorbate breakthrough on sorbent [27]. The time required for 50% sorbate-breakthrough concentration is designated as ' τ '.

2.10. Regeneration studies

The exhausted biomass was properly managed by regeneration/desorption to avoid the disposal problem of exhaust biosorbent [28]. Desorption of fluoride ion was achieved in continuous flow mode by using NaOH (0.1 M) at 5 cm bed height and 2 mL/min flow rate. The effluent was collected after the constant interval, used for the assessment of fluoride ion concentration.

3. Results and discussion

3.1. Characterization of the materials

Point of zero charge pH (pH_{pzc}) is pH of the solution at which surface charge of biomass become neutral. The surface of biosorbent becomes negative as pH of the solution increases above its pH_{pzc} . On the other hand, the surface gains positive charge and attract anion (fluoride) by a decrease in the pH of the solution bearing it below its pH_{pzc} [29]. The pH_{pzc} values of both biosorbent (PFR, PXFR) were found to be 7.1 and 6.9 respectively (Fig. 1). The slight decrease in pH_{pzc} of xanthate modified material could be due to the relatively more acidic character of sulfur being attached as a modifier.

Functional groups of PFR (simple) and xanthate modified were recorded before and after fluoride sorption on FTIR spectrophotometer (Cary 630-Agilent). The prominent bands for the functional groups found on the surface of PFR

Table 1
The models used to evaluate breakthrough curves

Models	Linear equations	Description	Reference
Bed depth service time (BDST) model	$t = \frac{N_o Z}{C_o v_1} - \frac{1}{K_a C_o} \ln \left(\frac{C_o}{C_b} - 1 \right)$	BDST plot expressed a linear relationship, time ' t ' vs ' Z ' bed depth, N_o = Adsorption capacity of biomass (mg/L), K_a = Rate constant (L/mg min) both parameters are calculated from the intercept and slope of the equation.	[26] [22]
Yoon-Nelson (Y-N) model	$\ln \left(\frac{C_o}{C_o - C_e} \right) = k_{\text{YN}} t - \tau k_{\text{YN}}$	Yoon and Nelson evaluated the linear correlation of $\ln \left(\frac{C_o}{C_o - C_e} \right)$ vs time. k_{YN} = Rate constant (min^{-1}), τ = Time require for 50% effluent concentration (min).	[30] [27]

and PXFR, before and after defluorination is provided in (Table 2). Spectra identified the presence of oxygen(O), nitrogen (N), and sulfur (S) containing groups such as; carboxylic (C=O), hydroxyl (O–H), amine (NH₂), and xanthate (C=S). Remarkable variation in FTIR spectra was observed after protonation of xanthate modified material. After protonation of biomass, amines (-NH₂) are susceptible to become acid site (NH₃⁺) for fluoride (F⁻) binding. A shifting of the peak position for amines was observed from 1,455.111 to 1,451.273 cm⁻¹ (corresponding to protonated amines), as shown in Fig. 2 (I) [31]. A sharp band (C–H) 2,914.401 cm⁻¹ of simple biomass shifted to 2,883.416 cm⁻¹ after xanthate modification [32]. A similar trend of distinct peak variation was observed after xanthantation of biomass as visible in the FTIR spectra of PXFR.

The topography and surface features of the biomass were observed by Scanning Electron Microscopy (SEM). The SEM-EDS micrographs of simple protonated and xanthate modified *Ficus religiosa* were obtained on Nova Nano 450 (Fig. 2). Comparison of SEM micrograph of PFR and PXFR has explored a distinct transformation of biosorbent after xanthation (insertion of Sulphur). The surface of xanthate modified biomass was more asymmetrical and rough compared with simple protonated biomass imparting the higher sorption capacity to PXFR. The EDS graphs of PFR and PXFR

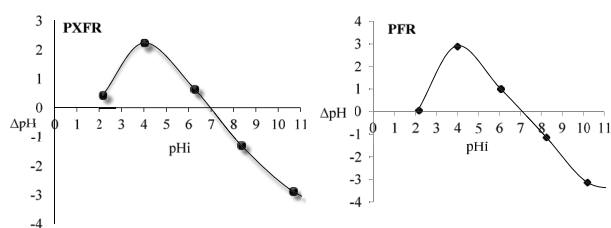


Fig. 1. Point of zero charge pH (pH_{pzc}).

Table 2
Functional groups peak values of simple protonated and xanthate protonated *Ficus religiosa*, before and after fluoride sorption

Absorbent	Wavenumber before sorption (cm ⁻¹)	Wavenumber after sorption (cm ⁻¹)	Functional group
PFR	3,334.840	3,332.937	O-H stretching
	2,914.401	2,917.890	C-H stretching
	1,649.438	1,632.014	C=C broadband
	1,455.111	1,451.273	NH ₂
	1,507.166	1,507.702	C=O
	1,226.897	1,229.141	C-N deformation
	1,030.002	1,029.738	C-O deformation
PXFR	3,322.866	3,353.118	O-H stretching
	2,883.416	2,913.918	C-H stretching
	1,634.052	1,592.428	C=C
	1,455.469	1,506.756	NH ₂ deformation
	1,506.772	1,419.541	C=O
	1,224.974	1,225.194	C-N deformation
	1,018.75	1,019.93	C=S deformation

contain carbon and hydrogen peaks while PXFR shows an additional peak of sulfur; that indicates the incorporation of xanthate on the surface of biosorbent, Fig. 2 (II).

The characterization of the biosorbent materials shows that XPFR is capable of attracting/adsorbing the negatively charged fluoride ions in an acidic pH, more effectively than PFR due to more roughness and S present in it.

3.2. Fixed bed column studies

3.2.1. Effect of concentration on fluoride biosorption

Biosorption of fluoride on PFR and PXFR was investigated using various initial fluoride concentrations of 25, 50 and 100 mg/L. Breakthrough curves for both PFR and PXFR were obtained on different concentration and bed heights (5, 15 and 30 cm) at a constant flow rate of 2 mL/min. A higher initial concentration should cause relatively faster enrichment of the column than at a lower concentration. The values of breakthrough and exhaust times decreased from 255 to 165 min and from 750 to 345 min respectively for PFR, when initial concentration increased from 25 to 100 mg/L. A similar trend was observed for PXFR. The initial concentration of fluoride solution was found to have an inverse relationship with breakthrough time (t_b) at a particular bed height (30 cm). The bed height showed a direct relationship with the breakthrough and exhaust times. It was founded that exhaust time value for both adsorbent PFR and PXFR were increased with bed heights (5–30 cm), from 105 to 705 min and from 150 to 1,065 min respectively at 50 mg/L concentration (Fig. 3). An increase in bed height exhibits an increase in the amount of adsorbent. Hence, the breakthrough, as well as exhaust times, increased with bed height for both of the adsorbents.

The values of removal efficiency $R\%$ and sorption capacity q_e for biosorbents (PFR and PXFR) were calculated via Eqs. (3) and (2) respectively (Table 3). Column bed height (5–30 cm) unveiled a direct relationship with $R\%$ (removal efficiency); $R\%$ values were significantly increased from 53.84% to 97.91% with increased bed height and slightly decreased from 96.00% to 92.59% with increasing concentration (25–100 mg/L) for XPFR, due to rapid enrichment of binding sites [33,34]. The same trend was observed for PFR.

3.2.2. Effect of bed height on fluoride sorption

Bed height of column has a linear relationship with the sorption efficiency of biomass. The quantity of biomass packed in the column increased from 1.3 to 7.8 g with bed height 5–30 cm. Sorption capacity and breakthrough times were found in direct relation with the bed height of the column. The surface of PXFR possesses more binding site compared with PFR, consequently, xanthate modified biomass contain more sorption capacity relative to simple adsorbent (Fig. 4). Bed height of column had a linear relationship with breakthrough time. As the height of bed increased from 5 to 30 min breakthrough time also increased from 30 to 255 min and from 60 to 375 min for PFR and XPFR respectively at 50 mg/L concentration. At constant bed height (30 cm) breakthrough time of fluoride decreased from 750 to 345 min and from 1,335 to 525 min for PFR and PXFR respectively with an increase in the concentration of fluoride (from 25

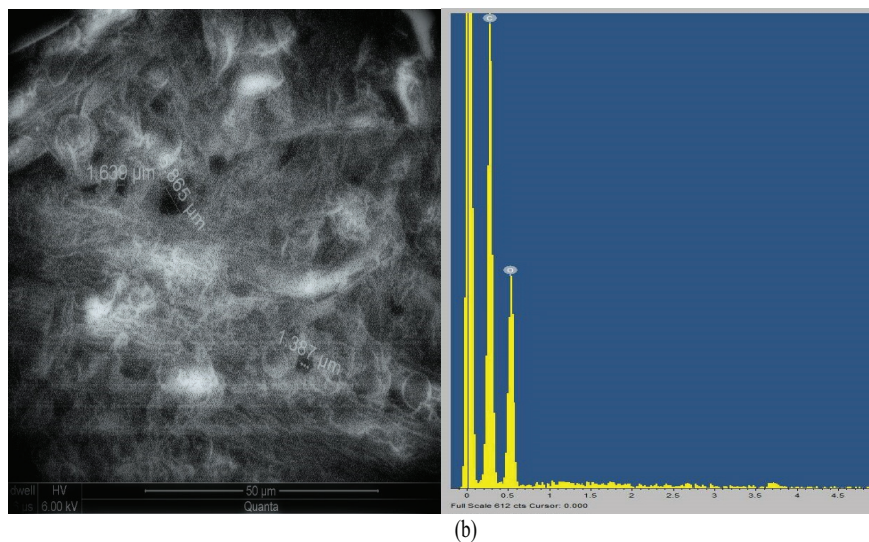
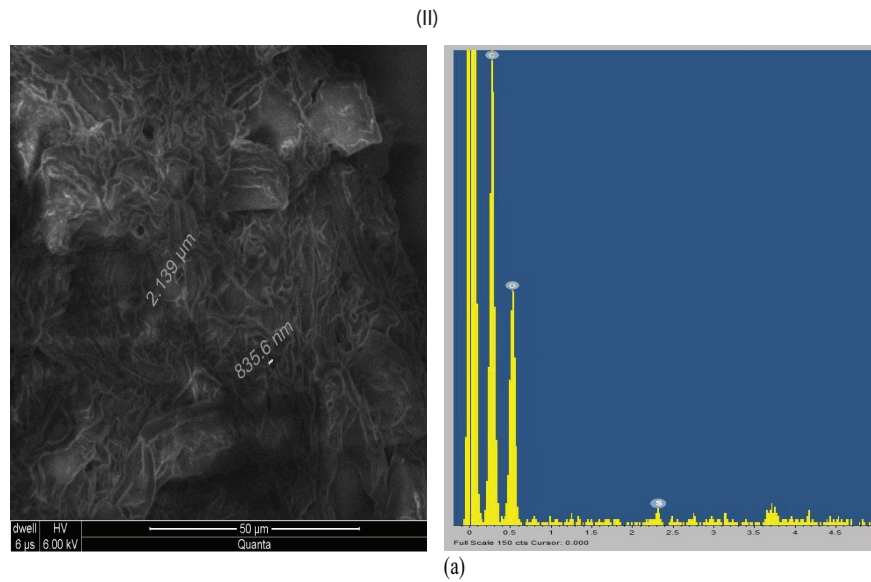
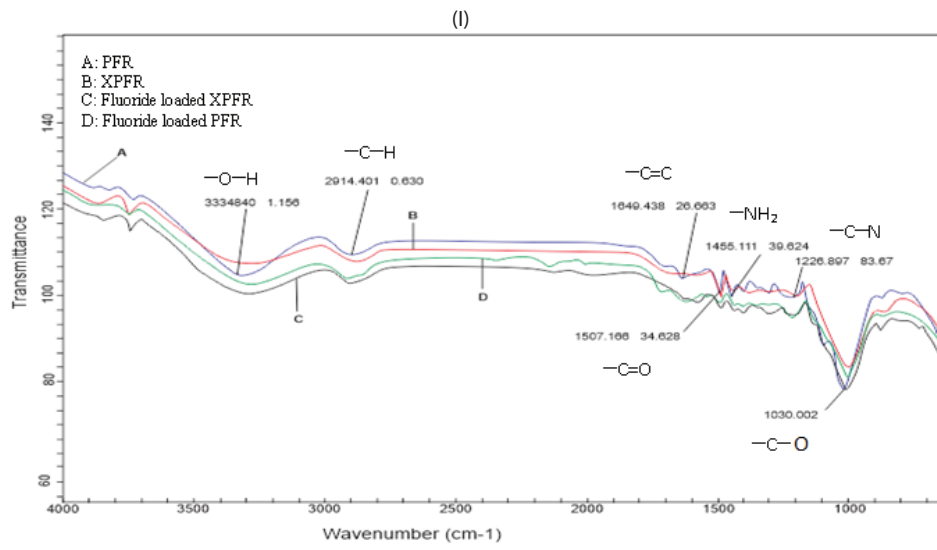


Fig. 2. (I) FTIR of (A) PFR, (B) XPFR, (C) Fluoride loaded XPFR, (D) Fluoride loaded PFR; (II) SEM-EDX of PXFR (a) and PFR (b).

to 100 mg/L). Exhaust time of column exhibited a similar trend for simple and xanthate modified biomass. Biosorption capacity q_e (mg/g) and $R\%$ values were increased with the concentration of fluoride solution [22].

3.2.3. Competitive sorption studies

A comprehensive summary of defluoridation studies in fixed bed column (with various materials) is provided in Table 4. The biosorbents such as Java plum (*Syzygium cumini*), *Eichhornia crassipes*, Sugarcane charcoal, Zr(IV)-loaded dried orange juice residue and Tamarind seed showed biosorption capacity ranging from 3.12 to 18.18 mg/g. While, the low sorption capacity was exhibited between 0.094 and 1.42 mg/g by Granular acid-treated bentonite and *Tamarindus indica* respectively. In present studies, the protonated xanthate modified *Ficus religiosa* showed high sorption capacity (19.72 mg/g) compared with other biosorbents as given in Table 4.

3.3. Mathematical modeling

3.3.1. Bed depth service time (BDST) model

BDST model is widely used for fixed bed sorption study. BDST model was applied to experimental data of fixed bed

column. The bed heights vs. service time at 10% and 90% column efficiency provided straight line plots. The model was successfully applied on experimental data obtained for simple (IPFR) and modified (IPXFR) adsorbent at a constant flow rate (2 ml/min) and concentration of fluoride solution (50 mg/L). The linear plots for both adsorbents (IPFR and IPXFR) are given in Fig. 5. BDST parameters (capacity of column (N_o) and (Rate constant (K_a)) were calculated by slope and intercept of equation respectively (Table 5). The value of the regression coefficient (R^2) was approximately 0.99 that indicates the validity of the BDST model. The K_a for IPXFR was found relatively greater than that for IPFR. A similar trend was observed for N_o values.

3.3.2. Yoon-Nelson(Y-N) model

In the present study, Y-N model parameters (k_{YN} and τ) were also evaluated using linear regression analysis. The results are provided in Fig. 6. The breakthrough time (τ) in this case was selected at 50% of C_o ; it meant that the column got enriched in 2τ time. The values of k_{YN} for both adsorbents (PFR and PXFR) indicated an inverse relation with bed height. As the height of the bed increased from 5 to 30 cm the value of k_{YN} was decreased (from 0.028 to 0.0098 min^{-1} and from 0.044 to 0.0108 min^{-1}) for IPFR and IPXFR respectively.

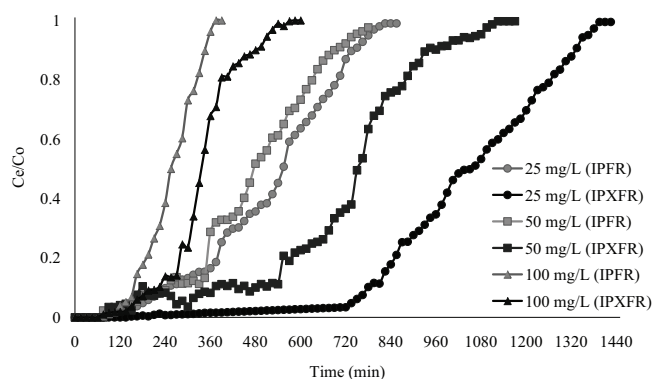


Fig. 3. Breakthrough curves of Fluoride biosorption on same bed height ($Z = 30$ cm) but on different concentrations (25, 50 and 100 mg/L).

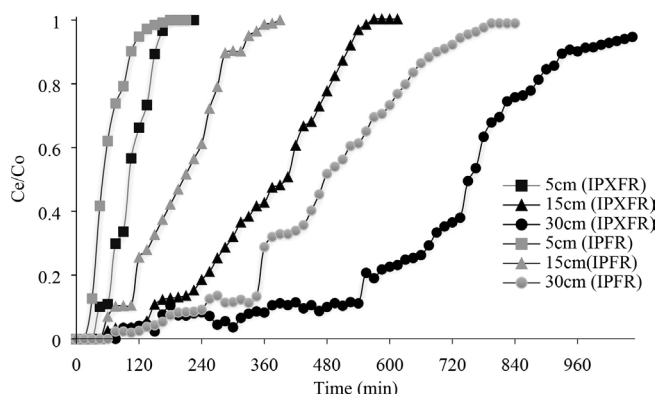


Fig. 4. Comparative breakthrough curves of Fluoride biosorption on different bed heights (5, 15 and 30 cm, $C_o = 50$ mg/L).

Table 3
Breakthrough parameters for Fluoride sorption on PFR and PXFR

Biomass	Fluoride concentration	Bed depth (cm)	Service time (min)		q_e (mg/g)		$R\%$	
			10%	90%	10%	90%	10%	90%
PFR	25	30	255	750	1.63	4.80	31.48	92.59
	50	5	30	105	2.30	8.07	15.38	53.84
	50	15	105	300	2.69	7.69	26.92	76.92
	50	30	255	705	3.26	9.03	35.41	97.91
	100	30	165	345	4.23	8.85	45.83	95.83
PXFR	25	30	780	1335	7.22	9.58	55.91	74.19
	50	5	60	150	6.66	16.66	33.33	83.33
	50	15	150	525	5.55	19.44	27.02	94.59
	50	30	375	1065	6.94	19.72	32.05	91.02
	100	30	225	495	8.33	18.33	39.47	86.84

The value of τ exhibited the linear relationship with bed height at constant fluoride concentration (50 mg/L) and flow rate of 2 mL/min. The experimental and calculated value of τ (time required for 50% effluent concentration) at 5, 15, and 30 cm bed height and 50 mg/L concentration show close proximity with each other detail provided in Table 6. The difference in experimental and calculated τ values is expressed as $D\%$ ($= 100 \times (\tau_{cal} - \tau_{exp}) / \tau_{exp}$). The difference was found to be less than 5% for all the cases. Hence, Y-N model could be applied for the column data. On the other side, the values of the coefficient of determination ranged from 0.98–0.94 indicated the validity of Y-N model in certain cases only. So, it can be concluded that Y-N model was not suitable for the experimental data in all cases. The comparison of both models indicated that R^2 values were greater than 0.98 for BDST rather than for Y-N; so BDST model was more suitable to explain the column data for the simple and modified materials for fluoride uptake.

As shown in Table 4, the comparative study of IPFR and IPXFR indicated the high efficiency of IPXFR compared with that of IPFR because more binding sites were available on the surface of protonated-xanthate-modified *Ficus religiosa*. Maximum sorption capacity values for simple and modified biomass were observed as 9.03 and 19.72 mg/g (at $C_o = 50$ mg/L, $Z = 30$ cm) respectively. So, IPXFR was found as a better candidate for the removal of fluoride ions from its aqueous solutions.

Table 4
Different plant materials were used for the remedy of Fluoride ion

Adsorbent	F ⁻ inlet concentration (mg/L)	Bed depth (cm)	Flow rate (mL/min)	Biosorption capacity (mg/g)	Model ^a	References
Granular acid-treated bentonite	2.85	28	2.42	0.094	T, EBCT	[35]
<i>Tamarindus indica</i>	2.0	15.0	2.0	1.42	T	[36]
Java plum (<i>Syzygium cumini</i>)	20.0	100	12.0	3.12	T, B	[37]
<i>Eichhornia crassipes</i>	10.0	18.0	1.7	4.4	L	[38]
Sugarcane charcoal	10.0	8.2	4.34	7.33	T, B	[39]
Zr(IV) loaded dried orange juice residue	14.3	2.4	2.55	10.38	B, T	[33]
Tamarind seed	20.0	8.2	2.0	18.18	T	[40]
Protonated Xanthate <i>Ficus religiosa</i>	50	5.0	2.0	19.72	Y-N, B	This study

^aB = Bed depth service time (Bohart-Adams) model; EBCT = Empty bed contact time; L = Lagergren plot; T = Thomas; Y-N = Yoon-Nelson.

Table 5
BDST parameters values for fluoride biosorption

Biomass	Initial concentration (mg/L)	Breakthrough concentration (%)	BDST equation for fluoride	R^2	N_o	K_a
PFR	50	10	$t = 9.0789Z - 21.316$	0.994	512.95	1.30E-03
		90	$t = 24.237Z - 33.947$	0.993	1369.3	8.17E-04
PXFR	50	10	$t = 12.789Z - 18.158$	0.983	722.57	1.53E-03
		90	$t = 36.553Z - 29.211$	0.999	2065.2	9.49E-04

3.4. Fluoride sorption mechanism

The stretches of NH_2 in FTIR spectra of protonated xanthate (Fig. 2-I) indicate the existence of hydrogen (H) bonding between fluoride (F^-) and (NH_3^+) protonated amine. C=S group also participated in binding of fluoride ions. Protonated xanthate biomass may act as hard acid (protonated NH_3^+) to bind with electronegative hard base fluoride ion.

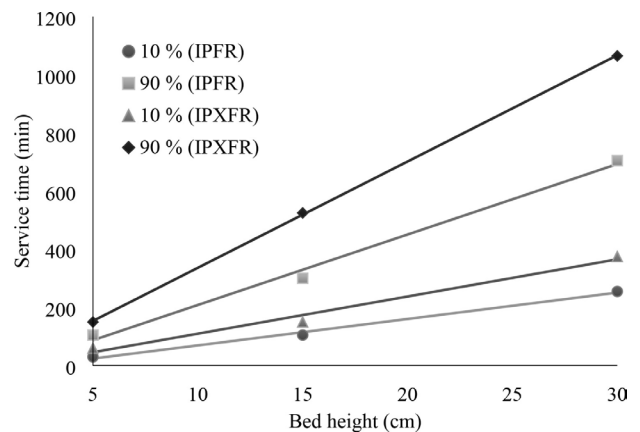


Fig. 5. BDST model for fluoride biosorption on IPFR and IPXFR ($C_o = 50$ mg/L and flow rate 2 ml/min).

Table 6
Yoon-Nelson model parameters for Fluoride biosorption

Biomass	Concentration	Bed height	$K_{YN}(\text{min}^{-1})$	τ calculated (min)	τ experimental (min)	D%	R^2
PFR	50	5	0.0284	47.83	50.0	2.16	0.96
		15	0.0244	209.70	210.0	0.29	0.94
		30	0.0098	477.44	480.0	2.55	0.98
PXFR	50	5	0.0445	100.79	105.0	4.20	0.96
		15	0.0195	401.12	405.0	3.87	0.98
		30	0.0108	752.56	755.0	2.43	0.96

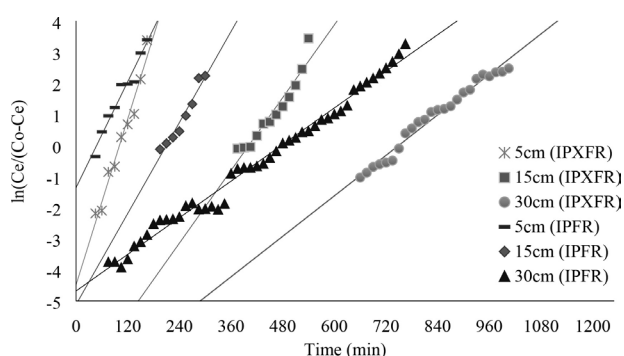


Fig. 6. Yoon-Nelson model applied on various bed height (5–30 cm) for fluoride sorption (C_o 50 mg/L, v = 2 mL/min).

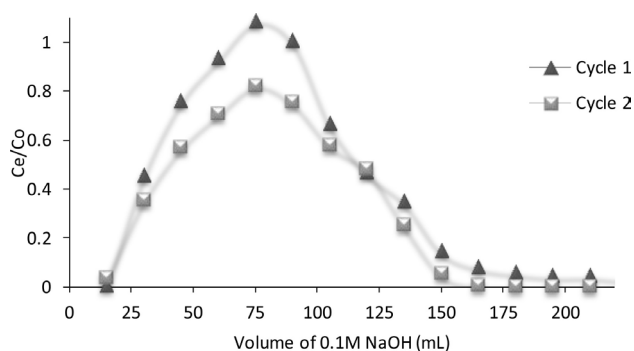


Fig. 7. Regeneration cycles of IPXFR in fixed bed column for defluoridation using 0.1 M NaOH solution (C_o = 50 mg/L, Z = 5 cm and v = 2 mL/min).

Fluoride was removed by electrostatic interaction between protonated amine, xanthate, and fluoride.

3.5. Desorption studies

To study the recycling ability of the studied biosorbent, desorption of sorbed fluoride ions is necessary. Being an anion, fluoride ion was desorbed by increasing the pH of solution above its pH_{pzc} . The pH was increased using NaOH (0.1M). Since IPXFR showed the better uptake results, so desorption was studied by the xanthate modified adsorbent. In addition, desorption was studied in a continuous mode. During the first cycle of desorption, the maxima was achieved in just 37 min (75 mL of eluting agent). The column was found to regenerate fully in 75 min (150 mL of eluting agent). The column was run for a second adsorption-desorption cycle. In

the second cycle, the times for maxima and full regeneration remained unchanged (Fig. 7). The removal percentage ($R\%$) of the column was relatively reduced during this cycle from 100% to 75.67%. The decrease in the percent removal could be attributed to the deterioration of IPXFR in the presence of a strong alkali solution.

4. Conclusion

The present studies reported the use of protonated and xanthate modified *Ficus religiosa* branch powder for the removal of fluoride ions from its aqueous solution in an industrially viable continuous flow mode. The branch powder was easily available, and the modification process is very simple as well as environmentally friendly. The materials were characterized by various analytical techniques. The breakthrough curves obtained for both types of materials was S-shaped. The effects of the amount of materials in column (bed heights) and the inlet fluoride concentration were studied at a fixed flow rate. The experimental data were applied for the BDST as well as Y-N models. The coefficient of determination and the model parameters indicated that the BDST model was a better fit than Y-N model. The breakthrough parameters indicated that xanthate modified material was a better adsorbent for fluoride ions in the continuous flow mode understudied set of conditions. The sorption capacity for simple material was 9.03 mg/g and that for xanthate modified material was 19.72 mg/g. The modified material was also studied for its recycling ability. It was found that NaOH (0.1M) was able to fully desorb fluoride ions in around 75 min, under continuous flow conditions. The results suggested that modified material was comparatively better than the simple one for the defluoridation of aqueous solutions in continuous flow mode.

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