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Statistical optimization and characterization of fluoride biosorption using dead microbial biomass

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Excessive fluoride consumption (> 2.0 mg/L) results in fluorosis, teeth staining, or bone weakening. It is critical to concentrate on the defluoridation of water. Adsorption has been a conventional method of fluoride removal in aqueous solution. Biosorbents are cost-effective, easily obtainable, and ecologically sustainable sources of adsorbents. In this study, aqueous fluoride solution is treated with dead bacterial biomass. Effects of process conditions like initial fluoride concentration, biomass dosage, pH, temperature, and contact time have been studied. Central Composite Design (CCD) with 30 experiments is performed. The centre point experimental conditions have been repeated 6 times. The optimum fluoride biosorption of 76.89% is observed after 8 h of biosorption with 3.25 mg L^{-1} initial fluoride concentration, 775 mg L^{-1} of biomass dosage, at temperature 55 ℃ and pH 4.5. R^2 value of the experimental design is found to be 0.92. Biosorption kinetic studies revealed that fluoride biosorption followed a pseudo-second-order kinetics and adsorption isotherm is best described by Freundlich isotherm. The biosorption efficiency of immobilised biosorbent is also studied using column approach. Biosorbent is characterised using SEM, FTIR and EDX techniques. The desorption and recyclability studies suggest that dead bacterial biomass could serve as a potential biosorbent for fluoride biosorption.

Keywords: Adsorption isotherm, Adsorption kinetics, Biosorbent, Defluoridation, Dead microbial biomass, Fluoride biosorption, Response surface methodology

Introduction

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 among the major pollutants of ground water contamination[1]. The World Health Organization (WHO) has recommended a permissible limit of 1.5 mg L^{-1} of fluoride in drinking water (UNEP, 1984). At trace quantity, fluoride is beneficial for maintenance of healthy bones and teeth in humans[2]. The deficiency of fluoride causes development of dental carries, lack of enamel formation and bone fragility [3]. However, consumption of drinking water with fluoride concentration higher than the intake limit influences the metabolism of calcium and phosphorus in human body. It leads to health disorders like dental and skeletal fluorosis, neurological disorders, thyroid disorder, infertility, liver and kidney damages[4]. Countries such as Mexico, South Africa, central and western China, and India are identified for excess fluoride concentration in drinking water [5]. Worldwide over 200 million people were reported to consume water with fluoride concentration higher than the permissible limits of consumption [6]. In India, more than 15 states have rich fluoride concentration in groundwater [7] and 25 million people are affected by excess fluoride consumption [8].

Fluoride contamination in water mainly happens through industrial effluents from semiconductors manufacturing, electroplating, glass and ceramic production industries, aluminium smelters and coal fired power plants[9]. It is also released into water naturally by weathering of rocks rich in fluoride [10]. Technologies such as nanofiltration[11], electro-coagulation [12], membrane separation [13], ion exchange process [14], reverse osmosis[15], adsorption[16], [17] chemical coagulation [18] and precipitation [6] have been adapted for defluorination of water. However, there are various limitations such as high cost, energy intensive and production of contaminants after treatment while employing these methods [19]. Adsorption is a conventional technique with relatively greater advantages in water treatment. Cost effectiveness [20], regeneration of adsorbents[21], easy implementation, and maintenance [22] are a few advantages of using adsorption over other strategies. Since, biosorbents are naturally abundant and have less harmful effects on environment they are preferred than chemical sorbents. Biosorbents can be prepared either from plant or animal sources[23], [24] and microbial sources

such as bacteria, fungi, algae[25-27]. In this study, bacterial isolate from fluoride-containing water was used as biosorbent. The present study focuses on studying the influence of process parameters such as biosorbent dosage, initial fluoride concentration, pH, temperature, contact time on fluoride biosorption. Furthermore, interactions among process conditions were studied using Central Composite Design (CCD) of response surface methodology (RSM). Biosorbents were characterized using Scanning Electron Microscopy (SEM), Fourier Transform Infra Red Spectroscopy (FTIR), and Energy Dispersive X-Ray spectroscopy (EDX).

Experimental Section

Preparation of biosorbent for fluoride adsorption

Water samples collected from the villages of Virudhungar district were serially diluted and spread in nutrient agar plates. Isolated colonies were grown in nutrient medium (Himedia, India) and glycerol stocks were maintained at -80 °C for future use. Overnight cultures of the 4 bacterial isolates with unique morphology were centrifuged at 10,000 rpm for 10 min. The pellets were rinsed with sterile double distilled water (ddH_2O) and autoclaved at 121°C, 15 psi for 20 min and used as biosorbent for fluoride biosorption.

Characterization of biosorbent

FTIR spectrum was used to identify the functional groups available at the surface of biosorbents that are responsible for fluoride binding from the solution onto biosorbent. The morphology and porosity of biosorbent was analysed using SEM. The surface images before and after biosorption were taken to study the changes in the surface topography of biosorbent. EDX was used for elemental analysis of the biosorbents before and after fluoride adsorption[28].

Fluoride estimation in aqueous solution

Fluoride estimation was performed using zirconium-alizarin red reagent method. About 0.03 g of Zirconiumoxychloride and 0.035 g of alizarin red were dissolved in 25 mL of double ditilled (dd) H_2O followed by the addition of 2 mL of conc. H_2SO_4 and 6mL of conc. HCl. It was then made upto 50 mL with ddH_2O. Standard fluoride solutions were prepared in the range of 2 to 10 mg L^{-1} from a stock of 100 mg L^{-1} prepared with NaF (221 mg NaF in 1 L of dd H_2O). 5 mL of each standard was taken and 0.5 mL of zirconium-alizarin red reagent was added and incubated in dark for about 5 min and absorbance was measured at 525 nm using spectrophotometer. A graph was constructed with fluoride concentration and absorbance[29].

Selection of biosorbents based on sorption efficiency

Briefly, 100 mg L^{-1} of each biosorbent prepared was added to NaF solution containing 5 mg L^{-1} fluoride (F^-) ions in separate flasks and kept in agitation at 160 rpm for about 24 h. The solution was then centrifuged (10,000 rpm for 10 min), and residual fluoride present in the supernatant was estimated. % fluoride biosorption was calculated using Eq (1)

$$\%\ Fluoride\ biosorption\ = \frac{(C_i - C_f)}{C_i} * 100 \qquad ...(1)$$

Where C_i is the initial fluoride concentration (mg L^{-1}) and C_f is the final fluoride concentration (mg L^{-1}).

Effect of process parameters on fluoride biosorption

The effects of process conditions on fluoride biosorption were determined one factor at a time. Fluoride biosorption studies were performed in 100 mL conical flasks with a working volume of 50 mL NaF solution. The effect of initial fluoride concentration (1, 2.5, 5, 7.5 mg L^{-1}), biosorbent dose (200 to 1000 mg L^{-1}), contact time (1 to 8, 12 and 24 h), temperature (25, 30, 35, 40, 45, 50 °C) and pH (2 to 9) were determined one at a timewhile keeping other parameters constant. Fluoride concentration in the supernatant was estimated after centrifugation. % fluoride biosorption was calculated using Eq. (1) whereas adsorption capacity was calculated using Eq. (2)

$$\boldsymbol{q_e} = \frac{(\boldsymbol{c_e} - \boldsymbol{c_i})\,\boldsymbol{V}}{\boldsymbol{w}} \qquad ...(2)$$

Where, q_e is the amount of fluoride adsorbed at equilibrium (mg g^{-1}), $c_e$is the equilibrium concentration (mg L^{-1}), c_i is the initial fluoride concentration in the solution (mg L^{-1}), V represents volume of solution (mL), and w is the weight of the biosorbent (mg). Adsorption kinetics and isotherm were studied with biosorbent dosage of 100 mg L^{-1} with initial fluoride concentration 5 mg L^{-1}, temperature 37 °C and pH 7.

Column approach for fluoride biosorption

Initially 2% (w/v) sodium alginate solution was mixed with 0.5% (w/v) of biosorbent and kept undisturbed for 12 h. Beads were then prepared in 200 mL of 0.2 M $CaCl_2$ solution for column preparation. Biosorbent immobilized sodium alginate beads were then packed in a glass column for fluoride

Table 1 — CCD for fluoride biosorption

Std	Run	A:Initial fluoride concentration mg L^{-1}	B:Biosorbent dosage mg L^{-1}	C:pH	D:Temperature °C	% fluoride biosorption	
						Actual	Predicted
1	11	3.25	325	4.5	35	89.94	91.37
2	14	7.75	325	4.5	35	83.69	76.60
3	2	3.25	775	4.5	35	80.26	79.92
4	6	7.75	775	4.5	35	69.87	64.87
5	30	3.25	325	9.5	35	78.65	76.68
6	10	7.75	325	9.5	35	59.23	62.92
7	16	3.25	775	9.5	35	77.58	72.00
8	9	7.75	775	9.5	35	55.25	57.17
9	19	3.25	325	4.5	55	86.52	83.21
10	25	7.75	325	4.5	55	72.48	78.19
11	29	3.25	775	4.5	55	80.45	76.89
12	18	7.75	775	4.5	55	70.25	70.77
13	23	3.25	325	9.5	55	59.24	65.21
14	3	7.75	325	9.5	55	62.32	61.21
15	4	3.25	775	9.5	55	60.03	65.67
16	17	7.75	775	9.5	55	61.89	60.57
17	8	1	550	7	45	96.52	96.71
18	1	10	550	7	45	75.69	76.82
19	7	5.5	100	7	45	70.36	68.03
20	24	5.5	1000	7	45	52.27	55.92
21	21	5.5	550	2	45	60.63	66.2
22	12	5.5	550	12	45	45.55	41.30
23	20	5.5	550	7	25	79.22	85.47
24	5	5.5	550	7	65	85.67	80.47
25	15	5.5	550	7	45	87.75	89.35
26	22	5.5	550	7	45	92.14	89.35
27	26	5.5	550	7	45	85.69	89.35
28	28	5.5	550	7	45	89.19	89.35
29	13	5.5	550	7	45	90.45	89.35
30	27	5.5	550	7	45	90.89	89.35

adsorption. 5 mg L^{-1} of fluoride solution (pH 7) was topped up to the column at the flow rate 100 mL h^{-1}[Ref 30]. Residual fluoride concentration was determined in outlet collected at the end of every hour.

Optimization of fluoride biosorption using Central Composite Design

Design expert 13 trial version was used to generate the design for optimization of fluoride biosorption and statistical analyses. Central composite design was used to investigate the response function of four independent variables namely initial fluoride concentration (A; X_1), biosorbent dosage (B; X_2), pH (C; X_3), temperature (D; X_4,) and % fluoride biosorption was taken as the response Y as shown in Table 1. The response of the model can be expressed using the following equation[31].

$$Y = f(X_1, X_2, X_3 \ldots\ldots, X_n) \pm e \quad \ldots(3)$$

Where, Y is the response, f is the response function, X_i are the independent variables and e is the experimental error. RSM calculates f using an appropriate polynomial for independent process variables. The quadratic model for RSM may be expressed as[32].

$$Y = \beta_0 + \sum \beta_i X_i + \sum \beta_i X_i^2 + \sum \beta_{ij} X_i X_j \; i = 1,2 \; and \; 3 \quad \ldots(4)$$

Where, Y is the predicted response, β_0 is the constant coefficient, βi is the linear coefficient, βij is the quadratic coefficients, Xi and Xj are the values of independent process variables.

Fluoride desorption from biomass

Fluoride desorption study was carried out to evaluate the potential of biosorbents for reuse. Briefly, after adsorption of fluoride ions onto the biosorbents (initial fluoride concentration – 1 mg L^{-1}, temperature – 45 °C, 8 h), the biosorbent was separated and added to aqueous solution at varying pH (4 to 12). 0.1 N HCl and 0.1 N NaOH were used to adjust pH of the aqueous

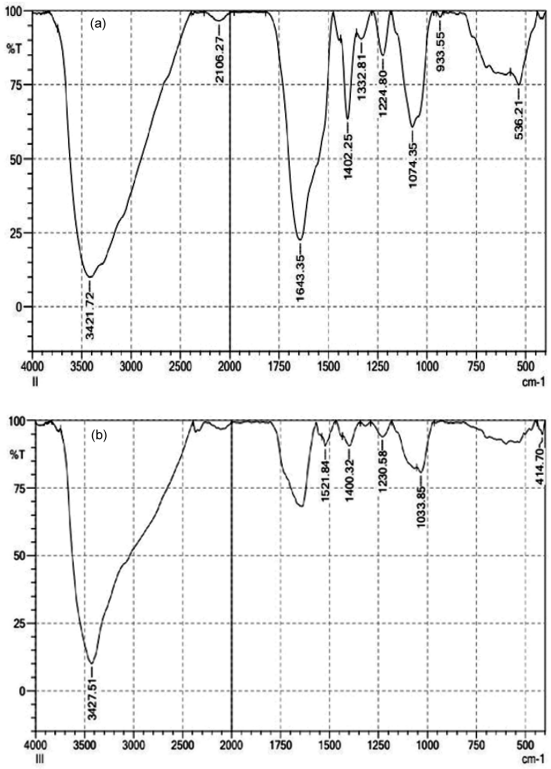

Fig. 1 — FTIR spectra of the biosorbent (a) before and (b) after adsorption

solutions. %fluoride desorption was calculated by estimating fluoride concentration in aqueous solution. The biomass was subjected to repeated cycles of adsorption and desorption after washing with deionized water followed by drying. The recyclability of the biosorbent was investigated[33,34].

Results and Discussion

Biosorbent characterization

FTIR spectrum revealed the presence of various functional groups present on the biosorbent surface for fluoride adsorption. Distinct peaks at 3421.72, 2106.27, 1643.35, 1402.25, 1332.81, 1224.80, 1074.35 and 536.21 cm^{-1} were observed in biosorbent before adsorption. The band at 3421.72 cm^{-1} represents the O-H stretching vibrations of alcoholic hydroxyl group (Fig. 1a). The bands at 1643 cm^{-1} and 1402.25 cm^{-1} may be to the asymmetric and asymmetric vibrations of carboxyl group respectively. Peak at 1074.35 cm^{-1} is because of C-O-C vibration. 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} were observed in biosorbent after fluoride adsorption (Fig. 1b). These shifts in the bands after sorption indicate their involvement in fluoride biosorption process. Presence of a peak at 1116.78 cm^{-1} reveals the C-F interactions in biosorbent after adsorption process which is missing in the FTIR spectrum of biosorbent before adsorption.

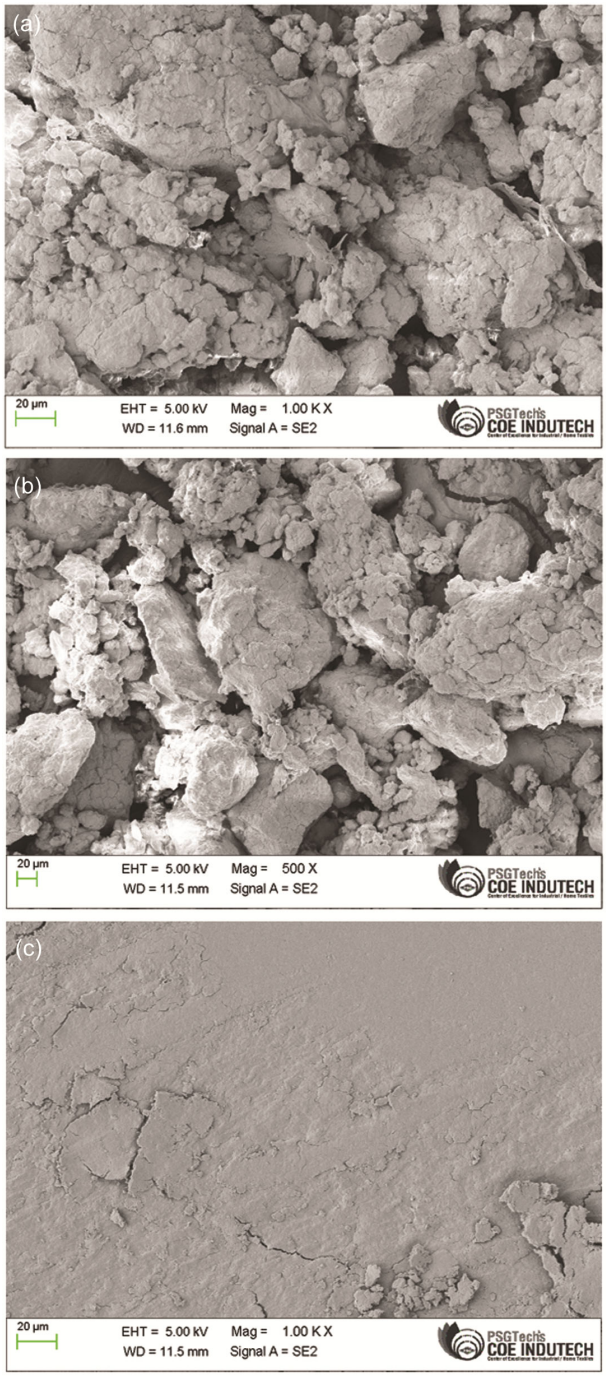

Fig. 2 — SEM images of the biosorbent (a) before adsorption, (b) added with dd H_2O and (c) after adsorption

SEM images taken before and after fluoride biosorption are shown in Fig. 2. Fig. 2a is the surface

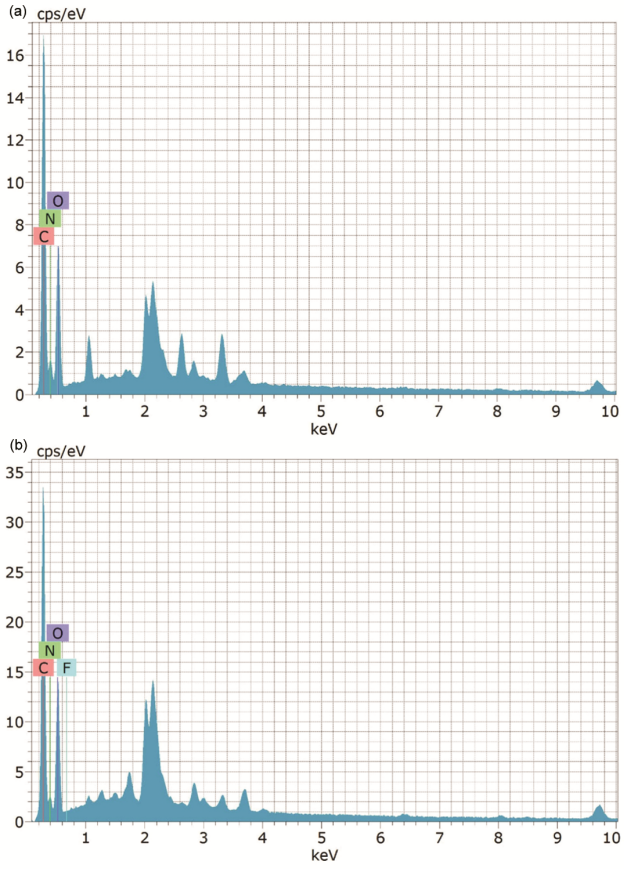

Fig. 3 — EDX analysis of the biosorbent (a) before and (b) after adsorption

image of biomass and Fig. 2b shows the surface characteristics of biomass treated with double distilled water and Fig. 2c shows the biosorbent characteristics after fluoride adsorption. Microporous structure of the biosorbent is clearly visible in the images captured before biosorption (Figs 2a and 2b) whereas in the images taken after biosorption (Fig. 2c), a structural modification has happened due to accumulation of fluoride on to the surface of biosorbent. Surface porous characteristic of adsorbent is an important feature that supports efficient adsorption. Since, biosorbent used in this study had microporous surface, its biosorption efficiency is comparable with the already reported results[35]. Moreover, the EDX results of biomass before (Fig. 3a) and after adsorption (Fig. 3b) clearly indicated the difference in elemental composition of biomass. The presence of fluoride in biomass after adsorption was confirmed.

Selection of biosorbent for fluoride biosorption

Fig. 4 shows %fluoride biosorption potential of biosorbents prepared using the isolates obtained from

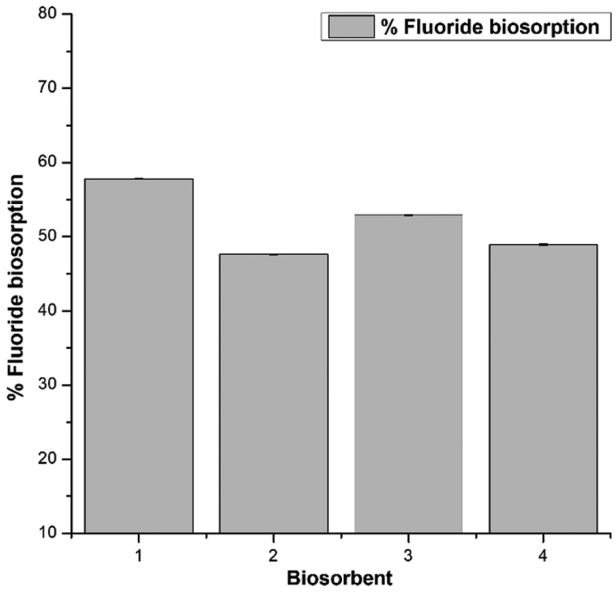

Fig. 4 — % Fluoride adsorption of biosorbents

water. The standard graph for fluoride estimation is given in Supplementary Information. Out of the four biosorbents, biosorbent-1 showed better fluoride biosorption efficiency. The %fluoride biosorption was around 60% which is higher than other biosorbents used in the experiment and comparable with the defluoridation efficiency of already reported dead bacterial biomass.

Effects of process parameters on fluoride biosorption

Effect of initial fluoride concentration

Fluoride biosorption with varying initial fluoride concentration (1, 2.5, 5, 7.5 mg L^{-1}) was studied. 99.49% fluoride biosorption was observed with 1 mg L^{-1} initial fluoride concentration. A drop in % biosorption was observed with increasing initial fluoride concentration (Fig. 5a). The reason for such an observation is at low initial fluoride concentration, number of adsorption sites available is more. The availability of adsorption sites is limited over an increased range of initial fluoride concentration in aqueous solution. Subsequently, the rate of adsorption also decreases. On the other hand, an increase in adsorption capacity was observed with an increase in initial fluoride concentration. Maximum adsorption capacity (2.4487 mgg^{-1}) was observed at 5 mg L^{-1}, and it is taken as the optimum initial fluoride concentration for fluoride biosorption. A similar trend had been reported in previous studies conducted using biosorbents prepared from jamun leaf ash, wheat

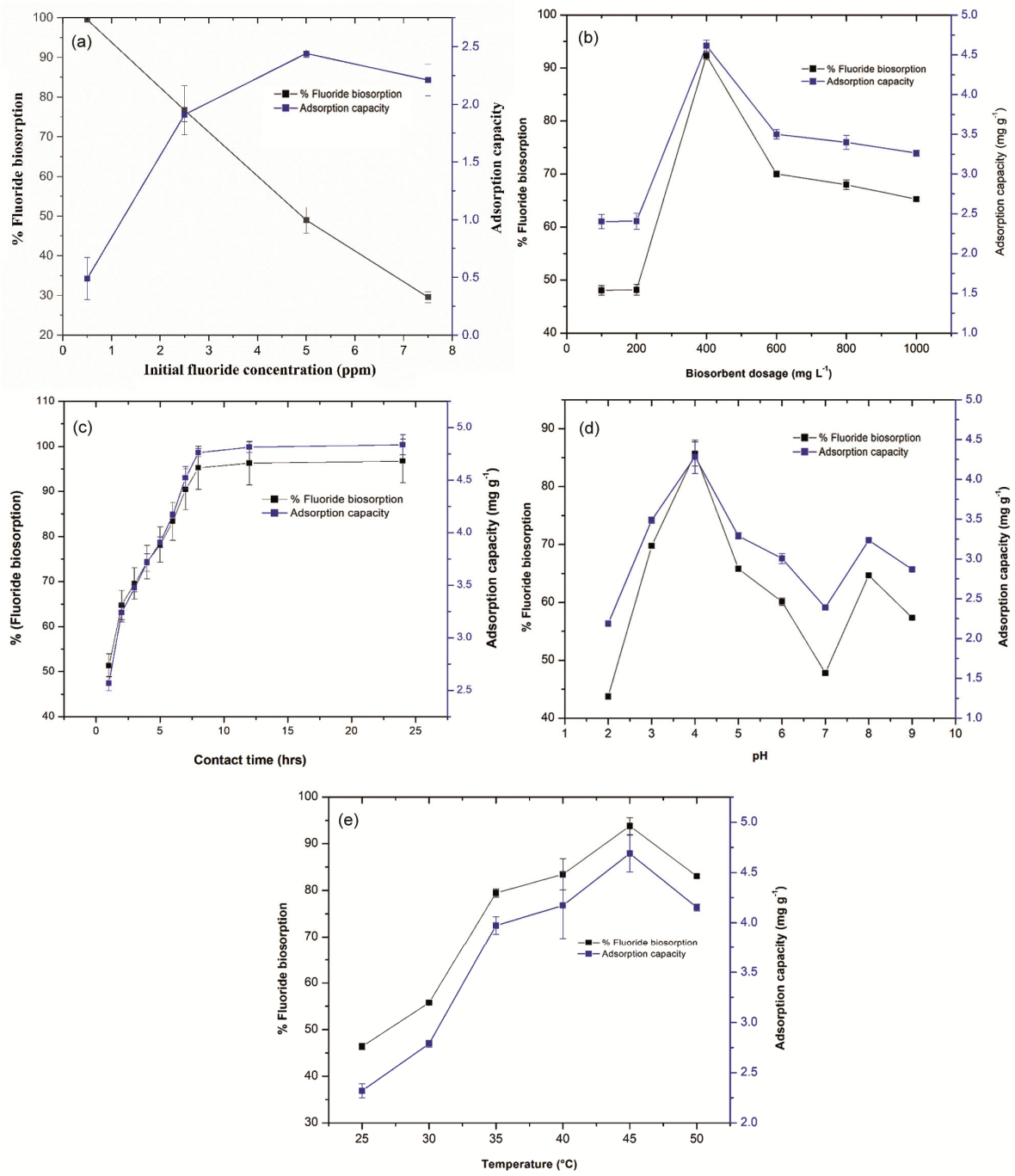

Fig. 5 — Effect of (a) initial concentration of fluoride, (b) biosorbent dosage , (c) contact time , (d) pH and (e) temperature on fluoride biosorption

straw and sawdust. A similar result was reported when fluoride was adsorbed onto Zn/Al hydrotalcite-like compound[34].

Effect of biosorbent dose

The effect of biosorbent dose on fluoride biosorption was studied. Initially, an increase in % fluoride biosorption with increase in biosorbent dose was reported owing to the availability of adsorption sites. Defluorination efficiency of biosorbent dosage of 400 mg L^{-1} was the highest (90%), after which a sharp decline in efficiency was noticed (Fig. 5b). Adsorption capacity calculated in this case was 4.614 mg g^{-1}. When higher dose of biosorbent was used,

aggregation of particles happens, and the adsorption sites are not exposed for further adsorption of fluoride.

Effect of contact time

The effect of time on fluoride biosorption was studied by allowing defluorination process to happen for different time. It was interpreted that both the % biosorption and adsorption capacity increased with increase in time up to 8 h with a maximum fluoride biosorption of 95% after which biosorption efficiency remained stationary (Fig. 5c). % fluoride biosorption reached an equilibrium state at around 8 h showing a plateau in the graph plotted against contact time and % fluoride biosorption. The increase in biosorption was due to exposed adsorption sites on the adsorbent surface, which remained filled after 8 h, showing no vacant sites for further fluoride adsorption.

Effect of pH

The pH of an aqueous solution is an important variable that influences the efficiency of biosorption process. The surface charges of biosorbents play a significant role in this experiment. The biosorbent was effective at pH 4 with maximum fluoride biosorption of 80%. A significant decrease in biosorption and adsorption capacity was observed at all other pH ranges (Fig. 5d). At acidic pH, the presence of hydroxyl and carboxyl groups imparts positive charge on the adsorbent surface, and since fluoride is highly electronegative, they establish an electrostatic interaction with adsorbent surface.

Effect of temperature

The effect of temperature (25, 30, 35, 40, 45, 50 °C) on fluoride biosorption was studied. The maximum fluoride biosorption (93%) and adsorption capacity of 4.68 (mg g^{-1}) was observed at 45°C (Fig. 5e). As reported earlier, fluoride biosorption follows chemisorption principle. Increase in temperature favours chemisorption and improves adsorption capacity until the process reaches an equilibrium point. The process is endothermic as increase in temperature results in favourable adsorption. At temperatures higher than the optimal temperature, there is an expected structural modification on the surface of biosorbents leading to the decrease in % fluoride biosorption.

Adsorption isotherm

Langmuir and Freundlich isotherm models are the most common models used for describing the adsorption mechanism[36]. Langmuir isotherm model considers a monolayer adsorption with no lateral interaction of adsorbate molecules on adsorbent surface. Langmuir adsorption isotherm can be expressed as in Eq. (5)

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

Where, c_e is the equilibrium concentration (mg L^{-1}), q_e is the amount of fluoride adsorbed at equilibrium (mg g^{-1}), q_m is the maximum fluoride adsorption capacity (mg g^{-1}), b is the constant (L mg^{-1}). The coefficient of determination (R^2 - 0.7688) obtained indicated the unsuitability of Langmuir model for fluoride biosorption. The affinity between the adsorbent and adsorbate can be calculated by a dimensionless factor R_L ($0 < R_L < 1$; favourable adsorption) which can be determined from the following Eq.(6)

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

Where, b is the Langmuir constant (L mg^{-1}) and C_0 is the fluoride concentration at time t = 0 in aqueous solution (mg L^{-1}). The $R_L$value for fluoride biosorption is 0.1678 indicating a favourable biosorption (Fig. 6a).

Freundlich isotherm is applicable on a heterogeneous surface and the eqn.(7) describes the linear form of the model

$$lnq_e = lnK_f + \frac{1}{n} lnC_e \quad ...(7)$$

Where, q_e is the fluoride adsorbed at equilibrium (mg g^{-1}), C_e is the equilibrium concentration (mg L^{-1}), K_f adsorption capacity (L mg^{-1}) and 1/n is the adsorption intensity (g mg^{-1}). Regression coefficient value for Freundlich isotherm was 0.9589 and value of 1/n was 0.402 (1/n < 0.5; favorable) indicating a good fit of isotherm (Fig. 6b).

Adsorption kinetics

Kinetics of fluoride biosorption was studied to determine the rate of biosorption process. Pseudo first order and pseudo second order kinetic equations were fitted to describe the biosorption process. The suitability of kinetic models can be determined by the closeness of R^2value to 1.

The equation for pseudo first order kinetics is given in Eq. 8

$$\ln(q_e - q_t) = lnq_e - k_1 xt \quad ...(8)$$

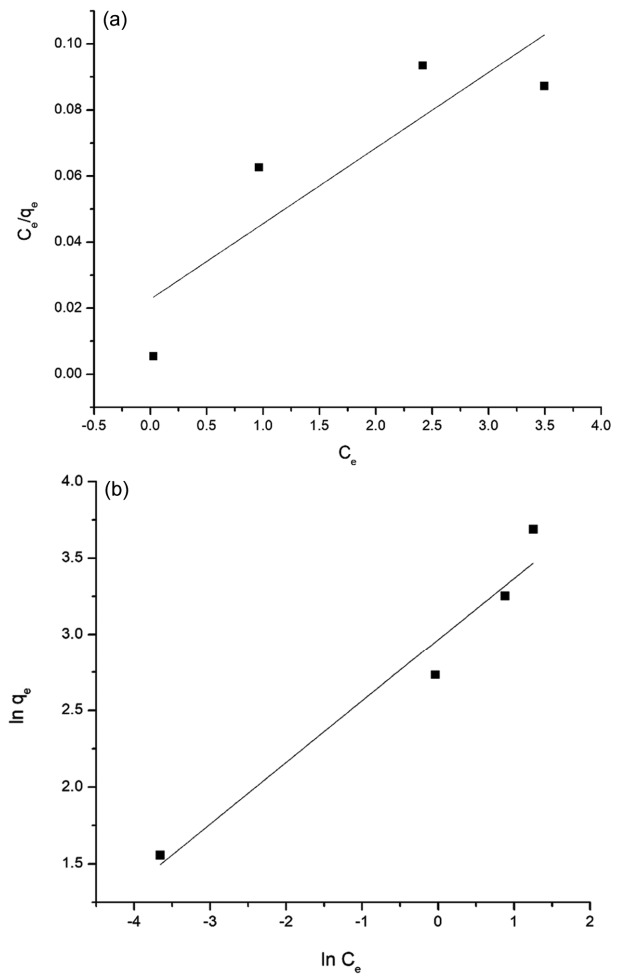

Fig. 6 — (a) Langmuir and (b) Freundlich adsorption isotherm for fluoride biosorption

Where, q_e is the fluoride adsorbed at equilibrium (mg g^{-1}), q_t is the fluoride adsorbed at time t, t is the time required for fluoride biosorption (h) and k_1 is the equilibrium rate (h^{-1}).

The pseudo second order equation is given in Eq. 9

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

Where, t is the time for fluoride biosorption (h), q_e is the fluoride adsorbed at equilibrium (mg g^{-1}), q_t is the fluoride adsorbed at time t and $k_2$is the second order kinetic constant (g mg^{-1} min^{-1}). The regression coefficient values (R^2) obtained for pseudo first order and pseudo second order equations are 0.4448 and 0.9825, respectively (Fig. 7a and 7b). Since the regression coefficient of pseudo second order equation is close to 1, it is more appropriate to choose second equation kinetics for describing fluoride biosorption.

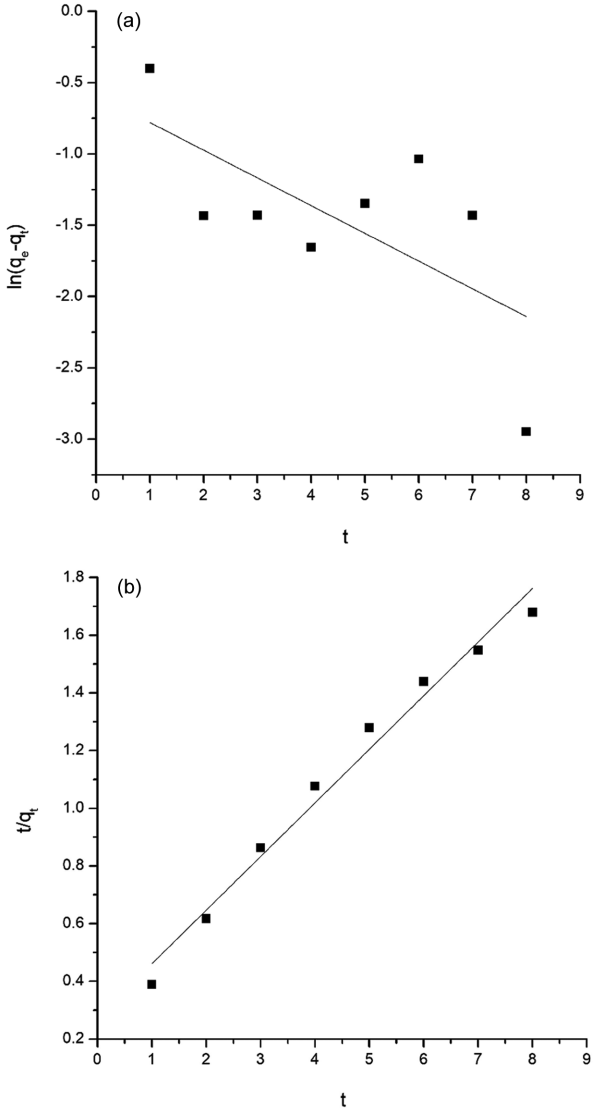

Fig. 7 — (a) Pseudo first order and (b) pseudo second order kinetic model for fluoride biosorption

Fluoride biosorption using column approach

The calcium alginate immobilized biosorbent was packed in the column and aqueous solution with 5 mg L^{-1} initial fluoride concentration was fed through it. Fluoride was estimated in the sample collected at the outlet at the end of every one hour. Fluoride biosorption was maximum (68%) at the end of 1 h after which decline in biosorption was observed (Fig. 8). The adsorption sites available on the surface of immobilized biosorbent were readily picking up fluoride ions present in aqueous solution. As time increases, adsorption sites become preoccupied with the already adsorbed fluoride ions leading to a sharp drop in biosorption efficiency.

Statistical optimization of fluoride biosorption using Response Surface Methodology

The design includes set of 30 experimental conditions and their responses were measured in terms of % fluoride biosorption. Run 8 (initial fluoride concentration – 1 mg L^{-1}, biosorbent dosage – 550 mg L^{-1} pH – 7, temperature – 45°C) showed maximum fluoride biosorption efficiency of 96.52%. Run 12 (initial fluoride concentration – 5.5 mg L^{-1}, biosorbent dosage – 550 mg L^{-1} pH – 12, temperature – 45°C) showed the lowest % of fluoride biosorption. The coefficient of determination (R^2) for the design was 0.9219 justifying the significance of the proposed model. The design suggested a quadratic polynomial model for the responses and the analysis of variance for the experiment is shown in Table 2. F-value of the model is 12.72 indicating that the model is significant. The current model for fluoride adsorption by biomass showed best fit to a quadratic equation as given in Eq. 10. Model terms with p-values less than 0.05 are assumed to have significant effects on fluoride biosorption. In this case, A (Initial fluoride concentration), B (biosorbent dosage), C (pH), D (temperature), B^2, and C^2 are the significant model terms. The contour plots describing the nature of interaction between the process parameters are given in Figs 9 (a-f). Fig. 9a shows that as the fluoride concentration and biomass dose increase, %fluoride biosorption also increases until a state of equilibrium is achieved. Further increase in the above variables results in a decrease in biosorption efficiency. A similar relationship is obtained with initial fluoride concentration and pH (Fig. 9b). Fig. 9c shows the interaction between temperature and initial fluoride concentration. As temperature and fluoride concentration increase, % biosorption also increases. The pH and biosorbent dose directly influence the biosorption up to a certain value after which a decrease in biosorption efficiency was noticed

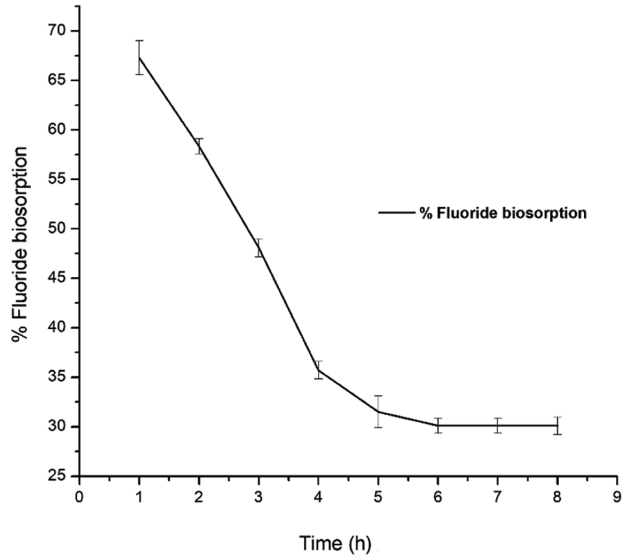

Fig. 8 — % Fluoride biosorption using immobilized biosorbent in column

Table 2 — 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	
A^2	10.49	1	10.49	0.3680	0.5531	
B^2	1287.13	1	1287.13	45.15	< 0.0001	
C^2	2179.56	1	2179.56	76.45	< 0.0001	
D^2	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				

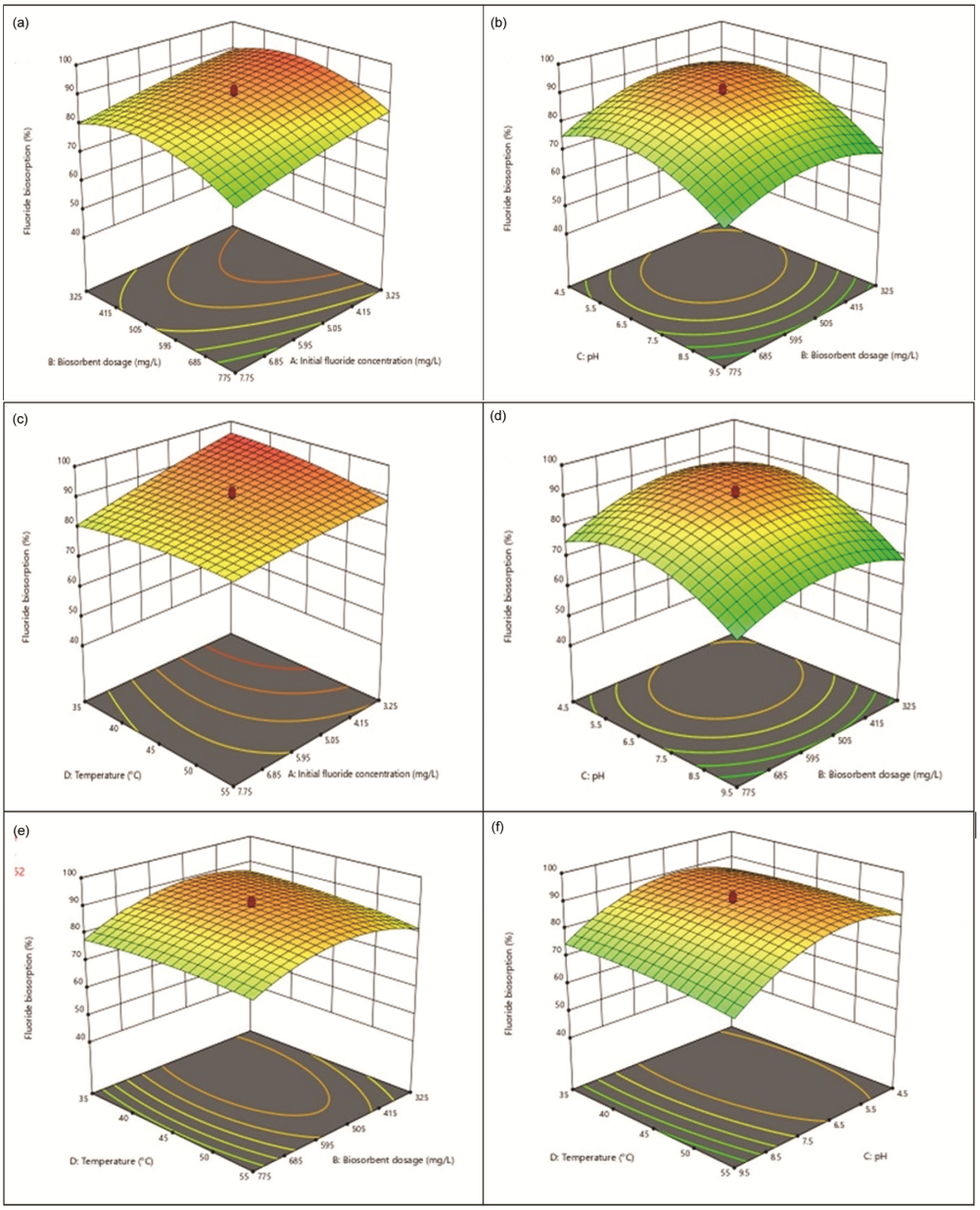

Fig. 9 — Effects of (a) initial fluoride concentration and biosorbent dosage, (b) initial fluoride concentration and pH, (c) initial fluoride concentration and temperature, (d) biosorbent dosage and pH, (e) biosorbent dosage and temperature and (f) pH and temperature on fluoride adsorption

(Fig. 9d). Fig. 9e demonstrates the influence of temperature and biosorbent dose on fluoride biosorption. pH and temperature should be optimum to support maximum biosorption (Fig. 9f)[37]. Based on the perturbation graph constructed using the design expert software, the robust operating conditions of the process parameters for increased fluoride biosorption were determined as 3.25 mg L^{-1} initial fluoride concentration, 775 mg L^{-1} of biomass dosage, at temperature 55 °C and pH 4.5.

$$\begin{aligned} \%\ fluoride\ biosorption &= 89.35 - (6.23 \times A) - (1.18 \times B) \\ &- (3.03 \times C) - (4.97 \times D) \\ &- (0.8231 \times A \times B) \\ &+ (1.69 \times A \times C) + 0.2544 \times A \times D \\ &+ (1.29 \times B \times C) + (2.44 \times B \times D) \\ &- (0.2769 \times C \times D) - (8.9A^2) \\ &- (1.56B^2 - (6.84 \times C^2) \\ &- (0.6468 \times D^2) \end{aligned} \quad ...(10)$$

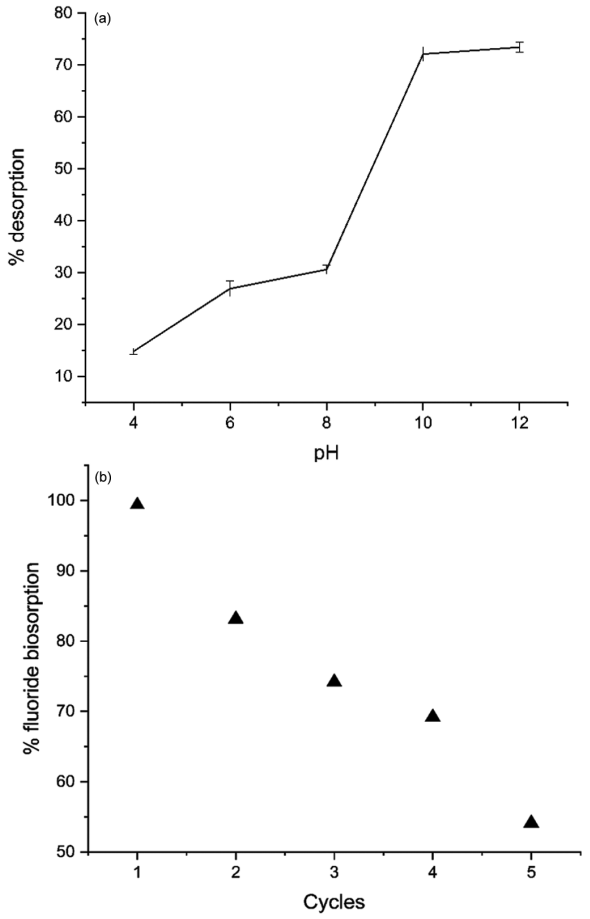

Fig. 10 — Plots for (a) Fluoride desorption from biosorbent and (b) recyclability of biosorbent

Desorption and recyclability of biomass

It was observed that the amount of fluoride desorbed gradually increased from acidic to alkaline aqueous solution as shown in Fig. 10a. Notably at pH 10, fluoride desorption was maximum and remained unaffected at pH more than 10. Over repeated cycles of biomass usage, adsorption capacity gradually decreased from 99.4% to 54.11% during 1st and 5th cycles respectively (Fig. 10b). The above results are consistent with the previously reported literature for fluoride biosorption. The decrease in fluoride adsorption over repeated cycles may be due to the degradation of fluoride biosorption sites. From the above results, it may be concluded that fluoride biosorption is reversible and the biomass can be reused for subsequent cycles of fluoride adsorption.

Conclusion

Based on the above results, it may be concluded that the biomass used for fluoride biosorption can be good biosorbent with less impact on environment. Also, they may be used for repeated cycles of fluoride biosorption.

References

1 Hussain J, Hussain I & Sharma K C, Fluoride and health hazards: Community perception in a fluorotic area of central Rajasthan (India): an arid environment, *Environ Monit Assess*, 162 (2010) 1.

2 Boldaji M R, Mahvi A H, Dobaradaran S & Hosseini S S, Evaluating the effectiveness of a hybrid sorbent resin in removing fluoride from water, *Int J Environ Sci Technol*, 6 (2009) 629.

3 Ayenew T, The distribution and hydrogeological controls of fluoride in the groundwater of central Ethiopian rift and adjacent highlands, *Environ Geol*, 54 (2008) 1313.

4 Nigri E M, Bhatnagar A & Rocha S D F, Thermal regeneration process of bone char used in the fluoride removal from aqueous solution, *J Clean Prod*, 142 (2017) 3558.

5 Meenakshi & Maheshwari R C, Fluoride in drinking water and its removal, *J Hazard Mater*, 137 (2006) 456.

6 He J, Siah T S & Chen J P, Performance of an optimized Zr-based nanoparticle-embedded PSF blend hollow fiber membrane in treatment of fluoride contaminated water, *Water Res*, 56 (204) 88.

7 Gupta S Banerjee S, Saha R, Datta J K & Mondal N K, Fluoride geochemistry of groundwater in Nalhati-1 block of the Birbhum district, West Bengal, India, *Fluoride*, 39 (2006) Please provide pages number

8 Arlappa N, Introduction, *Int J Res Dev Health*, 1 (2013) 97.

9 Bhatnagar A, Kumar E & Sillanpää M, Fluoride removal from water by adsorption-A review, *Chem Eng J*, 171 (2011) 811.

10 Ma L, Wang X, Tao J, Feng X, Liu X & Qin W, Differential fluoride tolerance between sulfur- and ferrous iron-grown Acidithiobacillus ferrooxidans and its mechanism analysis, *Biochem Eng J*, 119 (2017) 59.

11 Jadhav S V, Marathe K V & Rathod V K, A pilot scale concurrent removal of fluoride, arsenic, sulfate and nitrate by using nanofiltration: Competing ion interaction and modelling approach, *J Water Process Eng*, 13 (2016) 153.

12 Sandoval M A, Fuentes R, Thiam A & Salazar R, Arsenic and fluoride removal by electrocoagulation process: A general review, *Sci Total Environ*, 753 (2021) 142108

13 Ndiaye P I, Moulin P, Dominguez L, Millet J C & Charbit F, Removal of fluoride from electronic industrial effluentby RO membrane separation, *Desalination*, 173 (2005) 25.

14 Markovski J, Garcia J, Hristovski K D & Westerhoff P, 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 (2017) 1848.

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

16 Prasuna N V, Kumar R K & Damodharam T, Selective spectrophotometric determination of fluoride in water samples using an Alizarin red S complex as a colored reagent, *J Appl Sci*, 1 (2015) 18.

17 Alemu S, Mulugeta E, Zewge F & Chandravanshi B S, Water defluoridation by aluminium oxide–manganese oxide composite material, *Environ Technol*, 35 (2014) 1893.

18 Solanki Y S, Agarwal M, Gupta A B, Gupta S & Shukla P, Fluoride occurrences, health problems, detection, and remediation methods for drinking water: A comprehensive review, *Sci Total Environ*, 807 (2022) 150601.

19 Gentili F G & Fick J, Algal cultivation in urban wastewater: An efficient way to reduce pharmaceutical pollutants, *J Appl Phycol*, 29 (2017) 255.

20 Lee J I, Hong S H, Lee C G & Park S J, Fluoride removal by thermally treated egg shells with high adsorption capacity, low cost, and easy acquisition, *Environ Sci Pollut Res*, 28 (2021) 35887.

21 Blanco-Flores A, Arteaga-Larios N, Pérez-García V, Martínez-Gutiérrez J, Ojeda-Escamilla M, & Rodríguez-Torres I, Efficient fluoride removal using Al-Cu oxide nanoparticles supported on steel slag industrial waste solid, *Environ Sci Pollut Res*, 25 (2018) 6414.

22 Chen N, Zhang Z, Feng C Li M, Zhu D Chen R & Sugiura N, An excellent fluoride sorption behavior of ceramic adsorbent, *J Hazard Mater*, 183 (2010) 460.

23 Das D, Jaya S V C & Das N, Recovery of lanthanum(III) from aqueous solution using biosorbents of plant and animal origin: Batch and column studies, *Miner Eng*, 69 (2014) 40.

24 Kanaujia S, Singh B & Singh S, Removal of Fluoride from groundwater by Carbonised Punica granatum Carbon ('CPGC') bio-adsorbent, *J Geosci Environ Prot*, 3 (2015) 1.

25 Gupta V K & Rastogi A, Biosorption of lead(II) from aqueous solutions by non-living algal biomass Oedogonium sp. and Nostoc sp.--a comparative study," *Colloids Surf B*, 64 (2008) 170.

26 Vijayaraghavan K & Yun Y S, Bacterial biosorbents and biosorption, *Biotechnol Adv*, 26 (2008) 266.

27 Wang J & Chen C, Biosorption of heavy metals by Saccharomyces cerevisiae: A review, *Biotechnol Adv*, 24 (2006) 427.

28 Thakre D, Rayalu S, Kawade R, Meshram S, Subrt J & Labhsetwar N, Magnesium incorporated bentonite clay for defluoridation of drinking water, *J Hazard Mater*, 180 (2010) 122.

29 Bumsted H E & J C Wells J C, Spectrophotometric method for determination of fluoride ion, *Anal Chem*, 24 (1952) 1595.

30 Simate G S & Ndlovu S, The removal of heavy metals in a packed bed column using immobilized cassava peel waste biomass, *J Ind Eng Chem*, 21 (2015) 635.

31 Sahu J N, Acharya J & Meikap B C, Response surface modeling and optimization of chromium(VI) removal from aqueous solution using Tamarind wood activated carbon in batch process, *J Hazard Mater*, 172 (2009) 818.

32 Can M Y, Kaya Y & Algur O F, Response surface optimization of the removal of nickel from aqueous solution by cone biomass of Pinus sylvestris, *Bioresour Technol*, 97 (2006) 1761.

33 Amin F, Talpur F N, Balouch A & Bhutto M A, Biosorption of fluoride from aqueous solution by white—rot fungus *Pleurotus eryngii* ATCC 90888, *Environ Nanotechnol Monit Manag*, 3 (2015) 30.

34 Das D P, Das J & Parida K, Physicochemical characterization and adsorption behavior of calcined Zn/Al hydrotalcite-like compound (HTlc) towards removal of fluoride from aqueous solution, *J Colloid Interface Sci*, 261 (2003) 213.

35 Scheverin V N, Horst M F & Lassalle V L, Novel hydroxyapatite-biomass nanocomposites for fluoride adsorption, *Results Eng*, 16 (2022) 100648.

36 Mondal N K & Kundu M, Biosorption of fluoride from aqueous solution using lichen and its Ca-pretreated biomass, *Water Conserv Sci Eng*, 1 (2016) 143.

37 Kalsido A W, Meshesha B T, Behailu B M & Alemayehu E, Optimization of fluoride adsorption on acid modified bentonite clay using fixed-bed column by response surface method, *Molecules*, 26 (2021) 7112.