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Kinetics and thermodynamics of fluoride removal using cerium-impregnated chitosan

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ABSTRACT

The kinetics and thermodynamics of fluoride adsorption on cerium-impregnated chitosan (CIC) have been studied by the sets of experiments at various conditions (initial fluoride concentration, adsorption time and temperature). The characteristic of the adsorbent before and after fluoride adsorption was examined using Fourier transform infrared spectroscopy (FTIR), scanning electron microscope (SEM) and energy dispersive spectrum (EDS) techniques. Adsorption of fluoride was strongly affected by pH. Pseudo-second order kinetic model best described the reaction rate, and the adsorption capacity calculated by using model equation, was consistent with the actual measurement. Isotherms for the adsorption of fluoride on CIC were developed and the equilibrium data fitted well to the Freundlich, Langmuir, Temkin and Dubinin-Radushkevich (D-R) isotherm. The adsorption isotherms were compared for six different error functions i.e., the sum of the squares of errors (SSE), sum of the absolute errors (SAE), the average relative error (ARE), the hybrid fractional error function (HYBRID), the Marquardt's percent standard deviation (MPSD), and regression coefficient (R^2) to test the adequacy and accuracy of the model equations. Thermodynamic parameters such as enthalpy, entropy and free energy were calculated using Van't Hoff equations. The thermodynamics of fluoride adsorption on CIC indicates the spontaneous and endothermic nature of adsorption. Reusability of the CIC adsorbent material was tested up to nine consecutive cycles. Quantitative desorption of fluoride from CIC was found to be more than 93% at pH 12. The performance of the adsorbent material was studied with field water samples collected from a fluorosis endemic-region.

Keywords: Chitosan; Fluoride; Isotherms; Error-functions; Thermodynamics

1. Introduction

Water is essential for sustenance of all forms of life and the chemical nature of water is one of the most important criteria that determine its usefulness for a specific need. Fluoride contamination of water occurs due to natural and anthropogenic reasons. Fluoride is one of the essential elements for human health. The World Health Organization (WHO) guideline suggested a limiting value of 1.5 mg L^{-1} for fluoride present in drinking water [1,2]. Various methods have been tested for removal of excessive fluoride from drinking water including chemical methods (flocculation, softening, etc.) and separation methods such as ion exchange and membrane processes [3]. A number of research publications have reported various

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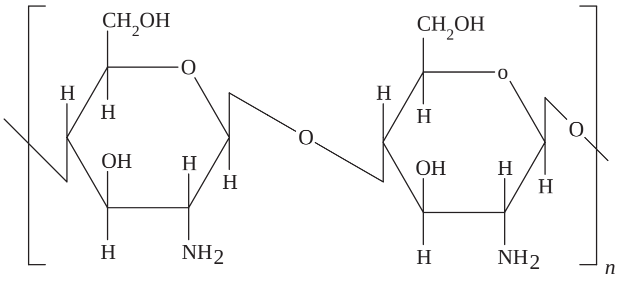


Fig. 1. Molecular structure of chitosan.

inorganic materials like alumina, calcium, ferrous-modified clays, etc., for the removal of fluoride from drinking water sources [4–6]. Apart from this, usefulness of synthetic resins in fluoride removal processes have also been investigated and compared for their process efficiency [7–10].

Fluoride possesses strong affinity towards multivalent metal ions like Al^{3+}, Ca^{2+}, Fe^{3+}, Zr^{4+} and a series of lanthanide metal ions [11]. Removal of fluoride using metal-impregnated polymeric materials, both natural as well as synthetic, was attempted by a number of researchers. For example, Tanaka et al. [12] reported the removal of fluoride using Zr-complexes of resins containing amine-N-acetate ligands, where the optimum pH for the adsorption of fluoride by the resins was reported in the range of 3–5. Zhou et al. [13] reported the use of a novel adsorbent material consists of La^{3+}-impregnated cross-linked gelatin for the removal of fluoride from aqueous medium. The maximum fluoride removal was obtained in the pH range of 5–7 which is suitable for drinking water treatment. The regeneration process for such kind of material was also optimized.

In this context, biopolymers are also used as suitable adsorbent materials for the removal of cations/heavy metal ions because of availability of a number of functional groups in the matrix [14]. Chitosan represents a natural polysaccharide material associated with various other features like biocompatibility, biodegradability and hydrophilicity. Basically chitosan (Fig. 1) is a derivative of chitin obtained from chitin deacetylation. Removal of harmful cations/anions from drinking water using chitosan biopolymer was investigated by number of researchers [15–21]. Metal-impregnated chitosan provides a suitable alternative for the removal of fluoride because of strong affinity of fluoride towards the specific metals present in the matrix. Viswanathan et al. [22,23] investigated the maximization of defluoridation capacity of chitosan beads by substitution of functional groups such as organic acids onto hydroxyl groups and chelation of amine groups with Fe^{3+}/La^{3+} ions. A reasonable mechanism for the removal process was also elucidated. Kamble et al. [24] studied the various physicochemical parameters such as pH, adsorbent dose, initial fluoride concentration and presence of interfering ions on adsorption of fluoride from ground water samples collected from Dhar district of Madhya Pradesh, India. The mechanism of adsorption processes on lanthanum modified chitosan was also elucidated in terms of the ligand exchange mechanism. However, reports regarding the removal of fluoride using cerium-impregnated various polymeric materials appears to be very few.

Cerium (Ce) is one of the trivalent elements with the highest pK_{sp} value with fluoride [25]. The sorption of fluoride ion with Ce-impregnated poly(hydroxamic acid) was reported by Haron et al. [26] and the results indicated that the fluoride level in the waste-water sample was reduced to below the permissible level by a single treatment with the adsorbent material. Preparation and defluorination performance of activated cerium oxide adsorbent material was reported by Xu et al. [27]. Interestingly, the adsorption capacity of fluoride ion on the adsorbent material found to increase by increasing Ce/Si ratio, showing the efficiency of metallic cerium to efficiently form complexation with fluoride ion. In this context more investigations using cerium impregnated polymeric materials for efficient removal of fluoride is quite worthful.

The objective of this investigation is to study the sorption behavior of fluoride on a cerium-impregnated chitosan (CIC) using batch adsorption technique. The physicochemical characteristics of the adsorbent were examined using C, H, N analyzer, Fourier transform infrared spectroscopy (FTIR), scanning electron microscope (SEM) and energy dispersive spectrum (EDS) techniques. The adsorption experiments were performed at different initial concentration of fluoride, different adsorption contact time, different pH and temperature of the medium. A particular objective of the investigation was to evaluate the kinetic and thermodynamic parameters of adsorption of fluoride on CIC. Experimental data were fitted to Freundlich, Langmuir, Dubinin-Radushkevich (D-R) and Temkin isotherm equation to determine the best-fit equation. Further, six different error functions i.e., sum of the squares of errors (SSE), sum of the absolute errors (SAE), average relative error (ARE), hybrid fractional error function (HYBRID), Marquardt's percent standard deviation (MPSD) and regression coefficient (R^2) were computed to test the adequacy and accuracy of the model equations. The suitability of adsorbent material with respect to elution and regeneration process was tested satisfactorily. Further, the efficiency of adsorption of fluoride was investigated with the real ground water samples collected from a fluoride affected region of Orissa State (Boden Block, Naupada), India. The detailed investigations reported in this work can find immense usefulness in exploiting the opportunity to use a low-cost biopolymer for fluoride removal processes.

2. Materials and methods

2.1. Materials

All chemicals used in the present study were of Analytical Reagent (AR) grade. Sodium fluoride, sodium chloride, sodium sulphate, sodium nitrate, sodium bicarbonate and sodium dihydrogen phosphate were obtained from E. Merck India Limited. Stock solution of fluoride was prepared by dissolving 2.21 g of sodium fluoride in 1 L deionized water. The required concentration of fluoride solution was prepared by serial dilution of 1,000 mg L^{-1} fluoride solution. The prawn shells were collected from Chilika lake, Orissa, India. Chitin was isolated from prawn shell using Hackman method as described previously [28]. Prawn shells were milled to fine particles using a rotary mill. Chitosan was prepared by deacetylation of purified chitin according to methodology followed by Muzzarelli et al. [29]. CIC was prepared by adding predetermined mass of chitosan to a certain volume of Cerium solution ($Ce(NO_3)_2 \cdot 6\ H_2O$) and the mixture was agitated continuously for 24 h after which both the metal solution and chitosan were further allowed to remain in contact for 48 h. The material was filtered, washed with enough quantity of deionized water and dried at 70 °C in vacuum.

2.2. Analytical measurements

The ash content of both chitin and chitosan were determined gravimetrically. The carbon, hydrogen, and nitrogen contents were determined using Vario EL Elemental analyzer. The FTIR spectra of all the sample materials were recorded at room temperature at a resolution of 4 cm^{-1} and 64 scans using Shimadzu IR Prestige-21 FTIR instrument. The surface structure of the adsorbent material was analyzed using SEM (Jeol, JSM 6390 LV) coupled with EDS technique.

2.3. Sorption studies

Batch experiment was carried out by adding fixed amount of the adsorbent material (CIC) to 100 mL of test solution in a conical flask which was kept in a rotatory shaker for a fixed time period. A rotation of 200 rpm was maintained at room temperature (25 ± 2) °C. Initial fluoride concentration was maintained at 10 mg L^{-1} for all the experiments except in those where the effects of initial fluoride concentration is to be studied. The pH of the solution was adjusted using either H_2SO_4 or NaOH. The effect of co-anions such as chloride, sulphate, nitrate, bicarbonate, phosphate upon the adsorption process were studied by adding required amount of NaCl, Na_2SO_4, $NaNO_3$, $NaHCO_3$, NaH_2PO_4 to a 100 mL of 10 mg L^{-1} fluoride solution. Concentration of fluoride in original and supernatant was checked using an ion selective electrode (Orion 720 A^+ Ion analyzer).

The reusability of the CIC was checked by adding 0.8 g of CIC to 100 mL of 10 mg L^{-1} fluoride solution. The adsorbent was filtered and dried in an oven at 70 °C in vacuum. Subsequently the same dried adsorbent material was used repeatedly for fluoride removal in various samples to determine the extent of adsorption. Further desorption studies were carried out by using the fluoride adsorbed CIC at different pH of the medium. Each experiment was carried out in duplicate and the average results were presented in the work.

3. Results and discussion

3.1. Characterization of chitin and chitosan

The percentage of ash, carbon, hydrogen, nitrogen of chitin and chitosan are summarized in Table 1. The percentage of ash for isolated chitin was found to be 4.0. The percentage of nitrogen in chitin and chitosan were 6.17 and 7.24, respectively, and the theoretical value of percentage of nitrogen in case of chitosan was calculated to be 8.7 %. Other researchers also reported similar kind of observations [29,30]. From the FTIR spectra of chitin and chitosan (Fig. 2), the degree of deacetylation (DD%) was calculated using the following equation [31]:

$$A_{1320}/A_{1420} = (0.3822 + 0.03133) \times \mathrm{DA} \tag{1}$$

where, A_{1320} and A_{1420} represented the absorbance at 1,320 and 1,420 cm^{-1}, respectively. DA represents

Table 1
Content of ash, carbon, hydrogen and nitrogen in chitin and chitosan

Content g/100 g of chitin/chitosan	Chitin	Chitosan
Ash	4.00	0.80
C	45.23	43.12
H	6.15	6.23
N	6.17	7.24

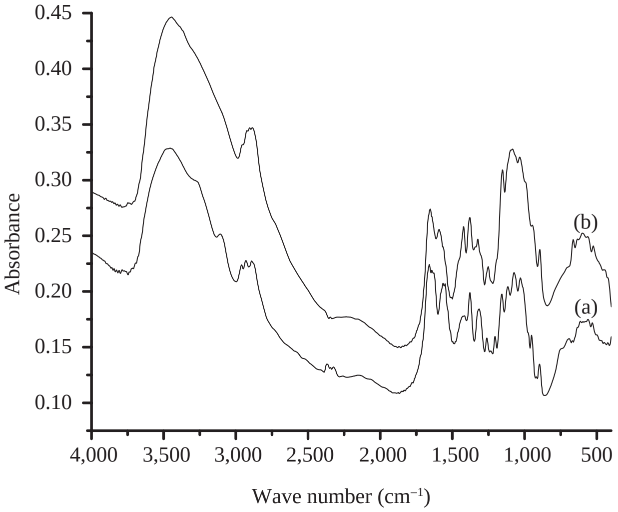


Fig. 2. FTIR spectra of (a) chitin and (b) chitosan.

the degree of acetylation (DA % = 100 − DD %). The degree of acetylation, in the present investigation, was calculated to be 84%.

The SEM (Fig. 3) of CIC surface indicates the CIC surface littered with whitish nodules after sorption with 10 mg L^{-1} fluoride solution. The corresponding EDS spectrum (Fig. 4) showed the signals generated from fluoride from the surface of CIC. The various other signals as found in EDS spectrum of sample material were N, O, C, and Ce. The presence of platinum signal in the spectra resulted from the platinum material that purposely coated to increase the electrical conduction, hence to improve the quality of micrograph.

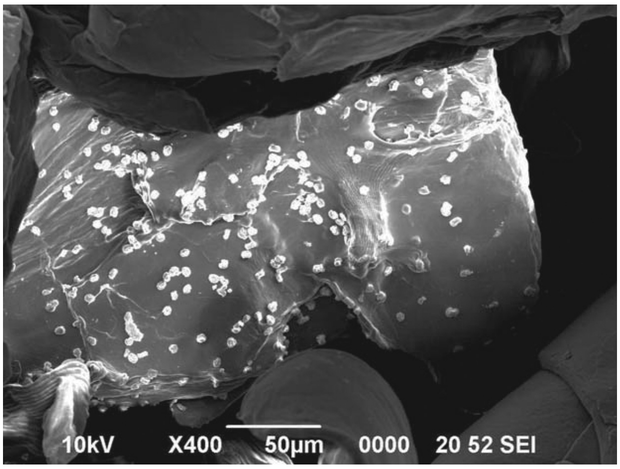


Fig. 3. Scanning electron micrograph of fluoride adsorbed on cerium-impregnated chitosan.

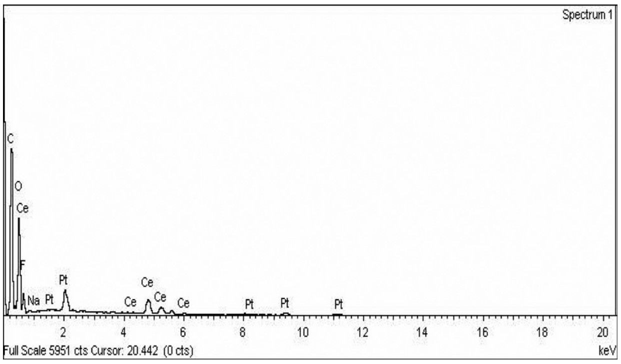


Fig. 4. EDS spectra of fluoride adsorbed cerium-impregnated chitosan (CIC).

3.2. *Effect of pH of the medium*

The solution pH is one of the important parameters in determining the sorption potential of a sorbent material. Adsorption of fluoride by CIC was studied in the pH range of 2–12. As shown in Fig. 5, the adsorption of fluoride increases within a pH range of 2–7 beyond which the adsorption decreases. The optimum removal of fluoride was found to be within a pH range of 6.5–7.0. A progressive decrease in fluoride removal was observed with increase in pH. The reason may be ascribed to the fact that in a solution, the competition of the hydroxyl ions with fluoride ion exist and subsequently with increase in pH value, the concentration and hence mobility of hydroxyl ion increases. In an acidic pH, the adsorption of fluoride is less due to the formation of weak H_2F^- ions [32].

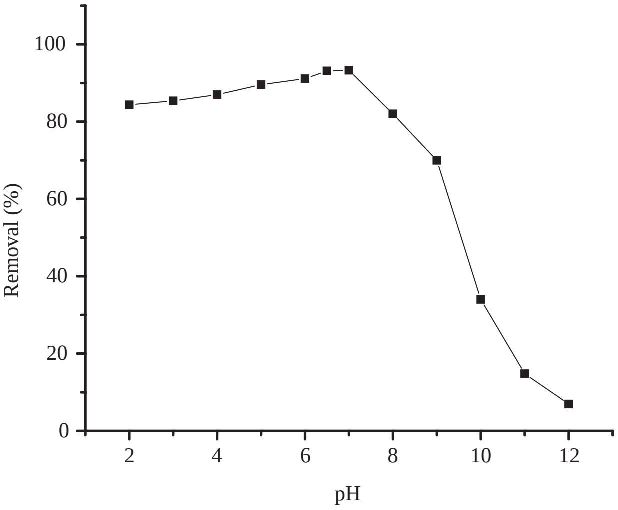


Fig. 5. Effect of pH of the medium upon removal of fluoride from solution. Adsorbent dose: 8.0 g L^{-1}, time of contact: 60 min; temperature: (25 ± 2) °C.

3.3. Adsorption kinetics

The kinetics of fluoride adsorption on CIC was verified using pseudo-first order, second order, first order reversible equation and intra-particle diffusion models.

The integrated pseudo-first order rate equation can be represented as [5]:

$$\log(q_e - q_t) = \log q_e - K_f t/2.303 \tag{2}$$

where q_e and q_t are the amount of fluoride adsorbed (mg g^{-1}) at equilibrium and at time 't', respectively. K_f (min^{-1}) is the rate constant of pseudo-first order adsorption reaction. A straight line of log ($q_e - q_t$) *vs* t suggests the applicability of these kinetic models. Both q_e and K_f can be determined from the intercept and slope of the curve, respectively.

The linear form of pseudo-second order kinetic model can be expressed as [5]:

$$t/q_t = 1/K_s(q_e)^2 + t/q_e \tag{3}$$

where, K_s is the rate constant for pseudo-second order reaction (g mg^{-1} min^{-1}). q_e and q_t are the amounts of solute sorbed at equilibrium and at any time 't' (mg g^{-1}), respectively. The straight line plot of t/q_t *vs* t for the kinetic data gives the values for q_e and K_s from the slope and intercept, respectively. On simplification, Eq. (3) can be rewritten as:

$$h = K_s q_e^2 \tag{4}$$

where 'h' is the initial sorption rate (mg g^{-1} min^{-1}).

The integrated form of the first order reversible equation is represented as [33]:

$$\ln[1 - U(t)] = K_B t \tag{5}$$

where, $U(t) = (C_{ao} - C_a)/(C_{ao} - C_{ae})$ and C_{ae} is the equilibrium solute concentration. $K_B = -k^{\#}$ and $k^{\#}$ is denoted as the overall rate constant. K_B can be calculated from the slope of the linear plot ln $[1 - U(t)]$ *vs* t.

The intra-particle diffusion model can be expressed as [5]:

$$q_t = K_i t^{1/2} + C \tag{6}$$

where, K_i is the intra-particle diffusion constant (mg g^{-1} $\text{min}^{-1/2}$) and C is intercept. The value of K_i is determined from the slope of the plot q_t *vs* $t^{1/2}$.

In the present study, the kinetic behavior was studied for an initial fluoride concentration of 10 mg L^{-1} and an adsorbent dose of 8.0 g L^{-1} keeping the pH fixed at 6.5 at room temperature to find out the minimum time of contact needed to attain maximum removal. The sorption of fluoride has been investigated as a function of time in the range of 10–60 min. The amount of removal of fluoride increases with increase in time and finally reaches a saturation value in a time period of 35 min where almost 95% of fluoride removal was achieved. This may be due to the fact that initially all adsorbent sites were available for the anion coordination and initial solute concentration gradient was also high. Once the saturation of metal sites was attained, the rate of fluoride uptake remained almost constant due to further decreases in number of available adsorbent site as well as amount of remaining fluoride ions in the solution.

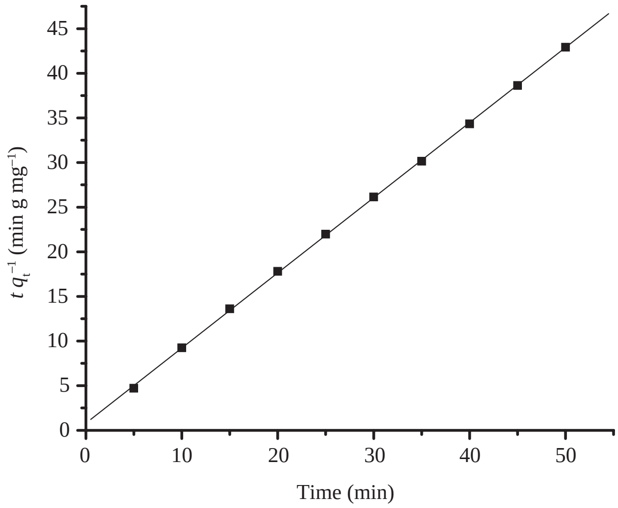


Fig. 6. Pseudo-second order kinetic plot for fluoride adsorption on CIC; Temp: (25 ± 2) °C; pH: 6.5; Fluoride conc.: 10 mg L^{-1}; adsorbent dose: 8.0 g L^{-1}.

The various kinetic parameters calculated from the slope and intercept of the linear plots (Figs. 6 and 7) are shown in Table 2. It was observed that the $q_{e,exp}$ and $q_{e,cal}$ values from the pseudo-second order kinetic model are very close to each other and the correlation coefficient R^2 found to be high (0.999). Therefore, the sorption kinetics can be represented by the pseudo-second order model for the adsorption fluoride onto CIC. The value of intercept C provides information about the thickness of boundary layer i.e., the resistant to the external mass transfer. The larger the value of intercept, higher is the external resistant [34]. The deviation of straight line from the origin, as shown in Fig. 7, may be due to the difference between the rate of mass transfer in the initial and final stage of adsorption which indicates that the pore diffusion is not the sole rate controlling step [35].

3.4. Adsorption isotherms

Equilibrium relationship between adsorbent and adsorbate are described by adsorption isotherm. Thus

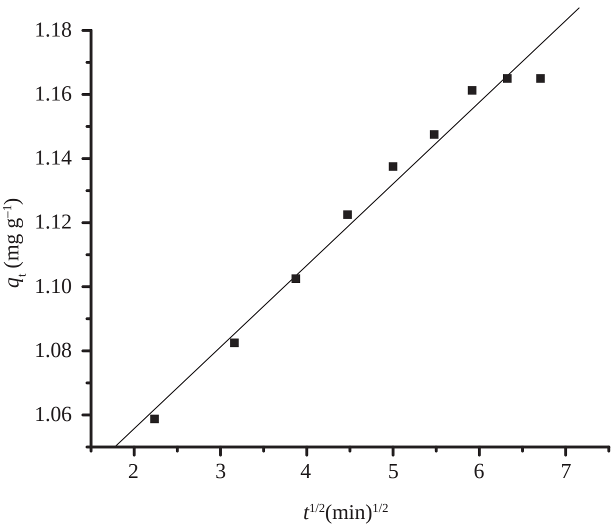


Fig. 7. Weber-Morris intra-particle diffusion plot for fluoride adsorption on CIC; Temp: (25 ± 2) °C; pH: 6.5; Fluoride conc.: 10 mg L^{-1}; adsorbent dose: 8.0 g L^{-1}.

the correlation of equilibrium data either theoretical or empirical equations is essential for practical design and operation of adsorption isotherm. In order to optimize the design of a sorption system for the removal of fluoride ions from aqueous solution by CIC, four isotherm equations have been used in the present study namely Langmuir, Freundlich, Temkin, and D-R.

The Freundlich expression is an exponential equation which assumes that the concentration of adsorbent on the adsorbent surface increases with the adsorbent concentration. Theoretically, using these expressions, an infinite amount of adsorption can occur. This equation is widely applied to heterogeneous system in which it is characterized by the heterogeneity factor 1/n. Thus the empirical equation can be written as [36]:

$$q_e = K_F C_e^{1/n} \tag{7}$$

The linearized form of the Eq. (7) can be written as:

$$\ln q_e = \ln K_F + 1/n \ln C_e \tag{8}$$

where, K_F and 'n' are the Freundlich constants that indicate the relative capacity and adsorption intensity, respectively. The values of K_F and 'n' are obtained, respectively, from the slope and intercept of the plot between ln q_e and ln C_e of the linearized Freundlich equation.

The Langmuir adsorption isotherm assumes that the adsorbed layer is one molecule in thickness and that all sites are equal resulting in equal energies and enthalpies of adsorption. The Langmuir equation can be described in the following equation [37]:

$$q_e = (q_m K_L C_e)/(1 + K_L C_e) \tag{9}$$

The linearized form of Eq. (9) can be written as:

$$1/q_e = (1/K_L q_m)(1/C_e) + 1/q_m \tag{10}$$

where, q_e is the amount of fluoride adsorbed at equilibrium (mg g^{-1}), C_e is the equilibrium concentration (mg L^{-1}), q_m is the mono-layer adsorption capacity (mg g^{-1}) and K_L is the Langmuir constant related to the free adsorption energies (L mg^{-1}). The value of q_m and K_L can be calculated, respectively, from the slope and intercept of the linear plot of $1/C_e$ *vs* $1/q_e$.

Temkin isotherm assumes that the decrease in heat of adsorption of all the molecules in the layer with coverage due to adsorbent-adsorbate interactions is linear rather than logarithm as implied in the Freundlich equation. Further it also describes that adsorption is characterized by uniform distribution of binding energies up to some maximum binding energy. Temkin isotherm is represented by the following equation [37]:

$$q_e = (\mathrm{RT}/b) \ln (K_T C_e) \tag{11}$$

The linearized form of the Eq. (11) can be written as:

$$q_e = B_1 \ln K_T + B_1 \ln C_e \tag{12}$$

where, $B_1 = \mathrm{RT}/b$ and K_T is the equilibrium binding constant (L mol^{-1}) corresponding to the maximum binding energy and the constant B_1 is related to the heat of adsorption. A plot of q_e *vs* ln C_e enables the

Table 2
Kinetic parameters for fluoride adsorption onto CIC at pH 6.5; adsorbent dose: 8.0 g L^{-1}, temp: 298 K, initial fluoride conc. 10 mg L^{-1}

	Pseudo-first order*			Pseudo-second order*			Reversible first-order*			Intra-particle diffusion*		
q_{exp}	K_f	$q_{e,cal}$	R^2	K_s	h	$q_{e,cal}$	R^2	K_B	R^2	K_i	C	R^2
1.165	0.0997	0.2418	0.8866	0.8739	1.234	1.188	0.999	0.997	0.886	0.0237	1.0118	0.962

* The units for q_{exp}, $q_{e,cal}$: mg g^{-1}; K_f: L min^{-1}; K_s, h: (mg g^{-1} min^{-1}); K_B: min^{-1}; K_i, C: mg (g min1/2)$^{-1}$.

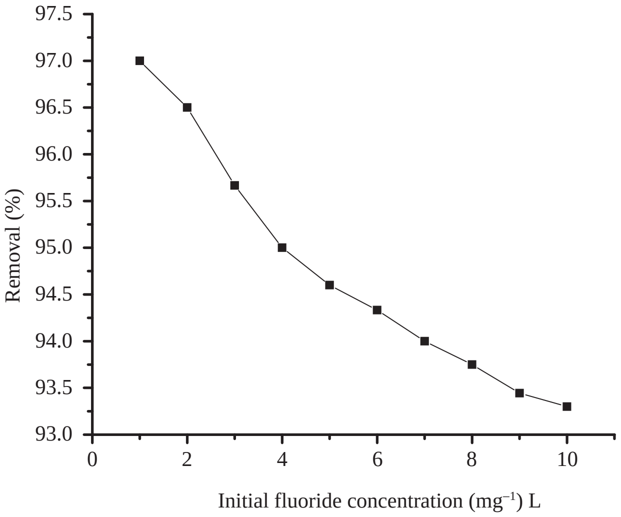


Fig. 8. Effect of initial fluoride concentration, adsorbent dose: 8.0 g L^{-1}; time of contact: 40 min; Temperature: (25 ± 2) °C; pH: 6.5.

constant B_1 and K_T to be determined from the slope and intercept, respectively.

However, the isotherm constants for Langmuir and Freundlich isotherms do not give any idea about the information regarding the adsorption mechanism. In order to understand the adsorption type, the equilibrium data was tested with D-R isotherm. The D-R isotherm can be represented as [37–39]:

$$q_e = q_m \exp\left(-K\varepsilon^2\right) \tag{13}$$

The linearized form of Eq. (13) can be written as:

$$\ln q_e = \ln\ q_m - K\varepsilon^2 \tag{14}$$

where, ε^2 is the Polanyi potential which is equal to RT ln $(1 + 1/C_e)$. q_e is the amount of adsorbate adsorbed at equilibrium per unit of adsorbent (g g^{-1}), q_m is the theoretical saturation capacity (g g^{-1}), C_e is the equilibrium solid concentration (g L^{-1}) and K is the constant related to adsorption energy. R is the gas constant and T is the temperature in Kelvin. The value of K and q_m, respectively, is obtained from the slope and intercept of the plot q_e *vs* ε^2.

In the present investigation, the effect of initial fluoride concentration upon adsorption process was investigated within concentration range of 1–10 mg L^{-1}. A contact time period of 40 min and adsorbent dose of 8.0 mg with volume of fluoride solution 100 mL was maintained as the experimental condition. The results are presented graphically in Fig. 8. It was observed that with increase in initial fluoride concentration, the percentage removal of fluoride decreases. This could be attributed to the fact that with increase in concentration of fluoride, the binding capacity of the adsorbent approaches saturation value, thus resulting in overall decrease in removal percentage.

Table 3
Linear and non-linear Freundlich, Langmuir, Temkin, and D-R isotherm constants related to the sorption of fluoride onto CIC

Model/parameters	Linear method	Non-linear method
Freundlich		
K_F	1.536	1.546
1/n	0.7161	0.7238
Langmuir		
K_L	3.225	1.065
q_m	1.352	2.728
Temkin		
b	7442.27	7442.27
A	30.37	30.37
D-R		
q_m	0.0096	0.0122
K	0.0066	0.0072

Theoretically predicted isotherm data were determined using the Microsoft excel for linear analysis and SPSS 13.0 statistic software for non-linear assessment and presented in Table 3. The fitting presentations are shown in Figs. 9 and 10 for linear and non-linear regression analysis, respectively.

Freundlich constants K_F and 1/n described about the adsorption capacity and adsorption intensity, respectively. Higher the value of 1/n, the higher will

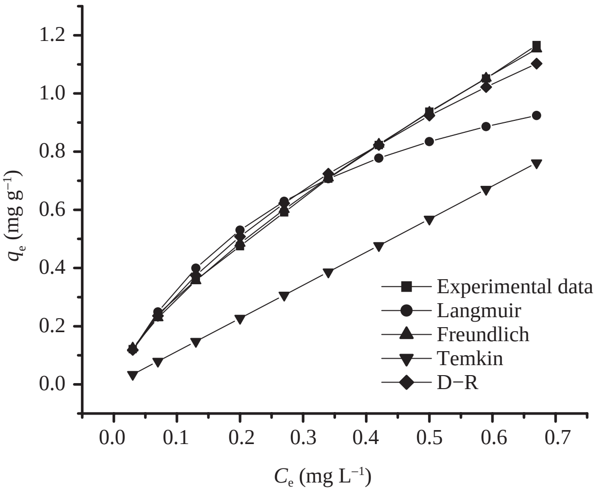


Fig. 9. Adsorption isotherm modeling of fluoride removal using CIC using linear regression analysis; adsorbent dose: 8 g L^{-1}; pH, 6.5, Temp, (25 ± 2) °C; contact time: 40 min.

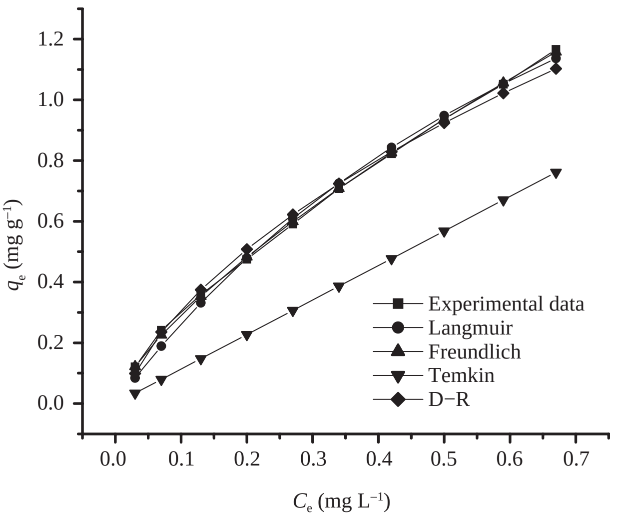


Fig. 10. Adsorption isotherm modeling of fluoride removal using CIC using non-linear regression analysis; adsorbent dose: 8 g L^{-1}; pH, 6.5, Temp, (25 ± 2) °C; contact time: 40 min.

be the affinity between the adsorbate and adsorbent and the heterogeneity of the adsorbent sites. The 1/n value indicates the relative distribution of energy sites and depends on the nature of the strength of the adsorption process [40]. It is found from the Table 3 that the values of 1/n lies between 0.1 and 1.0 confirms the favorable conditions of adsorption and also confirms that 71% of the active adsorption sites have equal energy.

The values of Langmuir constants q_m and K_L which determined by both linear and non-linear method analysis is also represented in Table 3. In order to find out the feasibility of isotherm, the essential characteristics of Langmuir isotherm can be expressed of a dimensionless constant separation factor or equilibrium parameter R_L [36,41] which is:

$$R_L = 1/(1 + K_L C_o) \tag{15}$$

where, C_o is the initial concentration of fluoride (mg L^{-1}). Values of $R_L < 1$ represents favorable adsorption where as, $R_L > 1$ represents unfavorable adsorption processes. The R_L for the initial fluoride concentration of 10 mg L^{-1} was found to be 0.03 and 0.08 by liner and non-linear regression analysis, respectively, indicating favorable condition of adsorption.

The value of the constant B_1 in Temkin isotherm relates to the heat of fluoride adsorption onto CIC and estimated to be 0.3,329 kJ mol^{-1}.

The D-R constant K gives the value of mean free energy of adsorption and the energy (E) per mole of the adsorbate denotes the energy required to transfer one mole of fluoride to CIC surface from infinite in solution which can be computed using the following equation [38,39]:

$$E = (-2k)^{-0.5} \tag{16}$$

The magnitude of E is quite useful for estimating the type of adsorption and if this value is between 8 and 16 kJ mol^{-1}, the adsorption type can be explained as ion-exchange. For the values of E < 8 kJ mol^{-1}, the adsorption process is physical nature [40]. The values of E in this study found to be 8.7 kJ mol^{-1}, which suggest that the adsorption proceeded by ion-exchange.

3.4.1. Error analysis

In order to find out the most suitable isotherm model to represent the experimental data, it is necessary to analyze the data using error analysis combined with the values of R^2 obtained from the regressive analysis. The six well known functions used in this study to calculate the error deviation between the experimental and predicted equilibrium data after both linear and non-linear analysis can be listed as (i) the SSE, (ii) the SAE, (iii) the ARE, (iv) the HYBRID and (v) the MPSD [42]. The values of the error functions are presented in

Table 4
Isotherm error deviation data related to the sorption of fluoride onto CIC using six commonly used functions

Error functions	R^2	SSE	SAE	ARE	HYBRID	MPSD
Linear approach						
Freundlich	0.999	0.000574	0.060442	1.468353	−0.02452	2.35678
Langmuir	0.994	0.104517	0.698432	8.713626	2.73054	11.96164
Temkin	0.9058	0.8882	2.813432	49.56936	61.96171	57.05894
D-R	0.9969	0.007757	0.212508	3.339724	−0.58987	4.356126
Non-linear approach						
Freundlich	0.999	0.000508	0.055969	1.355851	0.524555	2.509123
Langmuir	0.993	0.006889	0.218923	7.222194	6.453952	13.55663
Temkin	0.908	0.8882	2.813432	49.56936	61.96171	57.05894
D-R	0.997	0.008295	0.23826	5.043889	1.35889	7.831895

Table 4. By compiling the results of the values for the error functions, it can be concluded that Freundlich model is the most suitable model to satisfactorily describe the studied adsorption phenomenon basing on the highest R^2 value and lowest SSE, SAE, ARE, HYBRID, and MPSD values.

3.5. Effect of temperature on the adsorption

In order to study the effect of temperature upon adsorption process, the temperature of the medium was varied from 10 °C to 50 °C and at which various thermodynamic parameters were calculated. The thermodynamic equilibrium constant K of the material-anion interaction was calculated using the Van't Hoff Equation [43,44]:

$$\Delta G^o = -\mathrm{RT}\ln K \tag{17}$$

where, R is the universal gas constant ($8.314\ \mathrm{J\ mol^{-1}\ K^{-1}}$), T is the temperature (K), ΔG° is the change in free energy. Further, the relationship between K *vs* standard enthalpy (ΔH°) and standard entropy (ΔS°) factors can be written using the following equation:

$$\ln K = \Delta S^o/R - \Delta H^o/\mathrm{RT} \tag{18}$$

Here ΔH° and ΔS° parameters can be calculated, respectively, from the slope and intercept of plot of ln K *vs* $1/T$.

The relationship between the activation energy (E_a) and sticking probability (S^*) can be calculated from following equation:

$$S^* = (1-\theta)\ \exp(-E_a/\mathrm{RT}) \tag{19}$$

where, θ denotes the surface coverage which can be determined using the following equation:

$$\theta = 1 - C_e/C_o \tag{20}$$

where, C_o and C_e is the initial and equilibrium fluoride ion concentration, respectively.

Both the value of E_a and θ can be calculated, respectively, from the slope and intercept of the plot of ln $(1-\theta)$ *vs* $1/T$.

The experimental observation showed that percentage of removal of fluoride increases with increase in temperature of the medium (Fig. 11). The corresponding values of various calculated thermodynamic parameters are presented in Table 5. The negative values of ΔG° at all temperature confirm the spontaneous nature of sorption process of fluoride onto CIC. The decreasing values of ΔG° with increase in temperature shows the reaction is easier at higher temperature. The reason may be attributed to the fact that when fluoride ion reacts with the available cation on the surface of the adsorbent material, water molecule previously bonded to the metal ion get released and dispersed in solution, thus increasing the entropy factor. Similar trend was also reported by other authors [45]. The positive values of ΔH° and E_a confirms the endothermic nature of the sorption process. The positive values of ΔH° showed increasing randomness during the sorption of fluoride onto CIC. The values of S^* is found to be 0.0003 which is very close to 0 indicated that the adsorption follows chemisorption [46]. A proposed mechanism of fluoride removal by CIC is shown in Scheme 1 where the fluoride adsorption of CIC could be due to the exchange between water coordinated with Ce and F [25].

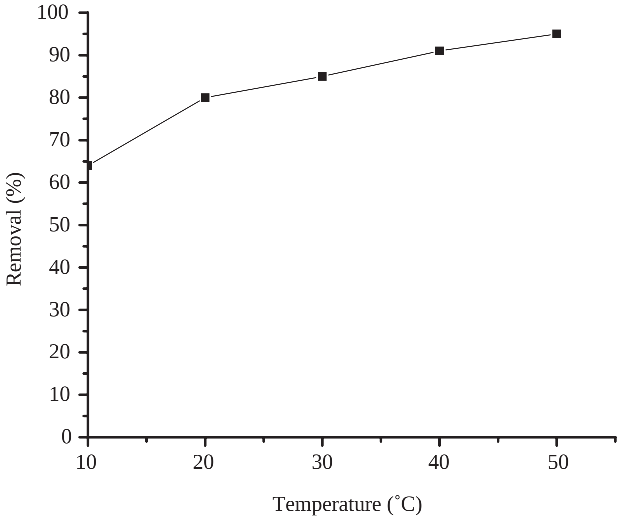


Fig. 11. Effect of variation of temperature of the medium; initial concentration of fluoride: 10 mg $\mathrm{L^{-1}}$; pH: 6.5; adsorbent dose: 8.0 g $\mathrm{L^{-1}}$; contact time: 40 min.

3.6. Effect of adsorbent dose

The effect of adsorbent dose on fluoride removal was studied at a fixed initial concentration of fluoride (10.0 mg $\mathrm{L^{-1}}$), pH 6.5, shaking speed of 200 rpm and contact time of 60 min. It was observed that percentage removal of $\mathrm{F^-}$ increased from 63 to 93% with increase in adsorbent dose and reached a maximum value of 93% at 8.0 g $\mathrm{L^{-1}}$ of CIC. However, after a dosage of 8.0 g $\mathrm{L^{-1}}$, no significant change in the percentage removal of $\mathrm{F^-}$ was observed. The saturation of the active sites could be resulted due to the overlapping of active sites at higher dosage as well as the decrease in the effective surface area resulting in the conglomeration of exchanger particles. However, it satisfies the

Table 5
Thermodynamic parameters for the sorption of fluoride on CIC

Temp (°C)	ΔH° (kJ mol^{-1})	ΔS° (kJ mol^{-1} K^{-1})	ΔG° (kJ mol^{-1})	E_a (kJ mol^{-1})S*	
10	21.719	0.131	−15.37	2.361	0.0003
20		−16.75			
30		−18.26			
40		−19.33			
50		−20.62			

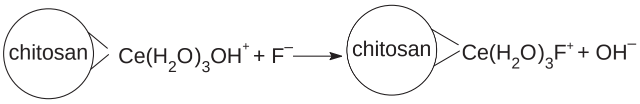
requirement of lowering the F^- level to 1.0 mg L^{-1} which is also the maximum permissible limit for F^- in drinking water [47].

3.7. *Effect of co-ions*

The effects of various diverse ions/competing co-ions upon adsorption of fluoride were investigated using sulfate, nitrate, chloride, bicarbonate and phosphate ions. The experimental condition for initial fluoride concentration was kept at 10 mg L^{-1} varying the initial concentration of co-ions from 25 to 600 mg L^{-1}. The results of the observation showed graphically (Fig. 12) indicated that NO_3^-, Cl^-, SO_4^{-2} had little effect upon fluoride removal processes. However, the experimental result showed that the presence of PO_4^{-3} and HCO_3^- significantly affected the fluoride removal process. Although it is expected that phosphate and bicarbonate may compete with the fluoride adsorption process, at present no satisfactory explanation could be drawn for such kind of observation which needs further experimental facts for conclusive proof.

3.8. *Comparison of removal of fluoride in field water and synthetic water*

The defluoridation capacity of CIC were tested in ground water samples collected from village of Nuapada (Boden block), Orissa, India, as well as synthetic water samples prepared by adding sodium fluoride to deionized water. The results of such investigations are presented in Fig. 13. It was observed that more amount of fluoride removal could be possible from synthetic water sample in comparison to collected ground water sample. The reason could be attributed to the fact that real ground water sample is always associated with a number of cations and anions, which could well interfere with the adsorption process. A summary of the characteristics such as pH, total hardness, alkalinity, presence of various metal ions, etc., of the field water samples collected from different places are given in Table 6. It is to be noted here that the presence of various cations and hence the total concentration of salts can also play a vital role in determination of adsorption of fluoride.



Scheme 1. Mechanism of fluoride adsorption on CIC

3.9. *Reuse and regeneration of adsorbent*

Effective reuse of adsorbent material directly affects the cost factor and hence its utility in continuous batch adsorption processes. The reusability capacity of CIC was performed with dried CIC. As shown in Fig. 14, the percentage of adsorption of fluoride by CIC was found to be reduced from 93 to 70% following a sequence of 1st to 9th cycle of batch operation study.

Desorption studies were carried out with variation of pH of the medium (Fig. 15). It was observed that

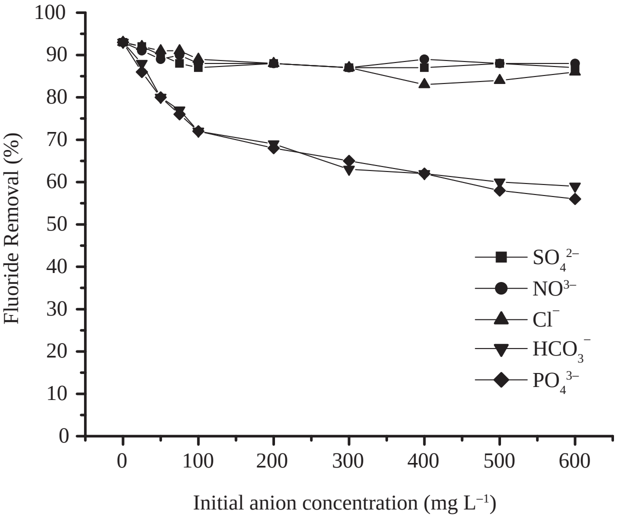


Fig. 12. Effect of co-ions upon removal of fluoride from solution; amount of adsorbent: 8.0 g L^{-1}; concentration of fluoride: 10 mg L^{-1}; time of contact: 40 min; Temperature: (25 ± 2) °C.

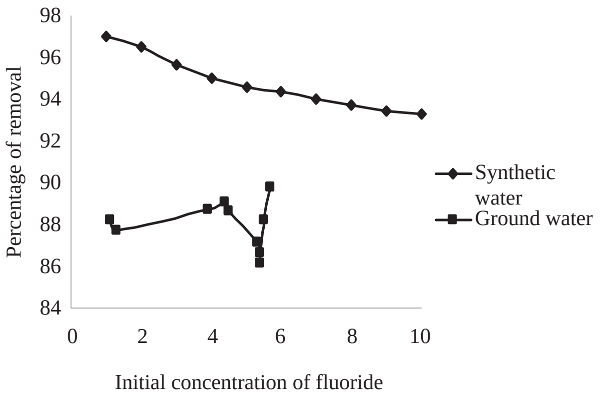


Fig. 13. Comparison of adsorption of fluoride in synthetic water and collected ground water sample; amount of adsorbent: 8.0 g L^{-1}; time of contact: 40 min; Temperature: (25 ± 2) °C.

leaching of fluoride from the adsorbent material was negligible in acidic pH of the medium. However in alkaline pH (pH > 8), substantial amount of fluoride could be eluted out and subsequently nearly 93% of the fluoride could be leached from the adsorbent material at pH 12. Therefore, it can be concluded that the regenerated CIC could be used successfully for a number of continuous cycles of operation in a batch technique.

4. Conclusions

The present investigation reports the preparation of a novel adsorbent material by impregnation of cerium upon chitosan which could be successfully utilized to remove the fluoride from drinking water. Some of the important conclusions of the study are:

Table 6
Characteristics of field water samples

Parameters	Values[a]
Turbidity (NTU)	0.6–5.0
Total hardness as $CaCO_3$ (mg L^{-1})	75–466
Total iron as Fe (mg L^{-1})	<0.07
Chloride as Cl (mg L^{-1})	42–340
Fluoride as F (mg L^{-1})	0.8–6.6
Nitrate as NO_3 (mg L^{-1})	10.5–203
Sulfate as SO_4^{2-} (mg L^{-1})	<120
Alkalinity as $CaCO_3$ (mg L^{-1})	198–576
Na (mg L^{-1})	42.7–482
K (mg L^{-1})	0.6–224
pH	7.1–8.8
Conductivity (μS)	484–2399
Mn (mg L^{-1})	<2.4

[a] All readings are reported as average of three values with RSD(%) 2.1–3.2.

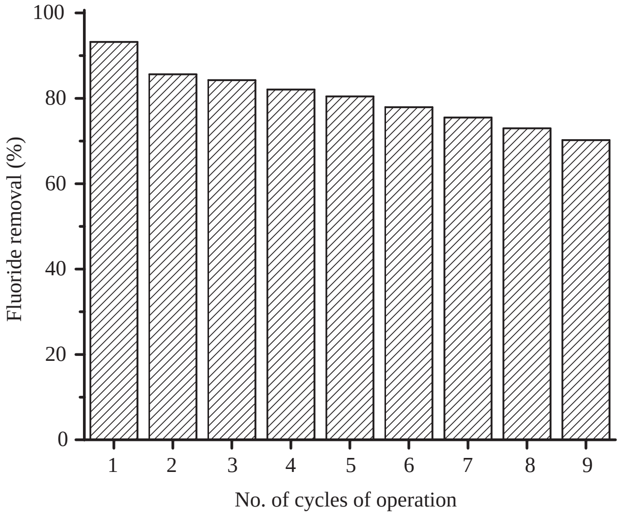


Fig. 14. Bar diagram showing the percentage of removal of fluoride by CIC in different cycle of batch operation.

1. Maximum fluoride could be removed at solution pH 6.5–7.0, therefore, CIC can be conveniently utilized for the removal of fluoride from drinking water sources without undertaking any further treatment facilities.
2. The adsorption process followed pseudo-second order kinetic model. By compiling the results of the values for the error functions, it can be concluded that Freundlich model is the most suitable model to satisfactorily describe the studied adsorption phenomenon based on the highest R^2 value and lowest SSE, SAE, ARE, HYBRID, and MPSD values.
3. The value of E found to be 8.7 kJ mol^{-1} suggesting adsorption processes to be ion-exchange in nature.

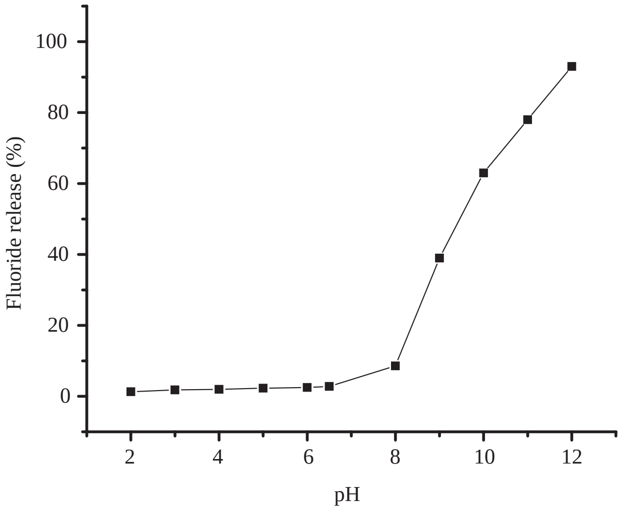


Fig. 15. Desorption of fluoride from CIC with variation of pH of the medium.

The negative values of ΔG° at all temperature confirm the spontaneous nature of sorption process of fluoride onto CIC with S^* value as very close to 0 indicating chemisorption.

4. The presence of co-anion such as NO_3^-, Cl^-, SO_4^{-2} did not have significant impact on removal of fluoride. Desorption study indicated that CIC can be conveniently regenerated and reused for the removal of fluoride.
5. The synthesized material is a low-cost efficient material which can find immense usefulness for the removal of fluoride in rural areas in a sustainable manner.

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