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Removal of Fluoride from Aqueous Solution Using Aluminum-Impregnated Chitosan Biopolymer

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Abstract: Aluminum impregnated chitosan (AIC) was prepared and applied as an adsorbent for the removal of fluoride from aqueous solutions. The process involved two stages: (i) isolation of chitosan from chitin, (ii) impregnation of aluminum in isolated chitosan at fixed pH. SEM and EDS techniques were used to characterize the composition of adsorbent AIC. Dynamic adsorption experiments on AIC were carried out at various pH, contact times, adsorption dosages, and initial fluoride concentration to determine optimum adsorption properties. The experimental data were analyzed using two adsorption models, Langmuir and Freundlich, with the later system providing the best fit. Thermodynamic parameters showed the adsorption process as spontaneous and endothermic. The adsorption process follows first-order kinetics for which a mechanism has been proposed. Reusability of the AIC was tested up to four consecutive cycles. The desorption experiment showed 92% elution of adsorbed fluoride at a pH of 12. Finally, the performance of the adsorbent material was studied on field water samples collected from a fluorosis endemic-region.

Keywords: Adsorption, adsorption model, chitosan, fluoride

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INTRODUCTION

The effect of fluoride in drinking water upon human health has been a subject of research interest since more than a decade. Fluoride is considered as an accumulative toxin and the presence of fluoride ion in potable water has adverse effect on human health (1,2). Fluoride is also considered as a necessary micronutrient both in case of man and animal, depending upon the total amount ingested and an excess fluoride ($>1.5\,\mathrm{mg\,L^{-1}}$) in drinking water is reported to be harmful to human health (3,4). Although fluoride has a beneficial effect for calcification of dental enamel and bone formation, an excess amount of fluoride intake may lead to mottling of teeth, fluorosis (dental and/or skeletal), as well as various neurological damages (5).

A number of defluoridation techniques have been suggested for the removal of excess fluoride and these can be classified into three major types, viz., chemical addition processes, adsorption processes, and ion-exchange mechanism (6). Membrane processes such as reverse osmosis, nanofiltration, electrodialysis, and Donnan dialysis were also recently investigated to reduce fluoride concentration in water (7–10). Activated alumina has also been successfully used to remove fluoride from contaminated ground water (11). However, fluoride removal using activated alumina is strongly pH dependant and hence the pH of both raw water as well as the regenerated bed needs to be adjusted accordingly. Apart from this, activated alumina particles are chemically unstable and are partly lost during the regeneration process. Use of selective ion-exchange resins (6,12–15) and various other synthetic resins were investigated by research teams (16–18) with respect to their efficacy in fluoride removal processes and advantages in operational procedure along with cost factor.

In this aspect, the polysaccharide chitosan, a copolymer of 2-glucosamine and N-acetyl-2-glucosamine derived from chitin, represents a suitable biopolymer that can be used as a porous carrier material. The presence of high concentration of amine groups favors coordination towards fluoride-selective metal ions which can be quite helpful in selective modification of such material for efficient use in the removal of fluoride from drinking water (1). Commercially chitosan is prepared by deacetylation of chitin in hot alkali. Recently, Ma et al. (19) studied the adsorption of fluoride on magnetic-chitosan particle from the water solution in the batch system. The kinetics of adsorption processes were evaluated by optimizing the parameters such as pH, temperature, etc. Kamble et al. (1) studied the removal of fluoride using lanthanum modified chitosan by optimizing the efficiency of the removal process with variation of pH of the medium. Although, a considerable amount of work has been done on developing new adsorbent materials using an impregnation technique, only a few studies have reported the deflouridation of drinking water using chitosan biopolymer (20).

The main objective of the present investigation is to study the removal of fluoride from drinking water using aluminum-impregnated chitosan material. In the present study, chitin was isolated from prawn shell (collected from Chilika Lake, Orissa) using a reported methodology (21). Further, chitosan was prepared by deacetylation of isolated chitin. The degree of deacetylation was calculated from the FTIR study. The adsorbent material was prepared by impregnation of chitosan with aluminum in molar ratio with optimization of pH of the solution. The effects of pH, adsorbent dose, concentration of fluoride, time of contact, the temperature, and the presence of interfering ions on adsorption of fluoride from solution were also investigated. Further, the efficiency of adsorption of fluoride was investigated in both laboratory and real ground water samples collected from a fluoride affected region of Orissa State (Boden Block, Naupada), India. Efficiency of the adsorbent material with respect to elution and regeneration process was optimized.

EXPERIMENTAL

Materials

All chemicals used in the present study were of AR grade. Sodium fluoride, sodium chloride, sodium sulphate, sodium nitrate, sodium bicarbonate, and sodium dihydrogen phosphate were obtained from E. Merck India Limited. A stock solution of fluoride was prepared by dissolving 2.21 g of sodium fluoride in one liter deionized water. The required concentration of fluoride solution was prepared by serial dilution of 1000 mg L^{-1} fluoride solution. The prawn shells were collected from Chilika lake, Orissa, India.

To maintain the accuracy of the experimental data, all adsorption experiments were conducted thrice to obtain reproducible results. Further, in order to reduce the analytical errors, the original fluoride solution (act as control) was used in all the experiments. All experimental errors were found to be well within an acceptable limit of 4%.

Preparation of Chitin and Chitosan

Chitin was isolated from prawn shell using Hackman method as described previously (21). Prawn shells were milled to fine particles using a rotary mill. Further Chitosan was prepared by deacetylation of purified chitin according to methodology followed by Muzzarelli et al. (22).

Characterization of Chitin and Chitosan

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 infra red spectra of all the sample materials were recorded at room temperature at a resolution of $4\,\mathrm{cm}^{-1}$ and 64 scans using Shimadzu IR Prestige-21 FTIR instrument. The surface structure of the adsorbent material was analyzed using Scanning Electron Microscope (SEM) (Jeol, JSM 6390 LV) coupled with energy dispersive spectrum (EDS) technique. Iso-electric points of adsorbent material in solution were determined by electrophoretic studies using Malvern Zeta meter (model Nano ZS).

Preparation of Aluminum Impregnated Chitosan

Aluminum impregnated chitosan (AIC) adsorbent material was prepared by adding required amount of chitosan to a solution of $Al_2(SO_4)_3 \cdot 16H_2O$ ($0.075\,\mathrm{mol\,L^{-1}}$) at different pH and the mixture was stirred continuously for 24 h at a temperature of (25 ± 2)°C. After a time period of 24 h, the stirring process was stopped but both the metal solution and chitosan were allowed to remain in contact for further 48 h to ensure the maximum loading of aluminum onto the chitosan material. The filtrate was analyzed for residual aluminum by EDTA titration. Then the impregnation was carried out at optimum pH by adding 5.0 g of chitosan to 50 mL of $0.075\,\mathrm{mol\,L^{-1}}$ $Al_2(SO_4)_3 \cdot 16H_2O$ solution and the filtered solid was washed with enough quantity of deionized water and dried at 70°C in vacuuo.

Removal of Fluoride Using AIC

The removal experiments were carried out by batch method in which a fixed amount of the adsorbent material (AIC) was added to 100 mL of test solution in a conical flask and kept in a rotatory shaker. A rotation of 100 r.p.m was maintained at room temperature (25 ± 2)°C. Initial fluoride concentration was maintained at $10\,\mathrm{mg\,L^{-1}}$ 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 100 mL of 10 mg L^{-1} fluoride solution. Concentration of fluoride in the solution, before and after adsorption, was determined using ion selective electrode (Orion 720 A^+ Ion analyzer).

To determine the reusability of the AIC, 0.7 g of AIC was added to 100 mL of 10 mg L^{-1} fluoride solution. After the adsorption, the adsorbent was filtered and dried in an oven at 70°C in vacuuo. The dried adsorbent material was used repeatedly for fluoride removal in successive fresh samples to evaluate the extent of adsorption process and hence its reuse.

Desorption Studies

Fluoride adsorbed AIC was used for desorption studies. 10 g of AIC was kept in contact with 10 mg L^{-1} fluoride solution for a time period of 1 h to attend the equilibrium. The fluoride adsorbed AIC, so prepared, was filtered and the filtrate was measured for residual fluoride content. Then desorption studies were carried out by using fluoride adsorbed AIC with varying pH by adding 0.01 mol L^{-1} H_2SO_4 or NaOH solutions. The leached fluoride concentration in the filtrate was measured using an Orion 720 A^+ Ion analyzer.

RESULTS AND DISCUSSION

Elemental and FTIR Characterizations of Chitin and Chitosan

The percentage of ash, carbon, hydrogen, nitrogen of chitin and chitosan are summarized in Table 1. The percentage of ash content for the isolated chitin was found to be 4.0. The percentage of nitrogen in chitin and chitosan were 6.17 and 7.24, respectively, in contrast to the reported

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

Content gm/100 gm	Chitin	Chitosan
Ash	4.00	0.80
C	45.23	43.12
H	6.15	6.23
N	6.17	7.24

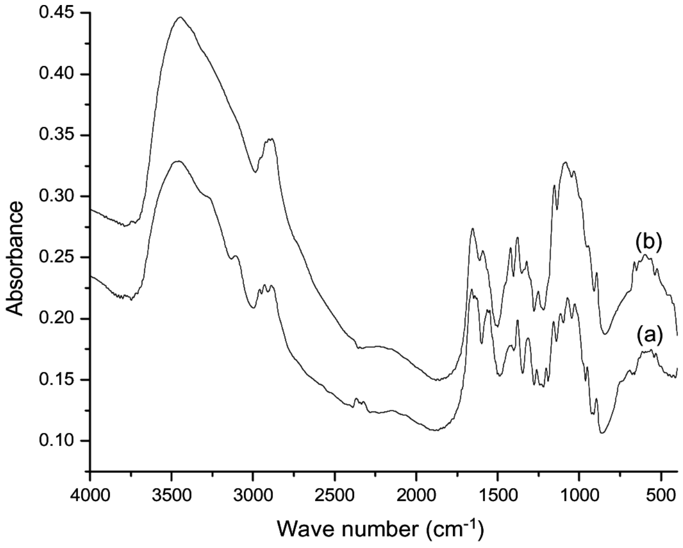

Figure 1. FTIR spectra of (a) chitin and (b) chitosan.

theoretical value of 8.7% for that of chitosan. Muzzarelli et al. (22,23) have reported similar kind of observations. From the FTIR spectra of chitin and chitosan, as shown in Fig. 1, the percentage degree of deacetylation (DD%) was calculated using the following equation (24):

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

where, A_{1320} and A_{1420} represented the absorbance at 1320 and 1420 cm^{-1}, respectively. DA represents the degree of acetylation (DA% = 100 − DD%). The degree of acetylation in the present investigation, was calculated to be 84%.

Electrophoretic Studies

The electrophoretic studies are important in view of determination of behavior of adsorbent materials in different electrolytic medium. The iso-electric point (IEP) of chitosan and the adsorbent AIC were determined using electrophoretic mobility in a solution of ionic strength 0.01 M NaCl and 0.001 M NaCl (Fig. 2). The point at which the zeta potential was found to be zero is termed as iso-electric point (25). From the electrophoretic studies shown graphically as a function of pH versus the zeta potential in mV (Fig. 2), the IEP values of chitosan and AIC

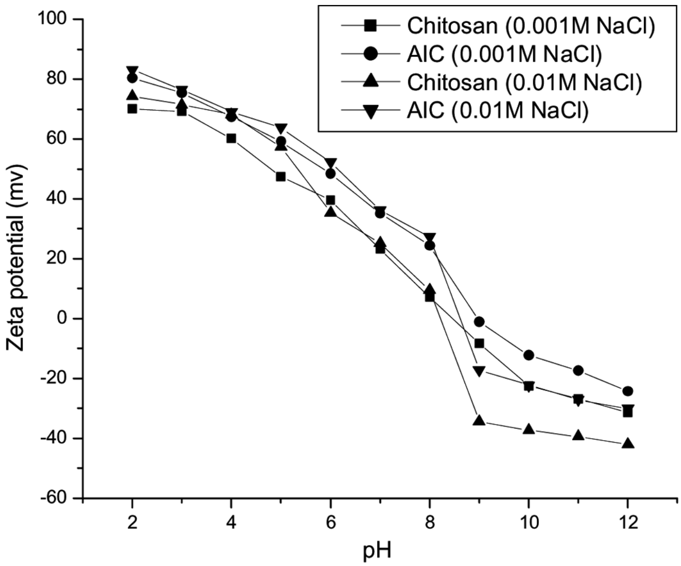

Figure 2. The zeta potential of chitosan and AIC as a function of pH using 0.01 M NaCl and 0.001 M NaCl as supporting electrolyte.

were found to be 8.2, 8.5, 8.6, and 9.0 respectively, at 0.01 M and 0.001 M NaCl solution. The IEP values of chitosan and metal-impregnated chitosan differs in different electrolytic medium indicating the surface modification of chitosan material with metal.

With increasing ionic strength, the IEP values of both the unmodified and modified chitosan material were found to be lower which could be due to the adsorption of the background electrolyte (NaCl) used as the medium. The anions could be adsorbed on the surface of the adsorbent materials, thus neutralizing the positive charge of the surface to some extent, resulting in lowering IEP values. Background electrolyte could also affect the surface of the adsorbent materials, therefore making it difficult to determine the exact point of the zero charge (pH_{pzc}).

Effect of Solution pH on Impregnation of Aluminum on Chitosan and the Mechanism of Aluminum Adsorption Process

The most important factor which controls the impregnation process is the pH of the medium. It is reported that in acidic medium ($pH < 4.0$), Al^{+3} remain as mostly predominant species in solution (26). In the present investigation, as shown in Fig. 3, the pH of the medium varies from

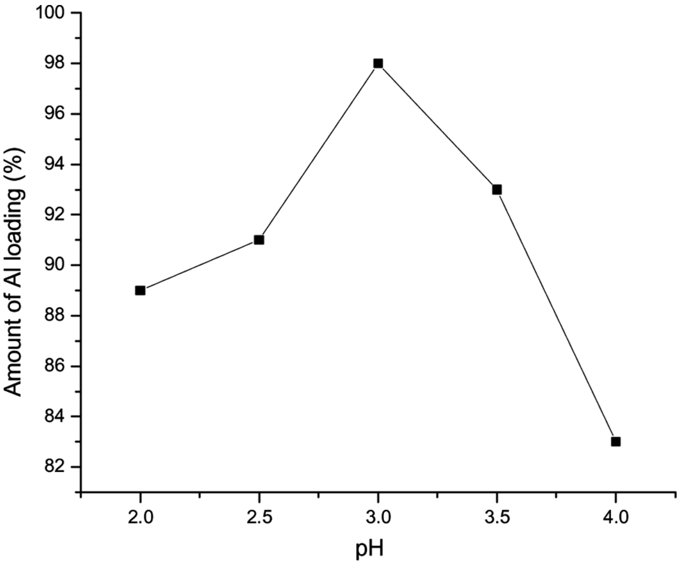

Figure 3. Al^{3+} loading on chitosan with variation of pH of the medium.

2.0–4.0 and it was observed that the percentage of the loading of aluminum (evaluated EDTA titration method) onto the chitosan material was maximum at a pH of 3.5. Increasing pH beyond 4.0 resulted in precipitation of aluminum as $Al(OH)_3$ which settled as sediment material at the bottom of the conical flask. The aluminum-impregnated chitosan was repeatedly washed with deionized water to remove the adherent physical deposition of aluminum upon the surface of the chitosan.

Since the maximum impregnation of aluminum on chitosan material was found at pH 3.5, therefore, the surface of the chitosan is expected to be positively charged because of the lower value of solution pH than the IEP values of chitosan that lies between 8.2 and 8.5. Although $pH < 4.0$ favors Al^{3+} as the mostly predominant species in solution, the possibility of the presence of other positively charged species in solution such as, $Al(OH)^{+2}$, $Al_2(OH)_2^{+4}$ and $Al_3(OH)_4^{+5}$ could not be ruled out (27). Since in the present study both the chitosan as well as metal species were positively charged, hence it was expected that impregnation of aluminum upon chitosan could not be possible only due to the electrostatic attraction or columbic attractive forces. Instead, it could be expected that a chemical interaction having sufficient energy to overcome the repulsive forces between the chitosan surface and aluminum hydro-complexes might occur in the solution medium.

Sorption Study

Effect of Adsorbent Dose

The effect of the adsorbent (AIC) dose on the removal of fluoride was studied at an ambient temperature of (25 ± 2)°C with a contact time period of 60 minutes. The initial concentration of fluoride in the solution was maintained at 10 mg L^{-1}. As shown in Fig. 4, it was observed that the percentage of the removal of fluoride increases with an increase in the adsorbent dose. The percentage of the maximum removal of fluoride was found to be 84.0 with 7.0 g L^{-1} of AIC. However, it is to be mentioned that no quantitative adsorption of fluoride was noticed with the isolated chitosan material.

Effect of pH of the Medium Upon Adsorption of Fluoride

The pH of the solution is an important parameter that controls the adsorption at the water-adsorbent interfaces. In the present investigation, as shown in Fig. 5, the adsorption of fluoride upon AIC was examined within a pH range of 2.0–12.0. It was observed that the adsorption of fluoride increases with an increase in pH of the medium. The percentage

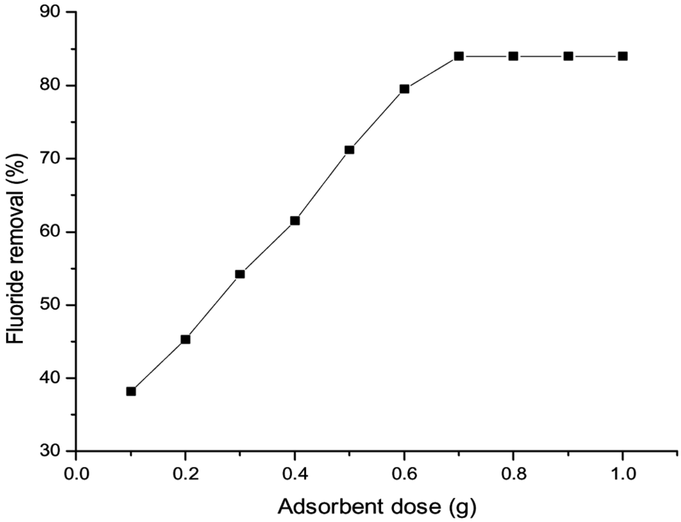

Figure 4. Effect of adsorbent dose for adsorption of fluoride; concentration of fluoride: 10 mg L^{-1}; pH: 6.5; temperature: (25 ± 2)°C; time of contact: 60 min.

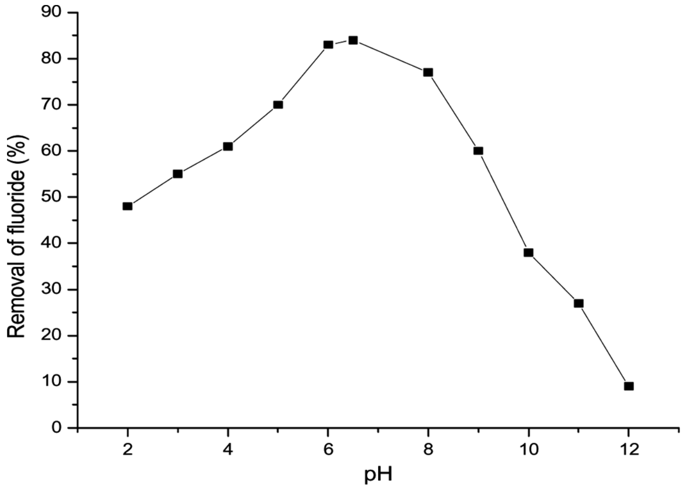

Figure 5. Effect of pH on adsorption of fluoride, adsorbent dose: 7.0 g L^{-1}, time of contact: 60 min; temperature: (25 ± 2)°C.

of the maximum removal of fluoride (~84%) could be possible at pH 6.5. With further increases in pH of the medium, the amount of removal of fluoride ion from the solution decreases. In an acidic medium, the formation of weak hydrofluoric acid often influences the amount of fluoride adsorption by the adsorbent material. At higher pH, the decrease in fluoride adsorption could be attributed to the strong competition of the hydroxyl ions with the fluoride in the solution.

Effect of Contact Time

The variation of contact time in Fig. 6, showed that the removal of fluoride increases with increase in the time period. A maximum removal of fluoride was possible within a time period of 10–30 minutes, after which the adsorption process became almost constant. This can be attributed 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 decrease in the number of available adsorbent sites as well as the amount of the remaining fluoride ions in the solution.

The kinetics of the adsorption process could be calculated using the Eq. (2). The rate of adsorption of fluoride was relatively fast during

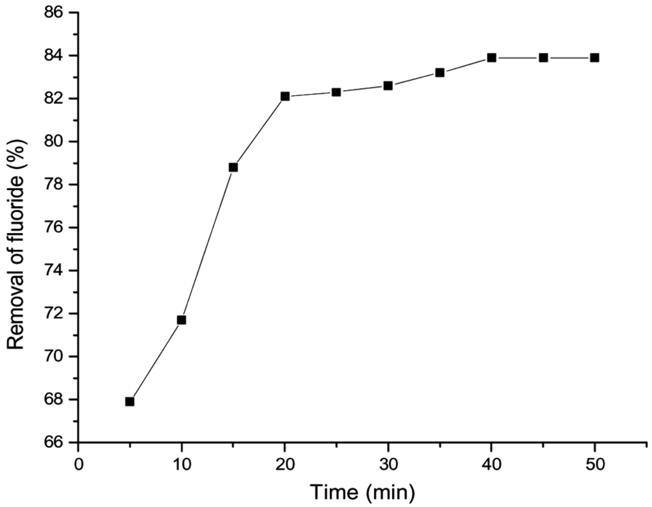

Figure 6. Effect of contact time on adsorption of fluoride; concentration of fluoride: $10\,\mathrm{mg\,L^{-1}}$; pH: 6.5; adsorbent dose: $7.0\,\mathrm{g\,L^{-1}}$; temperature: (25 ± 2)°C.

the first 5 minutes and thereafter the rate of fluoride adsorption slowed down, nearing the equilibrium. The rate constant (K_{ad}) for the sorption of fluoride was studied by Lagergren rate equation (2):

$$\log(q_e - q) = \log q_e - K_{ad}\left(\frac{t}{2.303}\right) \tag{2}$$

where q_e and q ($\mathrm{mg\,g^{-1}}$) are the amounts of fluoride adsorbed at equilibrium and at time ‘t’, respectively. The validity of the Lagergren equation following first-order kinetics was verified from the plot of log ($q_e - q$) versus ‘t’, in which a straight line was obtained with $r^2 > 0.99$. The adsorption rate constant (K_{ad}), calculated from the slope of the plot, was found to be $0.101298\,\mathrm{min^{-1}}$ for initial fluoride concentration of $10\,\mathrm{mg\,L^{-1}}$ under experimental condition.

Effect of Variation of Temperature

The effect of variation of temperature of the medium upon adsorption of fluoride was studied using optimum adsorbent dose $7.0\,\mathrm{g\,L^{-1}}$ and maintaining the concentration of fluoride at $10\,\mathrm{mg\,L^{-1}}$. The percentage removal of fluoride in Fig. 7, was found to increase within the range of study. A gradual increase in amount of adsorption was noticed within 20°C, beyond which the adsorption remained almost constant.

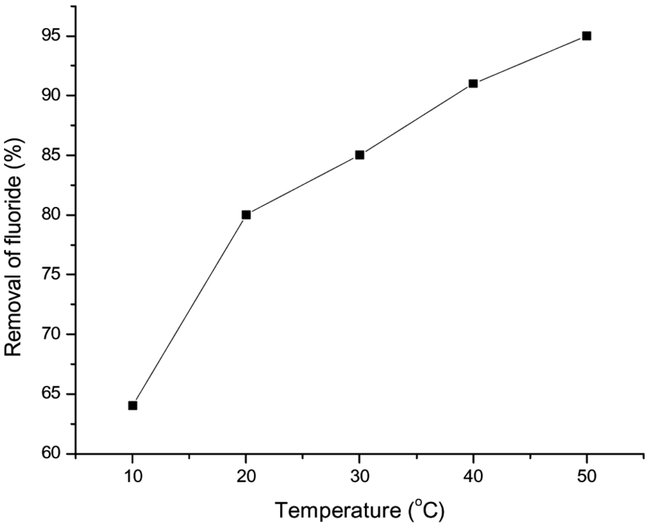

Figure 7. Effect of variation of temperature of the medium, concentration of fluoride: 10 mg L^{-1}, pH: 6.5; time of contact: 40 min; adsorbent dose: 7.0 g L^{-1}.

The various thermodynamic parameters such as change in free energy (ΔG), enthalpy (ΔH), and entropy (ΔS) were calculated using the following equations:

$$\log K_C = \frac{\Delta S}{2.303\ R} - \frac{\Delta H}{2.303\ RT} \tag{3}$$

$$\Delta G = \Delta H - T\Delta S \tag{4}$$

where ΔS and ΔH are the changes in entropy and enthalpy of adsorption, respectively. The value of ΔH and ΔS, evaluated from the slope and intercept of linear van't Hoff plot ($\log K_C$ vs $1/T$), were found to be 43064.09 kJ mol^{-1} and 160.29 kJ mol^{-1} K^{-1}, respectively. Thermodynamically, the positive value of entropy (ΔS) indicates increase in the degree of randomness in the adsorption process and hence a good affinity of fluoride with AIC could be expected. The negative value of ΔG at each temperature indicated the feasibility and spontaneity of ongoing adsorption process. A decrease in values of ΔG with the increase in temperature suggested more adsorption of fluoride at higher temperature. The endothermic nature of the process was once again confirmed by the positive value of enthalpy (ΔH). The positive value of enthalpy (ΔH) also suggested that the entropy factor is primarily responsible for a negative ΔG value. Therefore, the adsorption process could expect to be spontaneous due to the contribution of entropy.

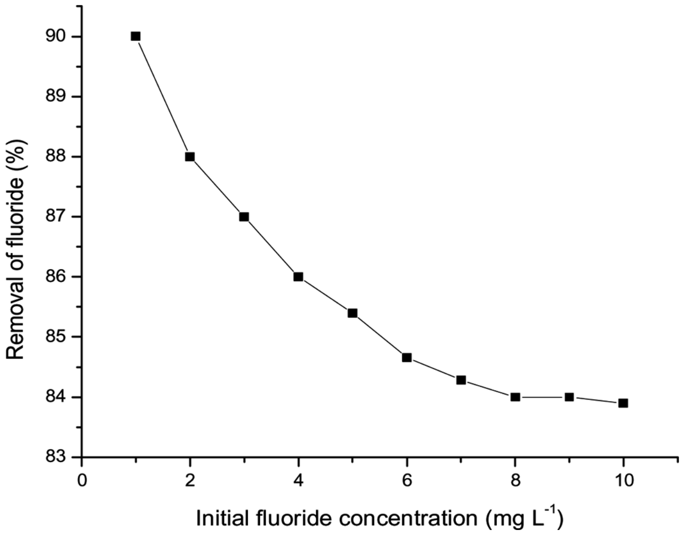

Figure 8. Effect of initial fluoride concentration, adsorbent dose: 7.0 g L^{-1}; time of contact: 40 min; temperature: (25 ± 2)°C; pH: 6.5.

Effect of Initial Fluoride Concentration

The effect of initial fluoride concentration upon the adsorption process was investigated within a concentration range of 1–10 mg L^{-1}. A contact time period of 40 minutes and an adsorbent dose of 7.0 g L^{-1} with the 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 an increase in the initial fluoride concentration, the percentage removal of the fluoride decreases. This could be attributed to the fact that with an increase in concentration of fluoride, the binding capacity of the adsorbent approaches saturation value, thus resulting in an overall decrease in the removal percentage. The adsorption process was further verified using the Langmuir adsorption isotherm model.

Adsorption Isotherm

Equilibrium relationships between the adsorbent and the adsorbate are best described by adsorption isotherms. Freundlich and Langmuir adsorption models are the two most widely accepted surface adsorption models for single-solute systems. However, the Freundlich isotherm is purely empirical in nature and the Langmuir isotherm model is applicable for monolayer sorption onto a surface with finite number of identical sites. The linearized form of the Freundlich equation can be written as:

$$\ln q_e = \ln K_F + 1/n \ln C_e \tag{5}$$

where, q_e is the solid phase sorbate concentration in equilibrium ($mg\,g^{-1}$), C_e is the liquid phase sorbate concentration in equilibrium ($mg\,dm^{-3}$), K_F is the Freundlich constant ($dm^3\,g^{-1}$), and $1/n$ represents the surface heterogeneity factor. The values of K_F and n, obtained from the slope and intercept of the plot between $\ln q_e$ and $\ln C_e$, were found to be 0.7919 and 1.2525, respectively.

For the purpose of comparison, the adsorption data obtained from the variation of the fluoride concentration were also fitted to linearly transformed Langmuir adsorption model. The linearized form of the Langmuir adsorption model, which is valid for the monolayer sorption onto a surface with finite number of identical sites, is given by:

$$1/q_e = 1/(K_L q_m) \times (1/C_e) + 1/q_m \tag{6}$$

where, q_e is the sorbate concentration in equilibrium ($mg\ g^{-1}$), C_e denotes the equilibrium adsorbate concentration in solution ($mg\ dm^{-3}$), q_m is the monolayer adsorption capacity ($mg\ g^{-1}$), and K_L ($l\ mg^{-1}$) is the constant related to the free adsorption energy. The values of q_m and K_L, obtained from the slope and intercept of the plot between $1/C_e$ and $1/q_e$, were found to be 1.73161699 $mg\,g^{-1}$ and 0.7822 $L\,mg^{-1}$, respectively.

In order to predict the adsorption efficiency of the adsorption process, the dimensionless equilibrium parameter was determined by using the following equation:

$$r = \frac{1}{1 + b\mathrm{Co}} \tag{7}$$

where, C_o is the initial concentration of fluoride. Values of r for an initial fluoride concentration of 10 $mg\,L^{-1}$ was found to be 0.1133. The value $r < 1$ thus indicated a favorable adsorption process.

Although the equilibrium data fitted well to both the adsorption models, the Freundlich model with the value of $R^2 = 0.9993$ exhibited a slightly better fit to the adsorption data than the Langmuir model with $R^2 = 0.993$.

Effect of Diverse Ions

The effects of various diverse ions/competing co-ions upon the adsorption of fluoride were investigated in case of sulphate, nitrate, chloride,

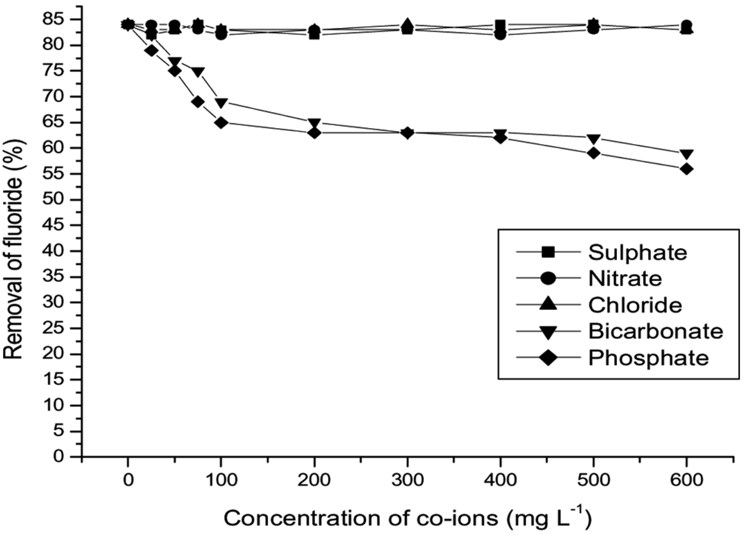

Figure 9. Effect of co-ions upon removal of fluoride from solution, amount of adsorbent: 7.0 g L^{-1}; concentration of fluoride: 10 mg L^{-1}; time of contact: 60 min; temperature: (25 ± 2)°C.

bicarbonate, and phosphate. The experimental condition for initial fluoride concentration was kept at 10 mg L^{-1} varying the initial concentration of co-ions from 50 mg L^{-1} to 600 mg L^{-1}. The results of the observation shown graphically in Fig. 9, indicated that NO_3^-, Cl^-, SO_4^{-2} had little effect upon the 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 but at present no satisfactory explanation could be drawn for such type of observation which needs further experimental facts for conclusive proof.

SEM and EDS Analysis of Fluoride Adsorbed AIC

The scanning electron micrograph (SEM) and energy dispersive spectrum (EDS) of AIC, after sorption with 10 mg L^{-1} fluoride solution, are presented in Fig. 10. The AIC surface appears littered with whitish nodules. The EDS spectrum clearly showed the evidence of signals generated from fluoride on the surface of AIC. The various other signals as found in the EDS spectrum of the sample material were Al, S, N, O,

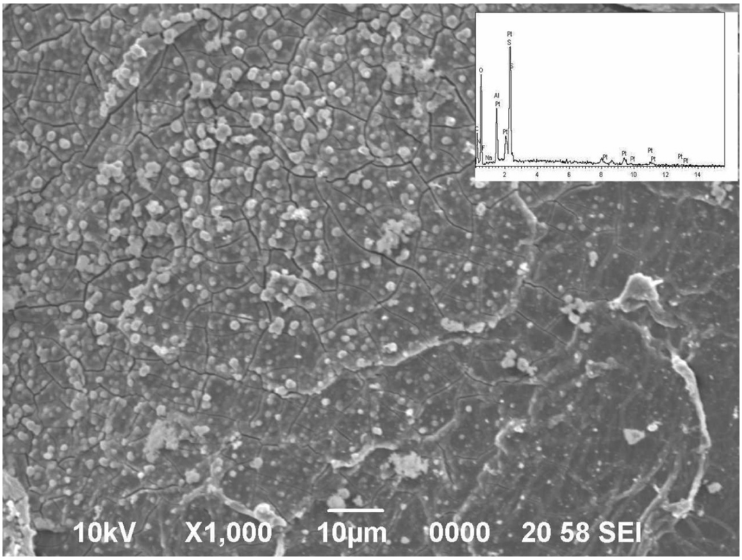

Figure 10. Morphological feature (SEM) of fluoride adsorbed AIC showing the presence of Al and F in the embedded EDS picture.

and C. The presence of a platinum signal in the spectra resulted from the platinum material that was purposely coated to increase the electrical conduction and hence to improve the quality of micrograph.

Adsorption Mechanism of Fluoride Upon Aluminum-Impregnated Chitosan

An attempt to elucidate the mechanism of adsorption of fluoride upon AIC is satisfactorily made here. As mentioned earlier, the IEP points of AIC were 8.6 and 9.0 at 0.01 and 0.001 M NaCl solution, respectively. At higher pH of the medium, the negatively charged surface of AIC could be expected to repel the fluoride ion from its surface. Therefore, the adsorption process was not expected to follow electrostatic or coulombic attraction, but it could be attributed to chemical surface precipitation. At a lower pH of the solution, the surface of adsorbent material AIC is positively charged, indicating the adsorption process due to both chemical and surface precipitation. The mechanism of ligand exchange reactions can be conveniently represented by following equations:

$$\mathrm{SOH} + \mathrm{H}^{+} \longleftrightarrow \mathrm{SOH}_2^{+} \tag{8}$$

$$SOH_2^+ + F^- \longleftrightarrow SF + H_2O \tag{9}$$

$$SOH + H^+ + F^- \longleftrightarrow SF + H_2O \tag{10}$$

where S represents the Al^{+3} ion.

Comparison of Removal of Fluoride in Field Water and Synthetic Water Samples

The defluoridation capacity of AIC was tested in ground water samples collected from the 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. 11. It was observed that a greater amount of fluoride removal could be possible from synthetic water sample in comparison to the 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 physical parameters 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 2. It might be interesting to note that the presence of various cations and the total concentration of salts play an important role in the determination of adsorption of fluoride, for which detailed investigations would be our future goal.

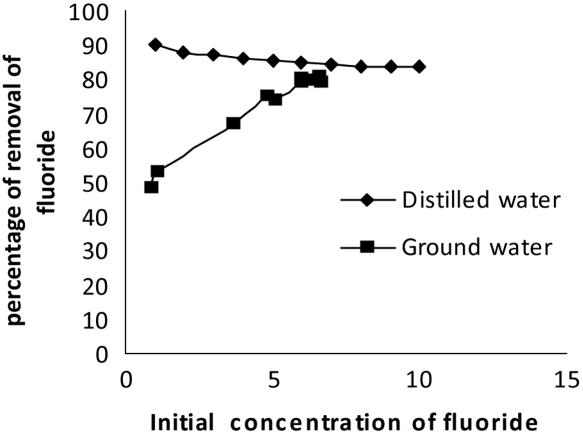

Figure 11. Adsorption of fluoride from synthetic laboratory and ground water samples, amount of adsorbent: 7.0 g L^{-1}; time of contact: 60 min; temperature: (25 ± 2)°C.

Table 2. 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
As ($mg\,L^{-1}$)	<1.8

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

Reuse of Adsorbent

Effective reuse of adsorbent material directly affects the cost factor and hence its utility in continuous batch adsorption processes. The reusability

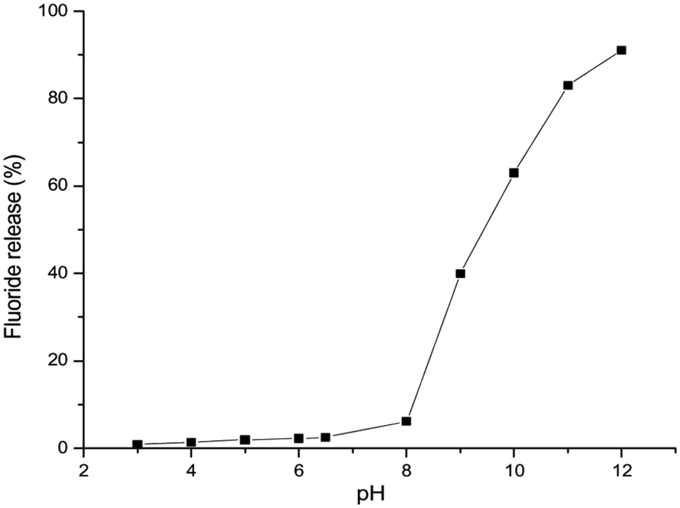

Figure 12. Desorption of fluoride from AIC with variation of pH of the medium.

capacity of AIC was performed with dried AIC. The percentage of adsorption of fluoride by AIC was found to be 84, 72, 61 and 45%, respectively, for 1st, 2nd, 3rd, and 4th cycle of batch operation study.

The desorption studies, as shown in Fig. 12, were carried out by varying the pH of the medium. It may be noted that a very small amount of fluoride could be leached in an acidic medium. However, beyond pH 8, a substantial amount of fluoride could be eluted out and at pH 12, nearly 92% of the fluoride could be removed from the adsorbent material. Thus, it can be concluded that the regenerated AIC can again be used for a number of cycles of operation using the batch technique. The optimization of the result is beyond the scope of the present work and shall be worked out subsequently.

CONCLUSION

The present investigation reports the preparation of an adsorbent material by impregnation of aluminum upon chitosan which could be successfully utilized to remove the fluoride from drinking water. Some of the salient features of the study are:

1. The impregnation of aluminum upon chitosan could be successfully carried out at solution pH 3.5.
2. Since maximum fluoride could be removed at solution pH 6.5, therefore, AIC can be conveniently utilized for the removal of fluoride from drinking water sources without any further treatment.
3. The adsorption process follows first-order kinetics as well as it obeys the Freundlich and Langmuir adsorption models within the range of studies.
4. The presence of co-anion such as NO_3^-, Cl^-, SO_4^{-2} did not have a significant impact on the removal of fluoride. However, the presence of PO_4^{-3} and HCO_3^- show a negative effect on fluoride removal process.
5. The desorption study indicated that AIC can be conveniently regenerated and reused for the removal of fluoride.

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