Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Sathish, R. Sai , Sairam, S. , Raja, V. Guru , Rao, G. Nageswara and Janardhana, C.(2008) 'Defluoridation of Water Using Zirconium Impregnated Coconut Fiber Carbon', Separation Science and Technology, 43: 14, 3676 — 3694

To link to this Article: DOI: 10.1080/01496390802222541

URL: http://dx.doi.org/10.1080/01496390802222541

Separation Science and Technology, 43: 3676–3694, 2008
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ISSN: 0149-6395 print/1520-5754 online
DOI: 10.1080/01496390802222541

Defluoridation of Water Using Zirconium Impregnated Coconut Fiber Carbon

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Abstract: In this study the applicability of Zirconium ion impregnated coconut fiber carbon (ZICFC) as an adsorbent for fluoride removal from water was investigated. The dependence of fluoride adsorption on the physicochemical properties includes pH, agitation time, adsorbent dosage, temperature, and the initial concentration of the adsorbate. Maximum defluoridation was obtained at an original pH value of 4.0 with a rapid 93% adsorption being achieved within 10 min of contact with ZICFC. Adsorption data for fluoride onto ZICFC were better correlated to the Langmuir isotherm and pseudo-second order chemical reaction provided the best fit for the experimental data as obtained from kinetic studies. A combination of chemisorption and physisorption processes in hand with intraparticle diffusion, account for the high defluoridation ability of ZICFC, with the thermodynamic parameters indicating an endothermic phenomenon. The fluoride adsorption capacity of ZICFC when compared with those of other commonly used fluoride adsorbents highlights the substantial improvement in fluoride adsorption capacity of coconut fiber carbon on zirconium impregnation.

Keywords: Coconut fiber carbon, defluoridation, impregnation, langmuir adsorption isotherm, reaction kinetics

INTRODUCTION

The access to safe drinking water, which is the elixir of human life, has been denied to over one billion people across the globe today. While the developed countries debate on policies with regard to fluoridation

Received 4 January 2008; accepted 6 April 2008.

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of their drinking water sources, the most populous developing countries– India and China reel under the effect of fluorosis (1). The Indian scenario is in a more pitiful state, with the quality of groundwater, which meets 80% of domestic needs in rural areas and 50% in urban areas in India, being contaminated by major inorganic pollutants like fluoride and arsenic which are geogenic in origin (2). The fluorosis problem prevails in 36,988 habitations, being the most widespread geochemical disease in India, with the states of Andhra Pradesh, Gujarat, and Rajasthan being the worst affected (1). Fluoride concentrations in groundwater here, ranges from 0.5 to 48 mg/L (3). This is a far cry from the recommendation standards set by WHO (4), which requires the fluoride concentration in drinking water in the range 1.0–1.5 mg/L. Leaving aside the geogenic leaching of fluoride into groundwater, unfortunately there has been a tragic increase in the fluoride ion concentration in groundwater and various other water bodies due to human contribution. Semiconductor manufacturing, uranium enrichment, coal power plants, fertilizer manufacturing, glass and ceramic production, and electroplating industries are mainly responsible for this contamination with fluoride rich effluents (5). Drinking water treatment with suitable adaptation to a novel, simple, efficient, and economical defluoridation methodology is hence the need of the hour.

The various defluoridation techniques available today can be broadly categorized as: precipitation, membrane, and adsorption processes. Each of these techniques has two sides to a coin, in terms of its advantages and limitations. With every new research publication, the human endeavor tends to shine one side of the coin- the advantages, brighter. This has been enshrined in techniques such as the use of waste residue from alum manufacturing process (6), nanofilteration membranes (7), alumina cement granules (8), donnan dialysis (9), plaster of Paris (10) and trimetal oxide adsorbent (11) for defluoridation. The current trend has also been to couple different processes to offer interesting alternatives, in search of the "Holy Grail" for defluoridation. Fluoride removal in this case has been achieved with the use of alum-impregnated activated alumina (12), electrocoagulation/flotation process (13) and adsorption on the natural chitosan followed by electrodialysis (14).

Considerable attention is being devoted to identify several low cost adsorbents, by increasing the adsorption efficiency of conventionally used absorbents by metal ion impregnation. Improved defluoridation of drinking water has been achieved with the use of lanthanum-modified chitosan (15) and metal ion loaded zeolites (16,17). Based on the details available from the literature (18) and from our previous study (19), it was found that activated carbons which are effective for fluoride removal, when impregnated with zirconium ion was found to have fluoride adsorption capacity, 25 to 30 times that of plain activated carbon (20), projecting the high affinity of zirconium for fluoride ion (21).

The objective of this defluoridation study was to test the defluoridation ability of Zirconium ion impregnated coconut fiber carbon (ZICFC) compared to the existing methods and even to our previously designed adsorbents whose equilibrium and kinetics of fluoride adsorption were studied (20).

MATERIALS AND METHODS

Adsorbent Material Development

Zirconium ion impregnated activated carbon was prepared as per the procedure gathered from literature (22) and our previous experimental study (20) from coconut fiber. Impregnated ZICFC adsorbent was obtained on stirring 5% $ZrOCl_2$ solution (pH 1.6) with coconut fiber carbon (CFC) at a solution/solid ratio = 1.5: 2, at room temperature (298 K) for 5 days. The impregnated adsorbent was subsequently filtered, rinsed, and dried in an oven at 333 K. Quality assurance and quality control checks were performed on ZICFC, in order to study the possibility of zirconium ion leaching into the treated water samples. From the quantitative analysis of zirconium concentration in ZICFC, as obtained from the EDX spectra, before and after its use in the batch equilibrium and kinetic experiments, it was confirmed that there was absolutely no variation in the zirconium ion concentration. This is in confirmation of the fact that no leaching of zirconium has occurred from ZICFC, in support of the previous study (23), where no zirconium (<1 ppb) was found in the effluent solution. The fluoride adsorption capacity of ZICFC was then investigated by pursuing the batch equilibrium and kinetic experiments.

All the reagents used were of analytical grade. A stock solution of 1000 mg/L fluoride ion was prepared and various other fluoride standard test solutions were prepared by subsequent dilution of this stock. All the experiments were carried out at room temperature.

Method of Analysis

The concentration of fluoride ion in water samples was measured by a potentiometric method using an Orion potentiometer, Model SA 720, with a fluoride ion selective electrode (FISE) in combination with a single-junction Ag|AgCl reference electrode. The calibration curve was prepared with standardized solutions and provides for fluoride determination in the range 0.01 to 100 mg/L. pH measurements and sample agitation were achieved with the use of the pH meter (Systronics) and Remi shaking machine respectively.

Characterization of the Impregnated Carbon Surface

Scanning electron microscopy (SEM) images (Fig. 1) and Energy dispersive X-ray (EDX) spectrum (Fig. 2) were obtained with a Leica S-440I

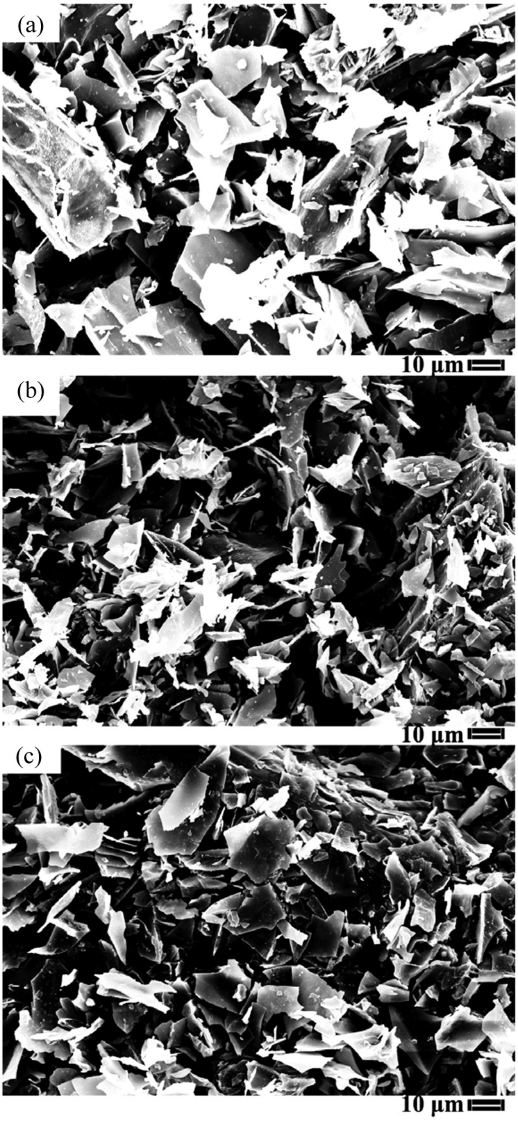

Figure 1. SEM Images. (a) Untreated CFC, (b) Acid treated CFC, (c) ZICFC.

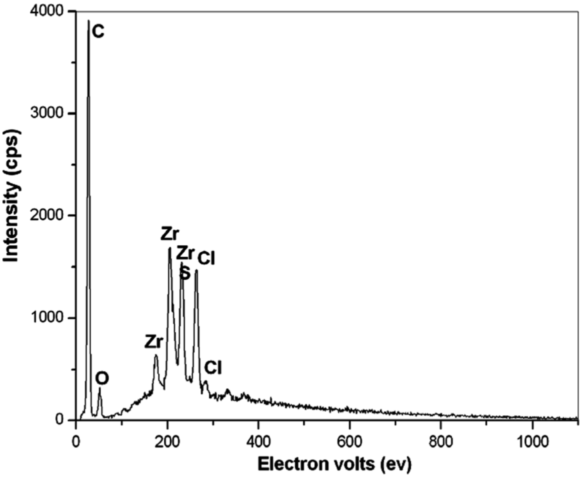

Figure 2. Energy dispersive X-ray (EDX) spectrum of ZICFC.

microscope fitted with an EDX spectrometer and Link ISIS detector. The pore size and surface area of ZICSC was evaluated using Quantachrome Autosorb-1 BET surface analyzer (Fig. 3).

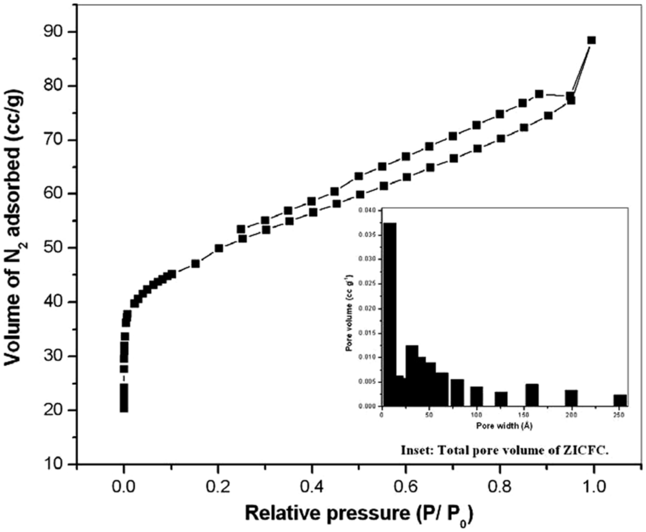

Figure 3. BET surface area analysis of ZICFC.

Point of Zero Charge Measurements

The pH drift method (24) was used to measure the pH at the potential of zero charge (pH_{pzc}) of ZICFC. The procedure involved adjusting the pH of a solution of 0.01 M NaCl between 2 and 8 by adding either HCl or NaOH. Dissolved carbon dioxide was removed from the solution by bubbling nitrogen at 25°C till the initial pH gets stabilized. ZICFC (0.15 g) was added to 50 mL of the solution, shaken for 24 hours and the final pH was then recorded. The graphs of initial versus final pH were used to determine the points at which initial pH and final pH values were equal and inturn the pH_{pzc} of the carbon.

Kinetic and Adsorption Experiments

The effect of H^+ and OH^- ions on fluoride uptake by ZICFC was studied at pH values from 2–11. The initial pH of the solution was adjusted to a fixed value by adding 0.1 M HCl or NaOH solutions to 100 mL of 20 mg/L standard test solution with a ZICFC adsorbent dose of 10 g/L. After the suspensions were shaken for 24 hours, they were filtered and the filtrates were immediately analyzed by FISE, to determine the optimum pH for defluoridation by ZICFC. The effect of agitation time and adsorbent dosage of ZICFC on fluoride removal were subsequently investigated by adopting appropriate experimental conditions. The sorption mechanism and adsorption kinetics of ZICFC and its fluoride uptake in comparison with other well known adsorbents was arrived at after standardization and optimization of the pH, agitation time and adsorbent dosage for ZICFC.

RESULTS AND DISCUSSION

Physicochemical Parameters/System Variables of the Adsorbent

Oxidation of CFC with unsaturated C=C bonds on the carbon surface was achieved with concentrated sulphuric acid at 373 K. This acidification step enhances the amount of carbon-oxygen surface chemical structures by remarkably generating more oxygen-containing surface functional groups (−COOH, −OH, >C=O) and yield large amounts of surface area available for metal uptake by improving its surface acidity and pore structure (25).

The hydrolysis of zirconyl chloride in aqueous solution, releases HCl, resulting in lowering the pH to 1.6 according to the reaction (26).

$$ZrOCl_2 + H_2O \rightleftharpoons ZrOOH^+ + H^+ + 2Cl^- \qquad (1)$$

At low pH value, activated carbon has high affinity for zirconium (22) and the physicochemical interactions could be expressed in terms of ion exchange and/or hydrogen bonding adsorption of $ZrOOH^+$ species. Another article (27) proposes a tetramer complex $[Zr(OH)_2{\cdot}4H_2O]_4^{8+}$ as the major species obtained on dissolution of $ZrOCl_2.8H_2O$ in aqueous medium. The coordinated water acts as the source of H^+ ions, inturn lowering the pH, as in the reaction.

$$[Zr(OH)_2 4H_2O]_4^{8+} \longleftrightarrow [Zr(OH)_{2+x}(4-x)H_2O]_4^{(8-4x)+} + 4xH^+ \qquad (2)$$

These positively charged precursors on either side of the equilibrium are adsorbed on the oxygen functionalities of the activated carbon surface through electrostatic interactions, forming C–O–Zr bonds through esterification (28). Once these zirconium based Lewis acid sites are generated by chemisorption on CFC as a monolayer, they are responsible for the very strong adsorption of Lewis bases, such as the fluoride ion.

The physiochemical properties on zirconium ion impregnation in CFC were studied with the use of SEM fitted with an EDX spectrometer and a BET surface analyzer. The working principle of an EDX involves the knocking out of the inner shell electrons of the ZICFC sample, by impinging an electron beam of specific energy. The outer electrons then filled the inner gap emitting X-rays that were characteristic of zirconium, confirming its presence. Based on the semi-quantitative EDX analysis of ZICFC, it was observed that 100 g of the adsorbent contained 2.1 to 2.6 g of zirconium. The intense sulphur signal in Fig. 2, is due to sulphonation of CFC before zirconium ion impregnation.

BET Surface Area and Total Pore Volume

The nitrogen adsorption isotherms were measured at relative pressures from 0–1 and at a 77.3 K adsorption temperature for monolayer formation. The surface area was calculated from the BET plots (Fig. 3), as 163.2 m^2/g. The pore volume of pore width in the range 5–10Å for ZICFC is the maximum (Fig. 3 inset), which are contributing to the surface area, as calculated by DFT Monte Carlo simulation based on the distribution of the surface area with respect to the different pore size, determined from the amount of nitrogen adsorbed.

A pH_{pzc} value of 3.715 was obtained for ZICFC, calculated using the pH drift method (24). This confirmed that the impregnated carbon used in this study is of the L-type which is more acidic in nature than the H-type.

The fluoride adsorption capacity of ZICFC, investigated by pursuing batch kinetic and adsorption experiments yielded the following results.

Effect of pH

Adsorption process is a pH dependent phenomenon as reflected in the fluoride sorption rate in Fig. 4. In a 24 hour agitation time, it was found that the q_e, which is the amount of fluoride ions adsorbed per unit weight of the adsorbent ZICFC (mg/g), was above 1.6 mg/g for the entire pH range of 2–8. A wide pH window, from strongly acidic to weakly basic conditions, makes ZICFC a promising fluoride adsorbent material. This ensures that no pH control is required in real time application to water treatment. However, as the maximum fluoride adsorption capacity, 3 mg F/0.5 g of zirconium ion impregnated activated carbon, was obtained at pH 4.0 (29) and the pH of a 100 mL fluoride test solution containing 1 g of ZICFC is self adjusted to around 4.0, this pH was adopted for our equilibrium and kinetic studies. For the pH window of 10–12, there was a drastic decrease in the extent of fluoride uptake with increase in pH of the solution. The fluoride adsorption capacity at higher pH 10–12 decreases, due to the competition of active sites on ZICFC surface between OH^- and F^-. In acidic pH, the H_3O^+ ion concentration was optimum to make the ZICFC surface positively charged and hence was accessible for fluoride ions. This helps recognize that desorption of fluoride on ZICFC can be achieved under strong basic pH. The broad

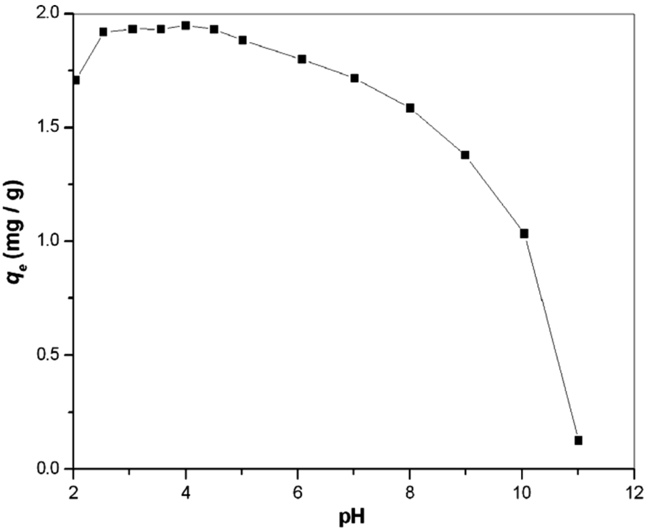

Figure 4. Effect of pH on fluoride adsorption onto ZICFC at room temperature. Adsorbent dose = 10 g/L, volume of sample = 100 mL, initial adsorbate conc = 20 mg/L, agitation time = 24 hours.

fluoride adsorption range of ZICFC makes it a promising adsorbent material for defluoridation of water.

Effect of Agitation Time

Figure 5 shows the effect of agitation time on the adsorption of fluoride ions on the adsorbent. A q_e of 1.77 mg/g, attained in 1 hour indicates a high degree of fluoride ion affinity and adsorption by ZICFC. An increase in agitation time, increases the removal of fluoride ions from water. This proportionality holds good till the saturation of fluoride ions on the available adsorption sites on ZICFC, after which, an increase in agitation time does not bring about increased fluoride uptake. The process was rapid with typically 1.74 mg/g being the amount of fluoride ions adsorbed per unit weight of the adsorbent ZICFC within 10 min of the contact for 100 mL of 20 mg/L fluoride standard test solution with a ZICFC adsorbent dose of 10 g/L, at the optimum pH 4.0. This initial rapid adsorption subsequently gave way to equilibrium and saturation, owing to lack of available active sites on the adsorbent surface at 6 hours, which was considered as the equilibrium time.

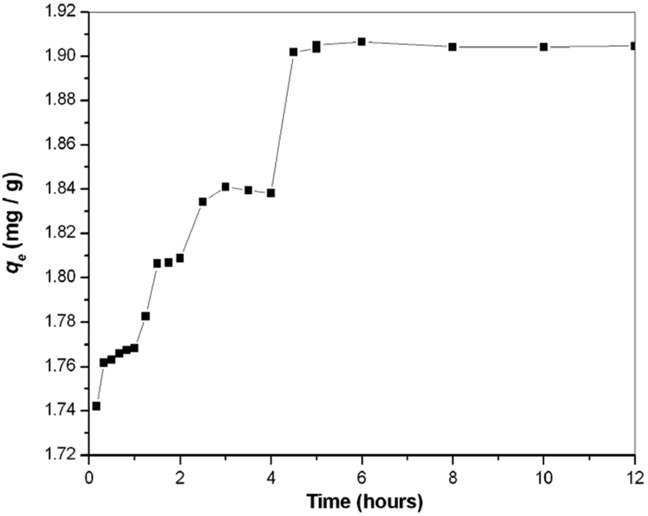

Figure 5. Effect of agitation time on fluoride adsorption onto ZICFC at room temperature. Adsorbent dose = 10 g/L, volume of sample = 100 mL, initial adsorbate conc = 20 mg/L, pH = 4.

Effect of Adsorbent Dose

Increasing adsorbent dosage increased the fluoride uptake with an optimum ZICFC dosage of 20 g/L being required for a quantitative fluoride removal. Fluoride adsorption as a function of ZICFC dosage for 100 mL of 20 mg/L fluoride standard test solutions at pH 4.0 is presented in Fig. 6. The fluoride removal efficiency increases up to the optimum dosage, as increasing the dosage provides greater surface area or adsorption sites. Beyond the ZICFC dosage of 20 g/L, there may be a slight improvement in fluoride removal efficiency but the adsorption density decreases.

Hence, maximum defluoridation of a fluoride rich water sample was achieved by maintaining the pH at 4, with 6 hours agitation time and 20 g/L of ZICFC adsorbent dosage as the optimum conditions.

Adsorption Isotherms

Langmuir, Freundlich, Redlich-Peterson, and Temkin sorption isotherm models were used to test the experimental data for fluoride adsorption on ZICFC (Fig. 7).

From the parameter values of the Langmuir and Freundlich isotherms presented in Table 1, it was found that the correlation coefficient

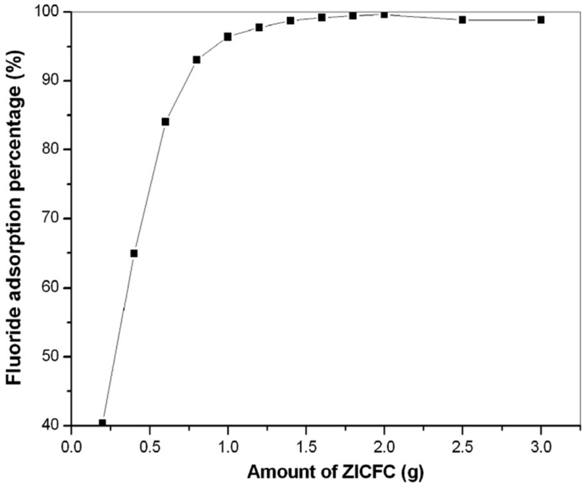

Figure 6. Effect of adsorbent dose on fluoride adsorption onto ZICFC at room temperature. Volume of sample = 100 mL, agitation time = 6 hours, initial adsorbate conc = 20 mg/L, pH = 4.

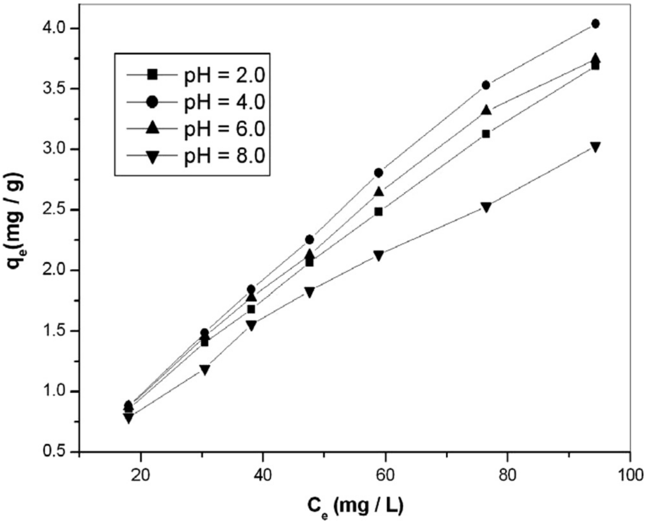

Figure 7. Adsorption isotherms of ZICFC as a function of pH values at room temperature.

R^2 value for the Langmuir model is near to unity for the pH range 2–8, hence the defluoridation process using ZICFC follows the Langmuir isotherm well. This suggests monolayer coverage and constant adsorption energy (10).

A minimization procedure was adopted to solve the Redlich-Peterson equation by maximizing the correlation coefficient between the theoretical data for q_e predicted from the equation and experimental data, that fitted well with Langmuir model in support of our previous conclusion.

Table 1. Isotherm parameters for F^- uptake by ZICFC

pH	Langmuir parameters			Freundlich parameters		
	q_m (mg/g)	b (1/mg)	R^2	k_f (mg/g)	n	R^2
2.0	16.026	0.003	0.999	0.068	1.132	0.999
4.0	40.016	0.001	0.999	0.061	1.073	0.997
6.0	20.109	0.003	0.999	0.069	1.124	0.997
8.0	8.844	0.005	0.997	0.077	1.231	0.994
10.0	8.565	0.003	0.964	0.057	1.270	0.949

Tempkin Model

Heat of adsorption and the adsorbate-adsorbate interaction on adsorption isotherms were studied by Tempkin and Pyzhev (30). The heat of adsorption of all molecules in the layer would decrease linearly with coverage due to adsorbate-adsorbate interactions. This isotherm has been used in the form as

$$q_e = \frac{RT}{b} ln(AC_e) \tag{3}$$

where R is the gas constant (8.314 J/mol/K), T is the room temperature (298 K) with $RT/b = B$, q_e is the amount of fluoride ions adsorbed per unit weight of the adsorbent ZICFC (mg/g) and C_e is the equilibrium fluoride ion concentration (mg/L). The constants A and b were obtained from a plot of q_e vs. $\log C_e$, where a very low, A value of 0.32 L/g with a R^2 value of 0.97 indicates least adsorbate–adsorbate interactions in ZICFC over the entire pH range of 2–10 and accounts for the excellent fluoride adsorption from water.

Thermodynamic Parameters

The thermodynamics of F^- on ZICFC indicates spontaneous adsorption, with an increase in the thermodynamic equilibrium constant (K_0) with rise in temperature. Increase of temperature from 20 to 45°C increased the sorption of fluoride, indicating the process to be endothermic. The increases in uptake of F^- with temperature may be due to the changes in the size of pores and the enhanced rate of intraparticle diffusion of adsorbate, as diffusion is an endothermic process.

The standard free energy (ΔG^0), and the equilibrium constant K_0 are presented in Table 2. A plot of q_e/C_e vs. C_e and extrapolating to zero q_e, provides K_0 as determined by Khan and Singh (31). The ΔG^0, ΔH^0, and ΔS^0 were calculated using the following equations:

$$\ln K_0 = \Delta S^0 R - \Delta H^0/RT \tag{4}$$

$$\Delta G^0 = -RT\, ln\, K_0, \tag{5}$$

ΔH^0 and ΔS^0 values were obtained from the slope and intercept of the linear plot of ln K_0 vs. $1/T$ (Fig. 8). The fluoride adsorption on ZICFC is a spontaneous process as indicated by negative ΔG^0 values. A positive value of 23.60 kJ/mol for ΔH^0 suggests that the adsorption process is endothermic. The ΔS^0 value of 125.77 J/mol/K for the adsorption

Table 2. Thermodynamic parameters for fluoride adsorption by ZICFC

Temperature (°C)	K_0	ΔG^0 (kJ/mol)	Fluoride adsorption percentage (%)
20	90.70	– 10.87	98.90
25	213.32	– 13.06	99.53
30	298.94	– 14.12	99.66
35	323.24	– 14.56	99.69
40	350.78	– 15.01	99.71
45	432.78	– 15.80	99.77

process, indicates an increased randomness at the solid solution interface during the adsorption of F^- on ZICFC.

Kinetics of Adsorption

The kinetics of fluoride removal has been carried out to understand the behavior of ZICFC, which is one of the important characteristics defining the efficiency of sorption.

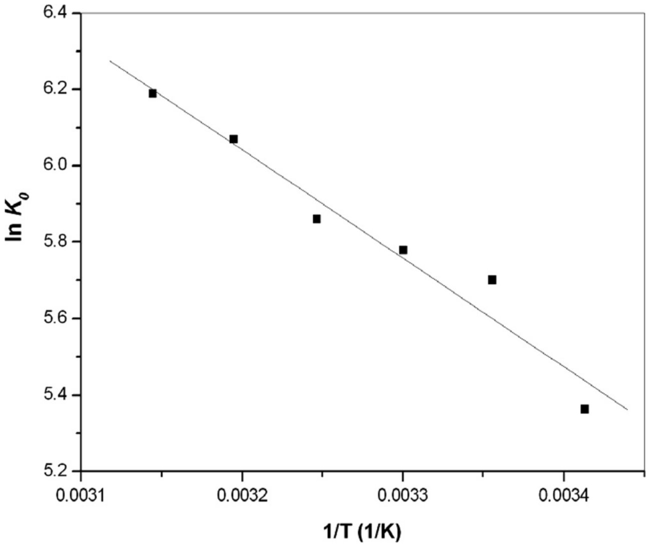

Figure 8. Van't Hoff isotherm for fluoride adsorption onto ZICFC. Adsorbent dose = 20 g/L, volume of sample = 50 mL, pH = 4.

Pseudo-Second Order Kinetic Model

The kinetics of fluoride adsorption on ZICFC is best described by a pseudo-second order model (32,33). The ZICFC–fluoride ion reaction in water maybe represented as-

$$\mathrm{ZrO(OH)Cl(adsorbed\ on\ CFC)} + 2\mathrm{F}^- \Leftrightarrow \mathrm{ZrOF_2} \qquad (6)$$

The rate law for a pseudo-second order reaction based on the fluoride adsorption equilibrium may be derived from Eq. (6) as

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \qquad (7)$$

where, q_t is the amount of fluoride adsorbed at time t (mg/g), k_2 is the rate constant for sorption (g/mg/h) and the initial sorption rate, h, can be defined as $h = k_2 q_e^2$. The applicability of the pseudo-second order kinetic model was tested with linear plots of $(t/\ q_t)$ vs. t, at different fluoride concentrations and this also yields k_2 and q_e from the intercept and slope respectively, as presented in Table 3.

The defluoridation process using ZICFC follows the pseudo-second order kinetic model, as the correlation coefficient R^2 values for this model presented in Table 3, was near to unity as compared to the R^2 values obtained in the first order and pseudo-first order kinetic models. The initial fluoride adsorption rate was extremely rapid as indicated by the high h values, in support of our experimental observations. The process of fluoride uptake by ZICFC was fast with 93% of the adsorption taking place within 10 min of contact at the optimum pH 4.0 as seen from the effect of agitation time.

The study of adsorption isotherms, thermodynamic and kinetic parameters have helped in the better understanding of the modus-operandi of fluoride removal by ZICFC, which is 25 to 30 times that of plain activated carbon. The Langmuir adsorption isotherm and pseudo-second order kinetics, bring to light that the defluoridation ability of ZICFC,

Table 3. Pseudo-second order parameters for fluoride adsorption by ZICFC

Fluoride (mg/L)	k_2 (g/mg/h)	h (mg/g)	R^2
20	383.75	361.01	0.99
30	365.14	757.58	1.00
40	176.16	666.67	1.00
50	201.80	1195.55	1.00
60	50.68	401.61	0.99

occurs through a combination of chemisorption and physisorption processes through monolayer formation. A Lewis acid-base interaction coupled with the high affinity of zirconium for fluoride ion (21) is invoked to explain fluoride uptake by ZICFC. Fluoride ion, a Lewis base, coordinates strongly with the zirconium species adsorbed on CFC, which are Lewis acid sites. An exchange of the chloride and the hydroxide of the ZrO(OH)Cl species adsorbed on CFC, through a ligand exchange mechanism (15) by fluoride ion, leads to the formation of $ZrOF_2$ as described in Eq. (6) and is strictly a monolayer surface chemisorption phenomenon (10). The initial zirconium ion adsorption on CFC is a monolayer adsorption, and once these impregnated active sites are chemisorbed by a monolayer of fluoride ions, no other active sites are further available for sorption. A van der Waals interaction between the fluoride ion and activated carbon (19), and intraparticle diffusion of the hydrated fluoride ion, 3.52 Å in size (34) into the pores of ZICFC, which varies from 5–10 Å accounts for the physisorption process. The intraparticle diffusion process may be involved in the rate limiting step, for inspite of fluoride uptake by ZICFC was rapid with q_e at 1.74 mg/g within 10 min of the contact, this initial rapid adsorption subsequently gave way to equilibrium and saturation only at 6 hours. Physisorption involves a monolayer alone, as successive fluoride ions are repelled by physisorbed fluoride ions through electrostatic forces.

The existence of intraparticle diffusion in the adsorption process is further confirmed by a plot of q_t vs. the square root of time ($t^{1/2}$), based on the rate law represented as:

$$q_t = K_{id} t^{\frac{1}{2}} \tag{8}$$

where, the values for K_{id}, the rate constant for intraparticle diffusion, were obtained from the slope of the linear portions of the curves for each concentration of the fluoride ion. The values were found to be 0.0016, 0.0019, 0.0049, 0.0052, 0.0134 mg/g min$^{1/2}$ for the initial concentrations of 20, 30, 40, 50, 60 mg/L, respectively. This supports the fact that the diffusion process may be involved in the rate limiting step, as with an increase in the initial fluoride ion concentrations, K_{id} increases, inconsonance with an endothermic process. This suggests that intraparticle diffusion begins on subsequent saturation of the entire zirconium ion impregnated active sites with fluoride ions.

The desorption and regeneration of ZICFC was achieved by alkali wash with 0.02 M NaOH solution. Sodium hydroxide quantitatively desorbs all bound fluoride without harming the underlying zirconium species adsorbed on CFC (20). Four successive regenerations of the impregnated charcoal showed similar efficiency as the first set of defluoridation experiments.

Table 4. A comparative study of fluoride adsorption onto various adsorbents

Adsorbents	Fluoride adsorption percentage (%) pH 4	pH 7
ZICFC	99.2	97.4
Alumina	70.1	51.3
Phosphorus free carbon	33.4	24.1
Chitin	22.0	10.3
CFC	8.2	4.5

Comparative Study

A comparative study of fluoride adsorption on ZICFC as against various adsorbents at room temperature was investigated for 50 mL of 20 mg/L fluoride standard test solution with an adsorbent dose of 20 g/L and 6 hours agitation time. ZICFC has its fluoride removal efficiency at 99.2 and 97.4% at pH 4 and 7 respectively which is comparatively higher than rest of the adsorbents as presented in Table 4. This highlights the substantial improvement in fluoride adsorption capacity of coconut fiber carbon on zirconium impregnation.

CONCLUSIONS

Maximum defluoridation of a fluoride rich water sample was achieved by maintaining the system variables, pH at 4, with 6 hours agitation time and 20 g/L of ZICFC adsorbent dosage as the optimum conditions. The chemisorption process in hand with physisorption and intraparticle diffusion account for excellent defluoridation properties of ZICFC, following the Langmuir adsorption isotherm and the pseudo-second order chemical reaction kinetics. The present method, involving the use of ZICFC was superior compared to existing methods, even to our previously designed zirconium impregnated coconut shell carbon (ZICSC) whose equilibrium and kinetics of fluoride adsorption were studied (20). For the fluoride adsorption capacity of ZICFC with a $q_e = 1.95\,\mathrm{mg/g}$ is much higher than ZICSC with a $q_e = 0.99\,\mathrm{mg/g}$ which is in turn far greater than that of unimpregnated activated carbon having a $q_e = 0.038\,\mathrm{mg/g}$. An exceptionally high q_e value for ZICFC is due to its large surface area of $163.2\,\mathrm{m^2/g}$ with micropores in the range 5–10Å as compared to 2.82 $\mathrm{m^2/g}$ of ZICSC with mesopores in the range 30–300Å. Hence, ZICFC can not only be used for the preconcentration of phosphate, arsenic, selenium, mercury (18), chromium (VI) (22), but also for fluoride rich water samples. This data would be useful for developing an appropriate technology in designing a treatment plant for fluoride rich water. Our future research on the use of ZrO_2-carbon nanotube nanocomposites (28) for defluoridation is already underway, with the unique surface area properties of these materials being exploited to arrive at excellent fluoride uptake properties.

ACKNOWLEDGEMENT

The authors are grateful to the Chancellor, Bhagawan Sri Sathya Sai Baba, Sri Sathya Sai University, for his constant inspiration.

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