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 , Raju, N. S. R. , Raju, G. S. , Rao, G. Nageswara , Kumar, K. Anil and Janardhana, C.(2007) 'Equilibrium and Kinetic Studies for Fluoride Adsorption from Water on Zirconium Impregnated Coconut Shell Carbon', Separation Science and Technology, 42: 4, 769 — 788

To link to this Article: DOI: 10.1080/01496390601070067

URL: http://dx.doi.org/10.1080/01496390601070067

Separation Science and Technology, 42: 769–788, 2007

ISSN 0149-6395 print/1520-5754 online
DOI: 10.1080/01496390601070067

Equilibrium and Kinetic Studies for Fluoride Adsorption from Water on Zirconium Impregnated Coconut Shell Carbon

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Abstract: The batch adsorptive fluoride removal from water by Zirconium ion impregnated coconut shell carbon (ZICSC) was investigated. ZICSC was found to have fluoride adsorption capacity, 25 to 30 times that of plain activated carbon. The effect of various parameters such as pH, agitation time, and adsorbent dosage on fluoride removal were studied. The fluoride adsorption by ZICSC was above 90% for the entire pH range of 2–9 and the adsorption rate was extremely rapid, with 91% of the adsorption being achieved within 10 min of ZICSC contact for an initial fluoride concentration of 10 mg/L. The experimental data have been analyzed by Langmuir, Freundlich, Redlich-Peterson, and Temkin sorption isotherm models and the adsorption data for fluoride onto ZICSC were better correlated to the Langmuir isotherm. The batch adsorption kinetics have been tested by first order, pseudo-first order, and pseudo-second order kinetic models with the subsequent determination of the rate constants of adsorption. The comparison of ZICSC with other adsorbents suggests that ZICSC provides a cost-effective working solution to the defluoridation problem in the developing countries by its great potential application in fluoride removal from water.

Keywords: Adsorption, fluoride, activated carbon, impregnation, reaction kinetics

Received 19 June 2006, Accepted 2 October 2006

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INTRODUCTION

Water pollution and its treatment to avail safe drinking water is a major concern of the 21st century. Of the various pollutants in water, the asymptotic fluoride is both tonic and toxic in nature depending on the amount of dosage. The recommendation standards set by WHO (1) require the fluoride concentration in drinking water in the range 1.0–1.5 mg/L. While it is an essential substance recommended in water for building healthy teeth, inhibiting dental caries and helps calcification of the dental enamel in infants at a concentration within 1.0 mg/L, excessive fluoride ingestion has physiological, chronic and toxic effects observed as permanent tooth and skeletal fluorosis (2). There has been a tragic increase in the fluoride ion concentration in groundwater and various other water bodies due to contamination by fluoride rich wastewater from semiconductor manufacturing, uranium enrichment, coal power plants, fertilizer manufacturing, glass, and ceramic production and electroplating (3). To encounter this fluoride menace, quantification of fluoride ions in environmental and industrial wastewaters is important, followed up with suitable adaptation of an effective defluoridation methodology.

Current defluoridation techniques that have been adopted can be divided into three categories: precipitation, membrane, and adsorption processes. Precipitation processes accomplished with the use of calcium and aluminum salts (4) result in the formation of fluoride precipitates or simultaneous co-precipitation of fluoride with a resulting precipitate, has its limitation due to the high probability of contamination of drinking water due to unwanted chemicals and waste disposal problems. Reverse osmosis, nanofiltration, electrodialysis, and donnan dialysis fit into the category of membrane processes, which have their disadvantage in terms of economic viability and maintenance cost (5). Hence adsorption on alumina, alum, charcoal, ash, zeolites, lime, clay minerals, and spent catalyst, involving water passage through a contact bed with subsequent fluoride removal is often the inexpensive method of choice to obtain safe drinking water (2, 6). Of late, the sorption of fluoride from aqueous solution has been achieved with the use of biomass of *Eichhornia crassipes* (7), biopolymer chitosan, aligned carbon nanotubes, amorphous alumina supported on carbon nanotubes (3) or by a hybrid process combining adsorption and donnan dialysis, but the focus has become more directed, with considerable attention being devoted to identify several other low cost adsorbents.

Zirconium and its metal complexes have been conventionally used for the colorimetric determination of fluoride due to the high affinity of zirconium for fluoride ion (8). The high charge density of the fluoride ion enables it to form stable fluoro complexes with tetravalent metal ions like zirconium (IV). Activated carbons which are effective for fluoride removal (2), when impregnated with metal ions have an increase in their fluoride adsorption capacity by 3 to 5 times that of plain activated carbon (9). As coconut shell (*Cocos nucifera* L.), is readily available in rural India from the agricultural sector, there is nil expenditure in procurement of this raw material and hence we have a low cost carbon preparation procedure (10). Further, a detailed literature survey has revealed that this zirconium ion impregnated activated carbon has already been used for treating phosphate (11), arsenic, selenium, mercury (12), and chromium (VI) (13) from water samples. But the limitation is, the presence of these co-ions (anions and cations) cause interference with fluoride ion uptake by principle of competition for the adsorption sites on zirconium ion impregnated activated carbon, as it was found that especially fluoride ions decreased the adsorption of As (V), Se (IV), and Hg (II) (12). Based on the details available from this literature and from our previous study (14), where, of the various metal ions, zirconium ion impregnated coconut shell carbon (ZICSC) proved to be the most effective defluoridating agent for treating effluents of lower fluoride concentrations from 10–2 mg/L, the current study was undertaken as an extension of this work.

The scope and objective of this defluoridation study was to investigate the fluoride adsorption capacity of ZICSC by pursuing the batch equilibrium and kinetic experiments, wherein the effect of various parameters such as pH, agitation time and adsorbent dosage were studied. An application oriented goal is to provide a working solution to the fluorosis menace problem of the Anantapur district located in southwestern corner of Andhra Pradesh state of south India. High levels of fluoride beyond 3.0 mg/L in ground water as source of drinking water is common in many of the 964 revenue villages included in 63 mandals of this district. Fluoride bearing minerals like apatite, micas, and clay minerals present in the country rocks like shales and pyroclastic materials of the study area are the main source of fluoride ion (F^-) in ground water. This is concluded from the positive correlation between the fluoride content in the bulk rock and F^- content in the nearby groundwater and also between the fluoride content in the soil leachates and F^- in the nearby surface water of the district. A good positive correlation between fluoride and lithogenic sodium is obtained, reflecting that weathering activity caused by a semi-arid climate and intensive irrigation practices are responsible for the leaching of F^- from mineralogical sources (15). Hence to reduce the fluoride levels to obtain safe drinking water, an effective defluoridation methodology is the need of the hour. In the previous study conducted by us (14), defluoridation of drinking water was carried out by the fixed-bed dynamic adsorption mode at room temperature with the use of ZICSC. 66.67 mL of fluoride rich drinking water was treated per unit mass of this adsorbent which could be subsequently applied in pilot and field studies as defluoridating columns.

MATERIALS AND METHODS

Adsorbent Preparation and Impregnation

Activated carbon was prepared as per the procedure (10) from coconut shell, where about 100 g of the crushed coconut shell was kept for 3 hours in a low temperature muffle furnace at 573–673 K, at which all of the material was completely carbonized. The carbonized material was then taken out of the muffle furnace, cooled, powdered, and kept in a beaker of 2-L capacity and 200 mL of concentrated sulphuric acid was gradually added to it, stirring the contents of the beaker continuously to ensure thorough mixing. The beaker was kept in a hot air oven at 373 K for 5 hours. The activated carbon was then cooled and left overnight and washed free of acid and dried at 110°C for 2 hours, then sieved using 40 mesh. Subsequently the activated carbon was further immersed in 1% Na_2CO_3 solution and washed free of alkali, providing the desired adsorbent for impregnation.

From the information gathered from literature (11–13) and our experimental study (14), the zirconium ion impregnation procedure was suitably modified by stirring 5% $ZrOCl_2$ solution (pH 1.6) with activated carbon (solution/solid ratio = 1.5:2) at room temperature (298 K) for 5 days. The impregnated carbon was then filtered, rinsed to confirm the effluent free from zirconium, dried in an oven at 333 K and subsequently used for defluoridation studies. The zirconium ion concentration in the effluents was determined using ammonia and alizarin red S (ARS) (16). Zirconium is generally nontoxic as an element or in compounds and the oral toxicity is low; OSHA standards for pulmonary exposure specify a TLV of 5 mg zirconium per m^3. As per the solubility product of zirconyl hydroxide ($K_{sp} = 6.3 \times 10^{-49}$), the solubility of it, is 26.7×10^{-15} g/L. Hence the amount of zirconium in our effluents is well below the safe limit. As solubility factor calculations could be at variance with experimental results, a quantitative analysis was further carried out to determine the concentration of Zr^{4+} ion in the effluents and in the treated water samples by using ARS as reagent to form ARS-Zr complex. This ARS is worthy of use as a reagent for spectrophotometric determination of Zr^{4+} at a wavelength of 520 nm, as it is sensitive towards small change of Zr^{4+} concentration and operates in the dynamic range of 5–35 mg/L at pH 2.5. All the tested samples had the Zr^{4+} ion concentration less than 5.0 mg/L. The fluoride adsorption capacity of ZICSC was then investigated by pursuing the batch equilibrium and kinetic experiments.

All the reagents used were of analytical grade. A fluoride ion stock solution of 1000 mg/L was prepared by dissolving 221 mg of anhydrous sodium fluoride in 100 mL distilled water in volumetric flask. Various other fluoride standard test solutions were prepared by subsequent dilution of the fluoride stock solution. All the experiments were carried out at room temperature.

Equipment

Fluoride ion concentration in water samples was measured by a potentiometric method using an Orion potentiometer, Model SA 720, with a fluoride ion selective electrode (FISE). This method requires the use of a calibration curve 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. Scanning electron microscopy (SEM) images (Fig. 1) and energy dispersive X-ray (EDX) spectrum (Fig. 2) were obtained with a Leica S-440I microscope fitted with an EDX spectrometer and Link ISIS detector. Further, the pore size and surface area of ZICSC was evaluated using a Quantachrome Autosorb-1 BET surface analyzer (Fig. 3).

Equilibrium and Kinetic Experiments

The effect of pH on the fluoride adsorption capacity of ZICSC was studied at pH values from 2–12. The role of H^+ and OH^- ions were examined by adjusting the initial pH of the solution to a fixed value by adding 0.1 M HCl or NaOH solutions to 100 mL of 10 mg/L fluoride standard test solution

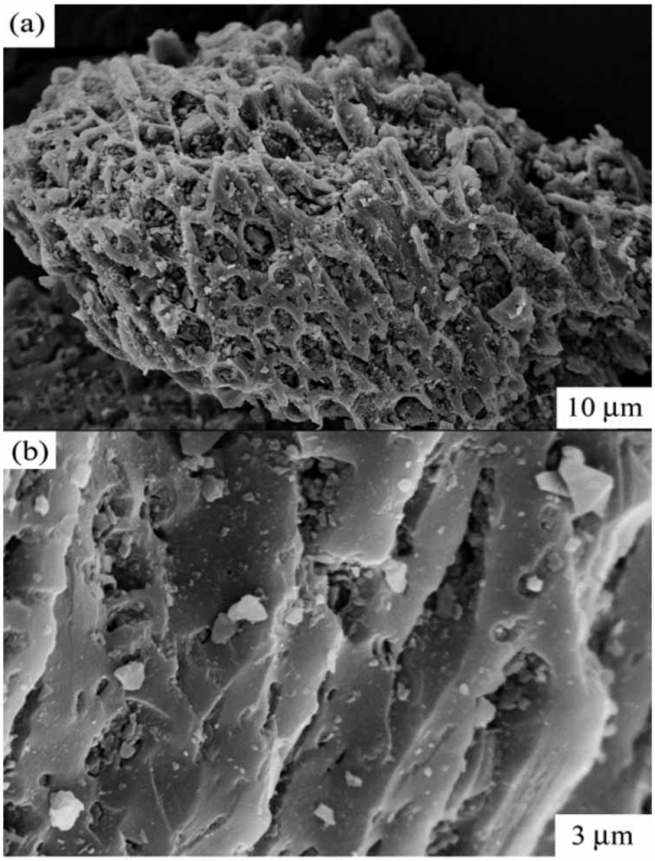

Figure 1. SEM images of ZICSC. (a) Low magnification; (b) High magnification.

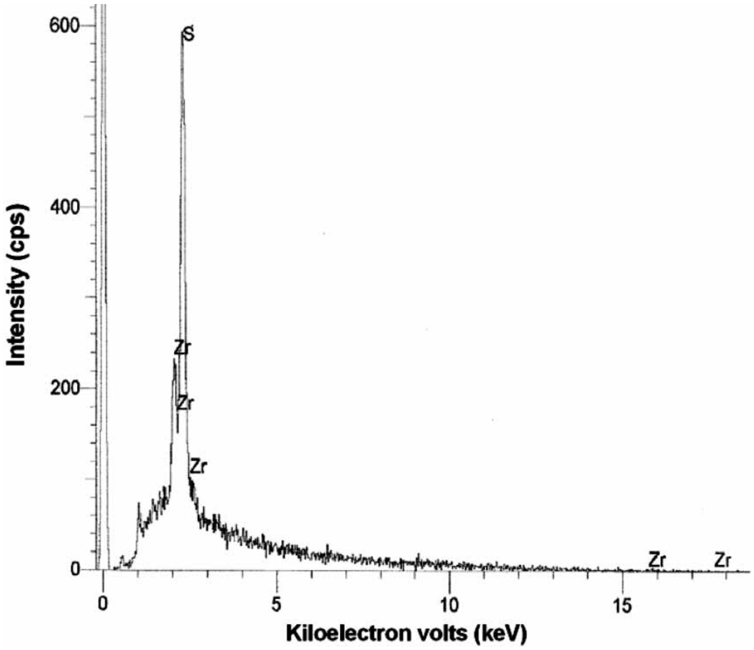

Figure 2. Energy dispersive X-ray (EDX) spectrum of ZICSC.

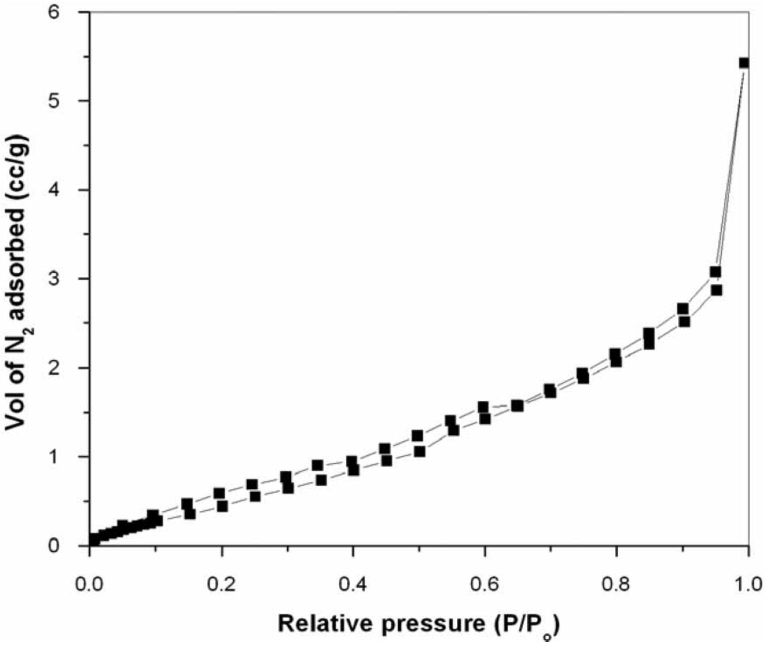

Figure 3. BET surface area analysis of ZICSC.

with a ZICSC adsorbent dose of 10 g/L. After the suspensions were shaken for 12 hours, they were filtered through 0.22-μm membrane filters and the filtrates were immediately analyzed by FISE, to determine the optimum pH for defluoridation by ZICSC. Subsequently the effect of agitation time and adsorbent dosage of ZICSC on fluoride removal were investigated by adopting appropriate experimental conditions. On standardization and optimization of the pH, the agitation time and adsorbent dosage for ZICSC, the experimental study was further extended to observe and determine the sorption mechanism and adsorption kinetics of ZICSC and its fluoride uptake in comparison with other well known adsorbents.

RESULTS AND DISCUSSION

Physicochemical Properties of the Adsorbent

Activated carbons are usually classified into two categories based on the acid-base behavior of the carbon. H- and L-type carbons are differentiated on the basis of pH of the carbon with L-type carbons being more acidic in nature and H-type being more basic (17). The carbons in this study are of the L-type. The carbon surface of coconut shell carbon (CSC) has unsaturated C=C bonds, which on oxidation with concentrated sulphuric acid at 373 K enhances the amount of carbon-oxygen surface chemical structures by remarkably generating more oxygen-containing surface functional groups and yield large amounts of surface area available for metal uptake by improving its surface acidity and pore structure (18).

The adsorption sites in activated carbons can be divided into two major types:

1. hydrophobic surfaces comprising of the graphene layers; and
2. oxygen functional groups which are primarily hydrophilic.

In the case of CSC, the oxygen functional groups consisting of carboxylic, hydroxyl and carbonyl, present on its surface, are involved in the physicochemical interactions with the metal ion. This suggests that surface modification of a carbon adsorbent with a strong oxidizing agent generates more adsorption sites on their solid surface for metal adsorption. This phenomenon has hence been exploited for removal of heavy metals (Ni, Cd, Pb, and Zn) from wastewater using CSC with high removal efficiency (19).

Zirconyl chloride behaves as a Lewis acid in aqueous solution and is hydrolyzed (20) according to the reaction

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

by freeing HCl. This results in lowering the pH to 1.6, where the activated carbon has been reported to have high affinity for zirconium (12). It was assumed that the physicochemical interactions that might occur during zirconium adsorption could be expressed in terms of ion exchange and/or hydrogen bonding mechanisms. In the ion exchange mechanism, the $ZrOOH^+$ species may compete with H+ from -COOH and -OH functional groups and be adsorbed at the CSC surface, with the hydrogen bonding mechanism also being available for adsorption of $ZrOOH^+$, thus providing two main possibilities for the adsorption of $ZrOOH^+$ species.

Hence, adsorption of zirconium ions from solutions by solid phase can occur with the formation of the surface complex between the oxygen functional groups (-COOH, -OH, $>C{=}O$) and the metal. The hydrogens on carboxylic and hydroxy groups occurring on the surface of activated carbons appear to be more labile, possibly as a result of electron density diversion to the Π-bond system of the graphite planes (17). Once these zirconium based Lewis acid sites are generated by chemisorption on CSC as a monolayer, they are responsible for the very strong adsorption of Lewis bases, such as the fluoride ion.

A scanning electron microscope fitted with an EDX spectrometer and BET surface analyzer was used to study the physiochemical properties on zirconium ion impregnation in CSC. In EDX, the ZICSC sample was impinged with an electron beam of specific energy that knocked out the inner shell electrons. The outer electrons then filled the inner gap emitting X-rays that were characteristic of Zirconium, confirming its presence. The CSC used for zirconium ion impregnation was previously sulphonated (10), which accounts for the intense sulphur signal in Fig. 2.

BET surface area and total pore volume—The surface area and total pore volume were determined by nitrogen adsorption, for monolayer formation. Here, the sample taken in a glass holder was degassed at around 423 K to desorb any of the adsorbed gases on the sample. The nitrogen adsorption isotherms were measured at relative pressures from 0–1 and at a 77.3 K adsorption temperature. The surface area was calculated from the BET plots (Fig. 3), as $2.82\ m^2/gm$. The total pore volume of ZICSC varies from 30–300 Å, which are contributing to the surface area, as calculated by DFT montecarlo simulation based on the distribution of the surface area with respect to the different pore size, determined from the amount of nitrogen adsorbed.

Batch equilibrium and kinetic experiments adopted to investigate the fluoride adsorption capacity of ZICSC yielded the following results:

Effect of pH

For any adsorption process, the pH of the test solution is a controlling factor. The influence of pH on the sorption rate was observed from Fig. 4. It was found that the q_e, which is the amount of fluoride ions adsorbed per unit weight of the adsorbent ZICSC (mg/g), was above 0.9 mg/g for the entire

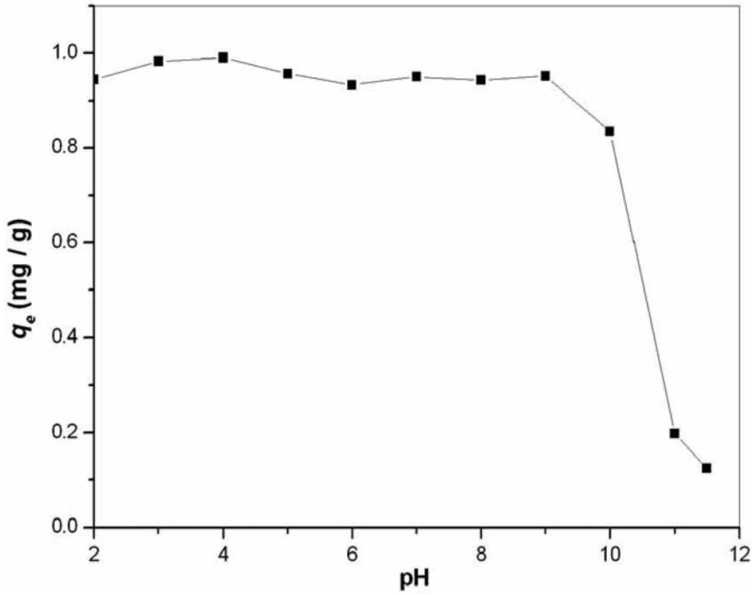

Figure 4. Effect of pH on fluoride adsorption onto ZICSC at room temperature. Adsorbent dose = 10 g/L, volume of sample = 100 mL, initial adsorbate conc = 10 mg/L, agitation time = 12 hours.

pH range of 2–9, in 12 hours agitation time. The broad fluoride adsorption range of ZICSC from strongly acidic to weakly basic conditions makes it a promising adsorbent material for defluoridation of water. Further, 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 (11), 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 ZICSC surface between OH^- and F^-. At pH values below 9, the H_3O^+ ion concentration was optimum to make the ZICSC surface positively charged and hence was accessible for fluoride ions.

Effect of Agitation Time

Agitation time studies reveal that a q_e of 0.94 mg/g was attained in 1 hour indicating a high degree of fluoride adsorption and affinity of ZICSC (Fig. 5). The removal of fluoride ions from water, increases with increase in agitation time to some extent, after which, increase in agitation time does not increase the fluoride uptake due to deposition of fluoride ions on the

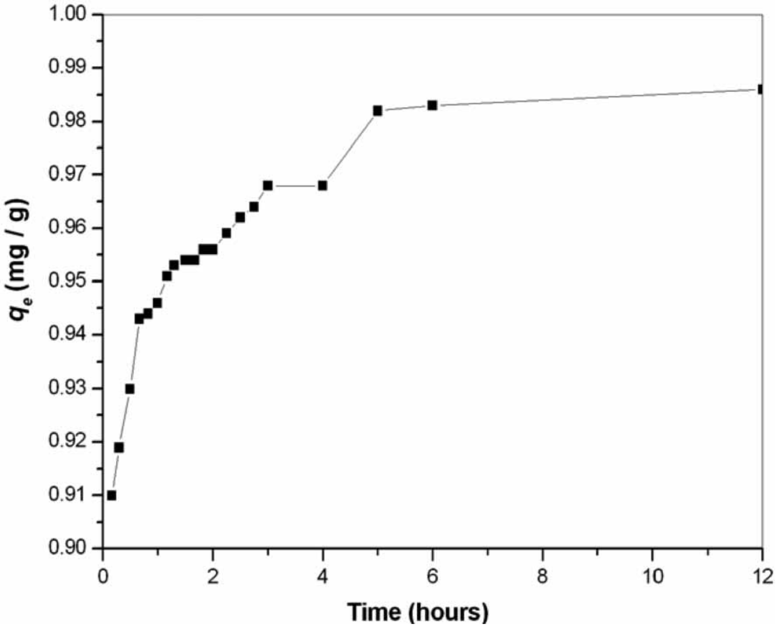

Figure 5. Effect of agitation time on fluoride adsorption onto ZICSC at room temperature. Adsorbent dose = 10 g/L, volume of sample = 100 mL, initial adsorbate conc = 10 mg/L, pH = 4.

available adsorption sites on ZICSC. Fluoride uptake by ZICSC at the optimum pH 4.0, indicates that the process was rapid with typically 0.91 mg/g being the amount of fluoride ions adsorbed per unit weight of the adsorbent ZICSC within 10 min of the contact for 100 mL of 10 mg/L fluoride standard test solution with a ZICSC adsorbent dose of 10 g/L. This initial rapid adsorption subsequently gave way to equilibrium and saturation at 6 hours, which was considered as the equilibrium time.

Effect of Adsorbent Dose

Figure 6 represents the adsorption of fluoride as a function of ZICSC dosage for 100 mL of 10 mg/L fluoride standard test solutions at pH 4.0. Increasing adsorbent dosage increased fluoride uptake, indicating that for a quantitative fluoride removal an optimum ZICSC dosage of 10 g/L was required. The results indicate that the fluoride removal efficiency increases up to this optimum dosage beyond which fluoride uptake has no significant change with ZICSC dosage. With the initial increase in the adsorbent dosage the fluoride uptake increased, as increasing the dosage provides greater surface area or adsorption sites. However, by increasing the adsorbent dosage beyond the optimum dosage, there may be a slight improvement in fluoride removal efficiency but the adsorption density decreases.

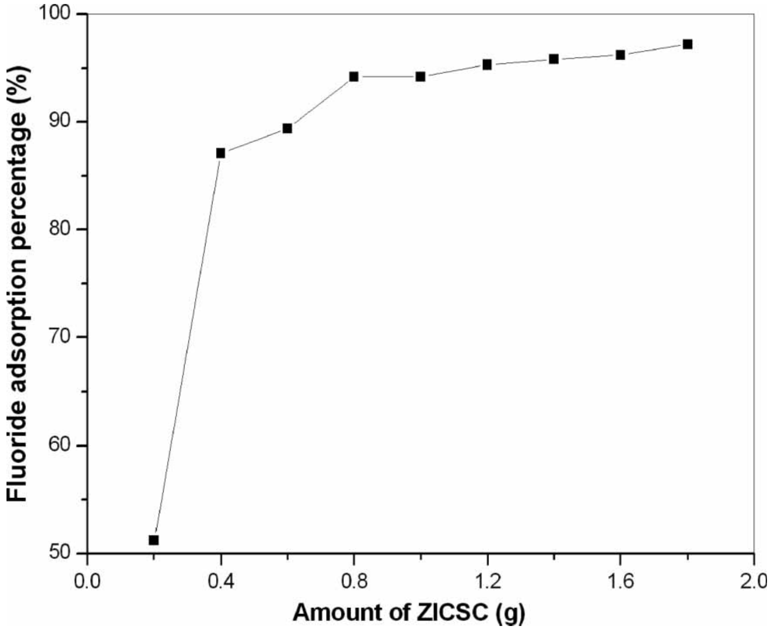

Figure 6. Effect of adsorbent dose on fluoride adsorption onto ZICSC at room temperature. Volume of sample = 100 mL, agitation time = 6 hours, initial adsorbate conc = 10 mg/L, pH = 4.

Hence, maximum defluoridation of a fluoride rich water sample was achieved by maintaining the pH at 4, with 6 hours agitation time and 10 g/L of ZICSC adsorbent dosage as the optimum conditions. The present method adopted was superior compared to existing methods as ZICSC can not only be used for the preconcentration of phosphate (11), arsenic, selenium, mercury (12), chromium (VI) (13) but also for fluoride rich water samples.

Kinetic Modeling

The experimental data for fluoride adsorption on ZICSC (Fig. 7) was analyzed using the Langmuir, Freundlich, Redlich-Peterson and Temkin sorption isotherm models.

Langmuir Isotherm

The linearized Langmuir adsorption isotherm, is expressed as

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{bq_mC_e} \tag{2}$$

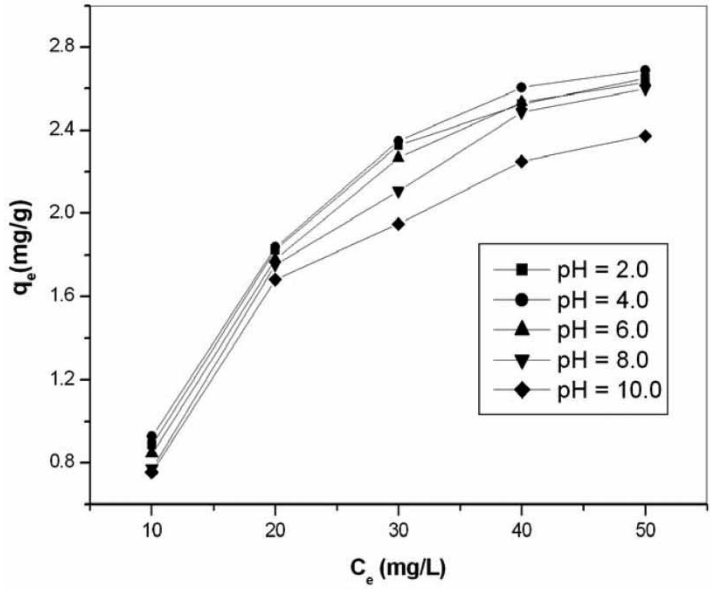

Figure 7. Adsorption isotherms of ZICSC as a function of pH values at room temperature.

where q_e is the amount of fluoride ions adsorbed per unit weight of the adsorbent ZICSC (mg/g), q_m is the maximum sorption capacity corresponding to complete monolayer coverage (mg/g), Langmuir constant b is indirectly related to the energy of adsorption (1/mg) and C_e is the equilibrium fluoride ion concentration (mg/L). Linear plots of $1/q_e$ vs. $1/C_e$, at different pH values were applied to confirm the applicability of the Langmuir isotherm as presented in Table 1 and this also yields $1/q_m$ and $1/bq_m$ as the intercept and slope respectively.

Freundlich Isotherm

Freundlich equation in its linear form can be expressed as

$$\log q_e = \log k_f + n \log C_e \tag{3}$$

where k_f and n are Freundlich constants and if $n < 1$, the bond energy increases with surface density, if $n > 1$, bond energy decreases with surface density, and for $n = 1$, all surface sites are equivalent. A plot of log q_e vs. log C_e delivers log k_f and n as the intercept and slope respectively as in Table 1.

From the parameter values of the Langmuir and Freundlich isotherms presented in Table 1, it was found that the correlation coefficient R^2 value for the Langmuir model is near to unity and hence the defluoridation process using ZICSC follows the Langmuir isotherm well.

Table 1. Langmuir and Freundlich isotherm parameters for fluoride adsorption by ZICSC

	Langmuir parameters			Freundlich parameters		
pH	q_m (mg/g)	b (1/mg)	R^2	k_f (mg/g)	n	R^2
2.0	6.77	0.02	0.98	0.20	0.69	0.93
4.0	6.41	0.02	0.98	0.22	0.67	0.94
6.0	7.51	0.01	0.98	0.18	0.71	0.94
8.0	9.11	0.01	0.97	0.15	0.75	0.94
10.0	6.64	0.01	0.97	0.17	0.70	0.92

Redlich-Peterson Isotherm

The features of both the Langmuir and Freundlich isotherms were incorporated by Redlich and Peterson (21) into a single equation and presented as a general isotherm equation

$$q_e = \frac{K_R C_e}{1 + a_R C_e^{\beta}} \tag{4}$$

where K_R, a_R and β are isotherm constants with the exponent, β, varying in the range 0 to 1. The two limiting behaviors here are: for $\beta = 1$, we have Langmuir form, while for $\beta = 0$, Henry's law is followed. A minimization procedure was adopted to solve the above equation by maximizing the correlation coefficient between the theoretical data for q_e predicted from the above equation and experimental data, which was provided by a value of $\beta = 1$, that fitted well with Langmuir model in support of our previous conclusion.

Temkin Isotherm

The Temkin isotherm has been used in the form as

$$q_e = \frac{RT}{b} \ln(AC_e) \tag{5}$$

where R is the gas constant (8.314 J/mol/K) and T is the room temperature (298 K) with $RT/b = B$. The effects of indirect adsorbate/adsorbate interactions on adsorption isotherms was considered by Temkin and Pyzhev (22). Further, the heat of adsorption of all molecules in the layer would decrease linearly with coverage due to adsorbate/adsorbate interactions. The constants A and b were obtained from a plot of q_e vs. log C_e, where a very low, A value of 0.24 1/g with a R^2 value of 0.98 indicates least adsorbate/adsorbate interactions in ZICSC over the entire pH range of 2–10 and accounts for the excellent fluoride adsorption from water.

Adsorption Kinetics

The residence time of the sorption reaction is governed by the kinetics of sorption describing the solute uptake rate, which is one of the important characteristics defining the efficiency of sorption. Hence in the present study, the kinetics of fluoride removal has been carried out to understand the behavior of ZICSC.

First Order Kinetic Model

The kinetics of fluoride adsorption on ZICSC was tested by the first order rate equation

$$\ln(1 - U_t) = -k\,t \tag{6}$$

where,

$$U_t = \frac{(C_0 - C_t)}{(C_0 - C_e)}$$

and C_0 and C_t are fluoride levels (mg/L) initially and at time t. k is the overall rate constant and U_t is the fractional attainment of equilibrium of fluoride calculated by considering the fluoride adsorption by ZICSC in a given time range of 0.08–0.5 hours. In the present study a concentration of fluoride over the range of 10 to 50 mg/L was examined (Fig. 8).

Pseudo-First Order Kinetic Model

The integrated rate law for a pseudo-first order reaction (23) is

$$\log\left(\frac{q_e}{q_e - q_t}\right) = \frac{k_1}{2.303}t \tag{7}$$

where, q_t is the amount of fluoride adsorbed at time t (mg/g) and k_1 is the equilibrium rate constant of the pseudo-first order sorption (1/min). Fluoride concentration in the range 10 to 50 mg/L was examined by Eq. (7) (Fig. 9).

Pseudo-Second Order Kinetic Model

A pseudo-second order model (23) alone describes the kinetics of fluoride adsorption on ZICSC. The ZICSC–fluoride ion reaction may be represented as:

$$\text{ZrO(OH)Cl(adsorbed on CSC)} + 2\text{F}^- \Longleftrightarrow \text{ZrOF}_2 \tag{8}$$

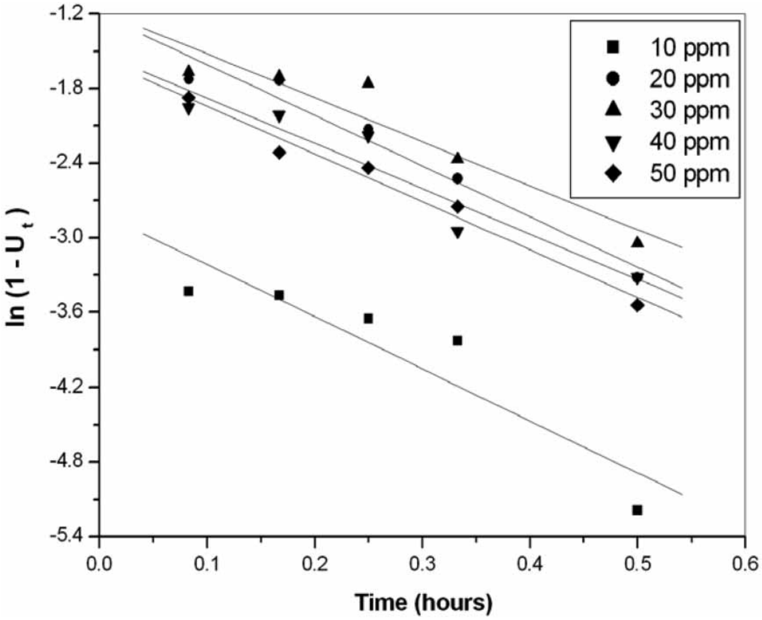

Figure 8. First order kinetic fit for fluoride adsorption onto ZICSC at room temperature. Adsorbent dose = 10 g/L, volume of sample = 100 mL, pH = 4.

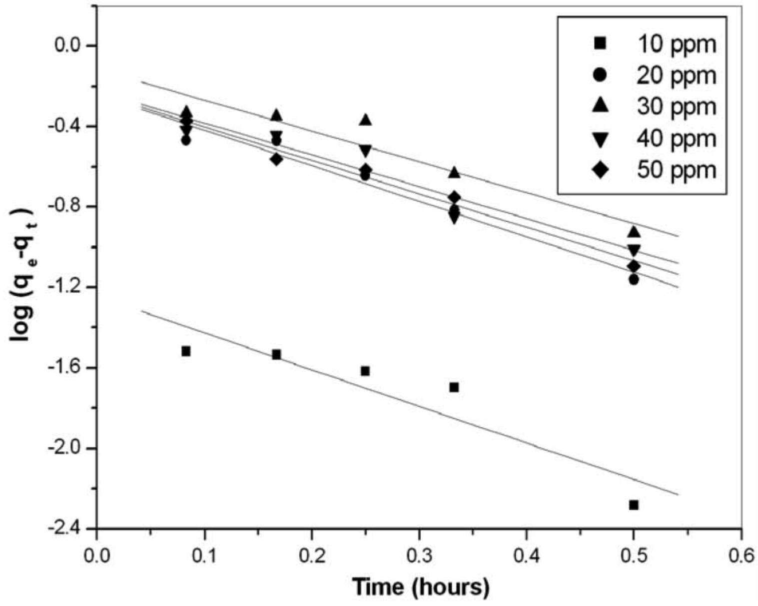

Figure 9. Pseudo-first order kinetic fit for fluoride adsorption onto ZICSC at room temperature. Adsorbent dose = 10 g/L, volume of sample = 100 mL, pH = 4.

An integrated rate law for a pseudo-second order reaction based on the fluoride adsorption equilibrium may be derived from Eq. (8) as

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}\, t \tag{9}$$

where k_2 is the rate constant for sorption (g/mg min) and the initial sorption rate, h, can be defined as $h = k_2 q_e^2$. Linear plots of (t/q_t) vs. t (Fig. 10), at different fluoride concentrations were applied to confirm the applicability of the pseudo-second order kinetic model as presented in Table 2 and this also yields k_2 and q_e from the intercept and slope respectively.

From the k_2 and h values of the pseudo-second order reaction presented in Table 2, it was found that the correlation coefficient R^2 values for this model was near to unity as compared to the R^2 values as obtained by plotting $ln(1 - U_t)$ vs. t in the first order kinetic model and by plotting log $(q_e - q_t)$ vs. t in the pseudo-first order kinetic model and hence the defluoridation process using ZICSC follows the pseudo-second order kinetic model well.

The high h values indicate that the initial fluoride adsorption rate was extremely rapid, in support of our experimental observations. As the effect of agitation time on fluoride uptake by ZICSC at the optimum pH 4.0, suggested that the process was fast with 91% of the adsorption within 10 min of contact.

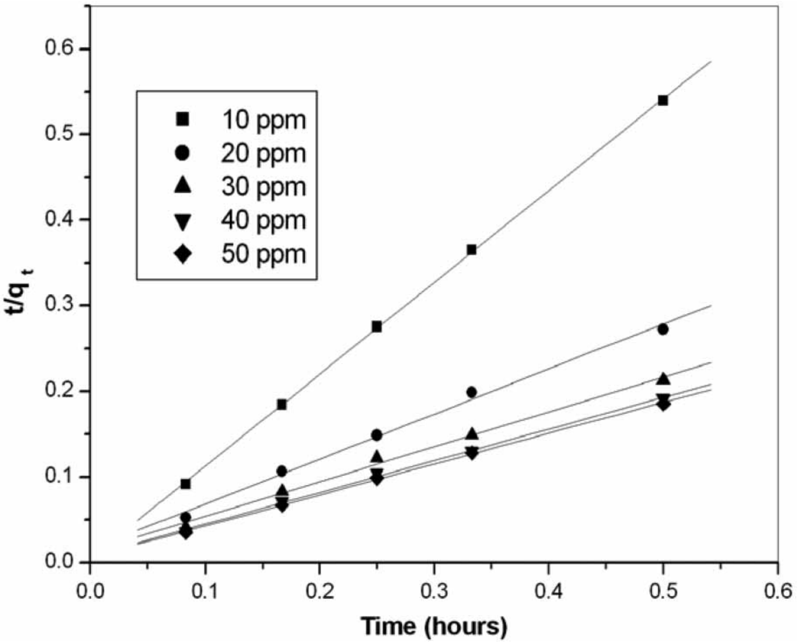

Figure 10. Pseudo-second order kinetic fit for fluoride adsorption onto ZICSC at room temperature. Adsorbent dose = 10 g/L, volume of sample = 100 mL, pH = 4.

Table 2. Pseudo-second order kinetic model parameters for fluoride adsorption by ZICSC

Fluoride (mg/L)	k_2 (g/mg min)	h (mg/g)	R^2
10	214.676	186.553	0.999
20	17.176	62.385	0.994
30	12.119	73.585	0.994
40	17.082	124.692	0.998
50	19.036	145.984	0.999

Hence it is very clear from the kinetic modeling and adsorption studies that the fluoride removal process using ZICSC follows the Langmuir adsorption isotherm and pseudo-second order kinetics. This brings to light that the defluoridation ability of ZICSC, which is 25 to 30 times that of plain activated carbon, occurs through a combination of chemisorption and physisorption processes through monolayer formation in accordance with Langmuir isotherm. Fluoride ion, a Lewis base, coordinates strongly with the zirconium species adsorbed on CSC, which are Lewis acid sites. The chemisorption mechanism of fluoride uptake, involves an exchange of the chloride and the hydroxide of the ZrO(OH)Cl species adsorbed on CSC by fluorides, leading to the formation of $ZrOF_2$ as described in Eq. (8) and is strictly a monolayer surface adsorption phenomenon (24). The zirconium ion adsorption on CSC is monolayer adsorption, and once these impregnated active sites are chemisorbed by a monolayer of fluoride ions, no active sites are further available for sorption. The physisorption process involves a van der Waals interaction between the fluoride ion and activated carbon, which accounts for fluoride adsorption on ash and CSC (10) and intraparticle diffusion of the hydrated fluoride ion, 3.52 Å in size (25) into the pores of ZICSC, which varies from 30–300 Å. It is this intraparticle diffusion factor that accounts for the fact that though fluoride uptake by ZICSC was rapid with q_e at 0.91 mg/g within 10 min of the contact, this initial rapid adsorption subsequently gave way to equilibrium and saturation only at 6 hours, indicating that the diffusion process may be involved in the rate limiting step. A monolayer alone is again supported by physisorption, as successive fluoride ions are repelled by physisorbed fluoride ions through electrostatic forces.

Further the regeneration of ZICSC is accomplished by eluting with 0.02 M sodium hydroxide solution. Washing the ZICSC particles with NaOH, quantitatively desorbs all bound fluoride without harming the underlying zirconium species adsorbed on CSC (24). Even after four regenerations the impregnated charcoal showed similar results as the first set of defluoridation experiments. This low-cost adsorbent can be disposed off easily and safely; they can be reused as filler material in low-lying areas (landfills) or in manufacture of bricks.

Table 3. Comparative study of fluoride adsorption onto various adsorbents at 298 K

	Fluoride adsorption percentage (%)	
Adsorbents	pH 4	pH 7
ZICSC	99.1	95.0
Alumina	59.6	41.2
Phosphorus free carbon	27.8	15.4
Chitin	14.8	6.2
Unimpregnated CSC	3.8	2.0

Comparison with Other Adsorbents

The fluoride adsorption capacity of ZICSC was compared with those of other commonly used fluoride adsorbents for 100 mL of 10 mg/L fluoride standard test solution with a ZICSC adsorbent dose of 10 g/L and 6 hours agitation time. Table 3 shows that ZICSC has its fluoride removal efficiency at 99 and 95% at pH 4 and 7 respectively which is comparatively higher than the rest of the adsorbents and in particular highlights the substantial improvement in fluoride adsorption capacity of CSC on zirconium impregnation.

CONCLUSIONS

The fluoride adsorption capacity of ZICSC from water was investigated in this paper, by pursuing the batch equilibrium and kinetic experiments, wherein the effect of various parameters such as pH, agitation time, and adsorbent dosage were studied. Maximum defluoridation of a fluoride rich water sample, with a pH, which is strongly acidic to weakly basic, can be achieved with 6 hours of agitation time and 10 g/L of ZICSC adsorbent dosage as the optimum conditions. Quantitative fluoride removal from water confirms the validity of these obtained results and the adsorption data for fluoride onto ZICSC were better correlated to the Langmuir than to the Freundlich isotherm. In the adsorption kinetic modeling studies, the pseudo-second order chemical reaction kinetics provided the best correlation of the experimental data for ZICSC. This kinetic data would be useful for developing an appropriate technology in designing a treatment plant for fluoride rich water. Further, the present method adopted was superior compared to existing methods as ZICSC can not only be used for the preconcentration of phosphate, arsenic, selenium, mercury, and chromium (VI) but also for fluoride rich water samples. This is a strong indication for its great potential application in fluoride removal from water as ZICSC provides a cost-effective working solution to the defluoridation problem in the developing countries.

ACKNOWLEDGEMENT

The authors are grateful to the Chancellor, Bhagawan Sri Sathya Sai Baba, Sri Sathya Sai Institute of Higher Learning, for his constant inspiration.

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