



Development of chitosan supported zirconium(IV) tungstophosphate composite for fluoride removal

Natrayasamy Viswanathan^a, S. Meenakshi^{b,*}

^a Department of Chemistry, Anna University Tiruchirappalli – Dindigul Campus, Dindigul 624622, Tamil Nadu, India

^b Department of Chemistry, Gandhigram Rural University, Gandhigram 624302, Tamil Nadu, India

ARTICLE INFO

Article history:

Received 17 July 2009

Received in revised form 10 October 2009

Accepted 9 November 2009

Available online 13 November 2009

Keywords:

Chitosan

Composite

Fluoride removal

Sorption

Zirconium(IV) tungstophosphate

ABSTRACT

A new biocomposite was prepared by incorporating inorganic ion exchanger namely zirconium(IV) tungstophosphate (ZrWP) into the chitosan biopolymeric matrix. The sorption behaviour of fluoride from aqueous solutions by this ZrWP/chitosan (ZrWPCs) composite has been investigated by batch technique. The fluoride sorption was studied as a function of contact time, pH, initial fluoride concentration, competing co-ions and temperature. The defluoridation capacity (DC) of the adsorbent was found to be 2025 mgF⁻ kg⁻¹. The composite was characterized using FTIR and SEM with EDAX analysis. The equilibrium sorption data were fitted to Freundlich and Langmuir isotherms. The kinetics of sorption was found to follow pseudo-second-order and intraparticle diffusion models. The values of thermodynamic parameters indicate the nature of sorption is spontaneous and endothermic. The biocomposite was successfully used for the removal of fluoride from the field water taken in a nearby fluoride endemic village.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

The presence of fluoride in water may be due to natural and anthropogenic sources. Fluoride ions present in aqueous environment are of great concern because of their possible accumulation and damage to the human tissues. The World Health Organisation suggested a limiting concentration of 1.5 mg L⁻¹ for fluoride content in drinking water [1–3]. Excessive intake of fluoride (>1.5 mg L⁻¹) leads to fluorosis. Recent research in the field of fluoride removal has focused on the development of sorbents with increased affinity, capacity and selectivity towards fluoride [4–6].

Ion exchangers have played a vital role in the domain of water treatment. In recent years, synthetic inorganic exchangers based on tetravalent metals have been objects of considerable study because of their selectivity towards the removal of toxic ions [7,8]. Zirconium-based ion exchangers have received attention because of their excellent ion-exchange behaviour and some important chemical applications in the field of ion exchange. The selectivity may be enhanced by varying the composition of the materials [7–11].

Nowadays, technology is devoted to the development of new materials which are able to satisfy the specific requirements in terms of both the structural and functional properties. The mod-

ern development of polymeric materials have introduced a new generation of composites. The main advantage of the polymeric composite materials resides in the possibility of combining the physical properties of the constituents to obtain new structural or functional properties. Composites can be shaped into any desired form viz., beads, candles and membranes. Due to the possibility of designing properties, polymeric composite materials have been used for field applications.

The powdered zirconium(IV) tungstophosphate (ZrWP) cannot be directly used in fixed bed columns or any other flow-through systems because it cause excessive pressure drops. To circumvent such technological bottlenecks, polymeric hybrid composites were prepared by dispersing powdered ZrWP particles onto porous polymeric substrates. Styrene supported zirconium(IV) tungstophosphate composite was prepared and used in the exchange of cations and sorption of pesticides [10,11]. Currently, the biopolymers namely chitin and chitosan possess the unique properties like biodegradability, biocompatibility and bioactivity. These biopolymers also play a promising role in the removal of toxic ions present in water [6,12–14].

The main objective of the research work is to synthesize chitosan supported ZrWP by dispersing ZrWP into the chitosan biopolymeric matrix for fluoride removal. Various influencing parameters on the defluoridation capacity (DC) of the composite viz., contact time, pH, initial fluoride concentration, competing co-ions and temperature were optimized. The equilibrium data was fitted with isotherms and kinetic models. The suitability of the composite was tested with a water sample collected from a fluoride endemic village.

* Corresponding author. Tel.: +91 451 2452371; fax: +91 451 2454466.

E-mail addresses: natrayasamy.viswanathan@rediffmail.com (N. Viswanathan), drs.meena@rediffmail.com (S. Meenakshi).

2. Materials and methods

2.1. Materials

Chitosan (85% deacetylated) was supplied by Pelican Biotech and Chemicals Labs, Kerala (India). $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$, $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$, H_3PO_4 and all other chemicals used were of analytical grade. For the field study, water containing fluoride was collected from a nearby fluoride endemic village.

2.2. Synthesis of ZrWPCs composite

ZrWPCs composite was synthesized by mixing the solutions of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ (0.1 M), $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ (0.1 M), H_3PO_4 (0.1 M) and chitosan in the volume ratios of 1:1:3:1 respectively with constant stirring. The gel so obtained was left undisturbed for 24 h. Then the composite gel was washed with distilled water until the neutral pH reached and dried at 60 °C in an oven. Finally, the ZrWPCs composite was ground to fine powders of uniform size and used for fluoride sorption studies.

2.3. Fluoride sorption experiments

Defluoridation experiments were carried out by batch equilibration method in duplicate. In a typical case, 0.1 g of the sorbent was added to 50 mL of NaF solution of initial concentration 10 mg L⁻¹. The contents were shaken thoroughly using a thermostated shaker rotating at a speed of 200 rpm and the filtrate was analyzed for fluoride. The influence of various parameters like contact time, pH and presence of other anions on DC of the sorbent were investigated. For the kinetic studies, the effect of different initial fluoride concentrations viz., 9, 11, 13 and 15 mg L⁻¹ at three different temperatures viz., 303, 313 and 323 K on sorption rate was studied by keeping the mass of the sorbent as 0.1 g and the volume of solution as 50 mL at neutral pH. The solution was then filtered and the residual fluoride ion concentration was measured.

2.4. Analysis

The fluoride ion concentration was measured using an expandable ion analyzer EA 940 and the fluoride ion selective electrode BN 9609 with the relative accuracy of ± 1 significant digit, detection limit of 0.02 mg L⁻¹ and the reproducibility of $\pm 2\%$ [15]. The pH measurements were done with the same instrument with a pH electrode. All other water quality parameters were analyzed using the standard methods [16]. The pH at zero point of charge (pH_{zpc}) of the composite was determined by a pH drift method [17].

2.5. Composite characterization

Fourier transform infrared spectrophotometer (FTIR) spectra of the composite were obtained using JASCO-460 plus model to confirm the functional groups present in it. Surface morphology of the composite was examined with scanning electron microscope (SEM) with HITACHI-S-3000H model fitted with an energy dispersive X-ray analyzer (EDAX) which allows a qualitative detection and the localization of elements present in the composite. SEM images enable a direct observation of the surface of the fresh and the fluoride-sorbed composites.

2.6. Statistical tools

Computations were made using the Microcal Origin (Version 6.0) software. The significance of the data trends and the goodness of plot fit were discussed using the error bar plot, regression cor-

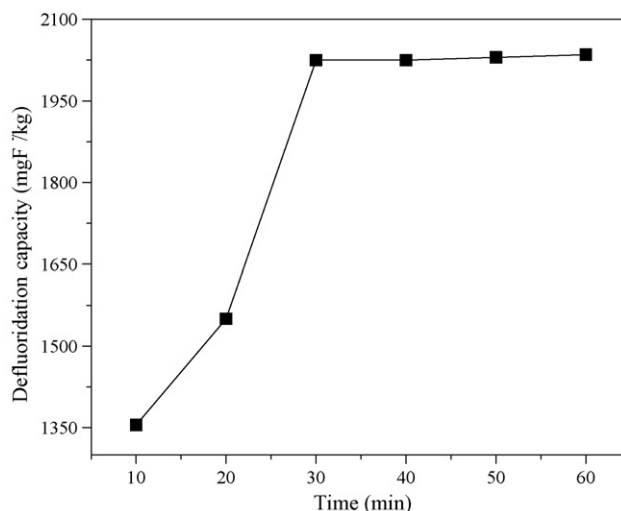


Fig. 1. Effect of contact time on DC of the sorbent in the presence of 10 mg L⁻¹ initial fluoride concentration with a dose of 0.1 g in neutral pH 7 at 303 K.

relation coefficient (r), chi-square analysis and standard deviation (SD).

3. Results and discussion

3.1. Effect of contact time

The DC of the sorbent may vary with the time of contact between the sorbate solution and the sorbent. The variation of DC of ZrWPCs composite with respect to contact time with sorbate solution was carried out with the different period of contact in the range of 10–60 min at 303 K. Fig. 1 shows that ZrWPCs composite reached saturation at 30 min, and hence for further studies the contact time was fixed as 30 min. The DC of ZrWPCs composite was found to be 2025 mgF⁻ kg⁻¹ at 30 min contact time.

3.2. Influence of pH of the medium

To determine the chemical condition at which fluoride ions are effectively sorbed onto ZrWPCs composite, the sorption studies were carried out at five different initial pH levels viz., 3, 5, 7, 9 and 11 by keeping all other influencing parameters like contact time, dose and initial fluoride concentration as constant at 303 K. The pH of the working solution was controlled by using 1 M HCl/NaOH solution. Fig. 2 shows the DC of ZrWPCs composite as a function of pH, which indicates that the DC of the sorbent was influenced by the pH of the medium. The composite recorded a maximum DC of 2142 mgF⁻ kg⁻¹ at pH 3 followed by a gradual decrease trend with increase in pH and a minimum DC of 1165 mgF⁻ kg⁻¹ was observed in pH 11. The reason could be in acidic environment the positive charged composite surface attracts more fluoride ions whereas in alkaline medium the hydroxyl groups will compete with fluoride ions in the active sites of the composite during sorption.

3.3. Effect of co-anions

The anions like Cl⁻, SO_4^{2-} , NO_3^- and HCO_3^- ions are commonly present in water. In order to know the effects of these ions on fluoride sorption by ZrWPCs composite was studied as a function of competing anion concentrations. Fig. 3 shows the dependence of DC of ZrWPCs composite in the presence of co-anions viz., Cl⁻, SO_4^{2-} , HCO_3^- and NO_3^- ions with a fixed initial concentration of 200 mg L⁻¹ prepared using sodium salts of the respective ions with 10 mg L⁻¹ as initial fluoride concentration for 30 min at 303 K. It

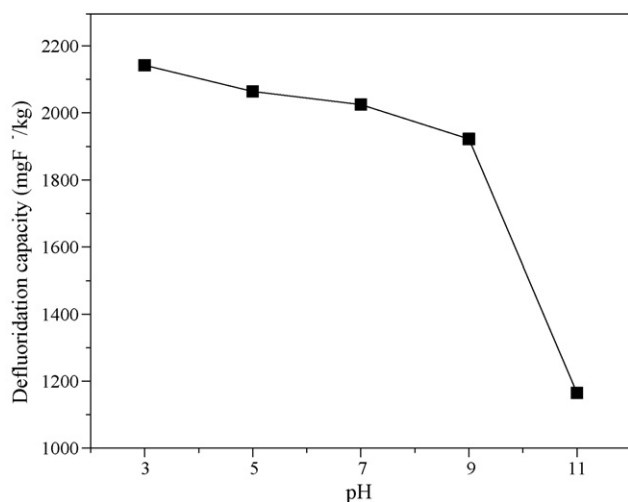


Fig. 2. Effect of pH on the DC of the composite with 10 mg L⁻¹ initial fluoride concentration with a dose of 0.1 g for 30 min at 303 K.

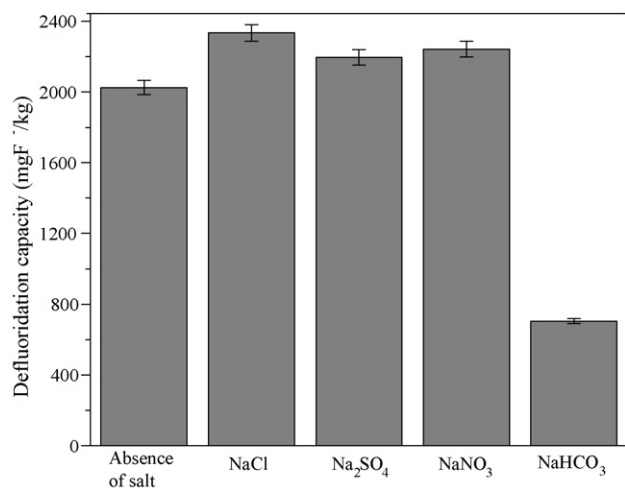


Fig. 3. Influence of foreign anions on the DC of the composite with 10 mg L⁻¹ initial fluoride concentration with a dose of 0.1 g at 303 K.

was inferred that there was no remarkable influence on the DC in the presence of Cl⁻, SO₄²⁻ and NO₃⁻ ions except HCO₃⁻ ion. Infact a slight increase in DC was observed in the presence of Cl⁻, SO₄²⁻ and NO₃⁻ ions. The decrease in the DC of ZrWPCs composite in the presence of bicarbonate ion may be due to on hydrolysis of NaHCO₃ it will release OH⁻ ions which will increase the pH of the solution and will compete with fluoride ions in the active sites of the composite.

3.4. Characterization of ZrWPCs composite

The characteristics of ZrWPCs composite are shown in Table 1. Fig. 4a and b represent the FTIR spectra of ZrWPCs composite and the fluoride-sorbed ZrWPCs composite. The band at

Table 1
Characteristics of ZrWPCs composite.

Constituents	ZrWPCs composite
Inorganic material	Zirconium(IV) tungstophosphate
Organic matrix	Chitosan
Particle size (nm)	435
Density (g cm ⁻³)	1.221
BET surface area (m ² g ⁻¹)	3.55
pH _{zpc}	2.84

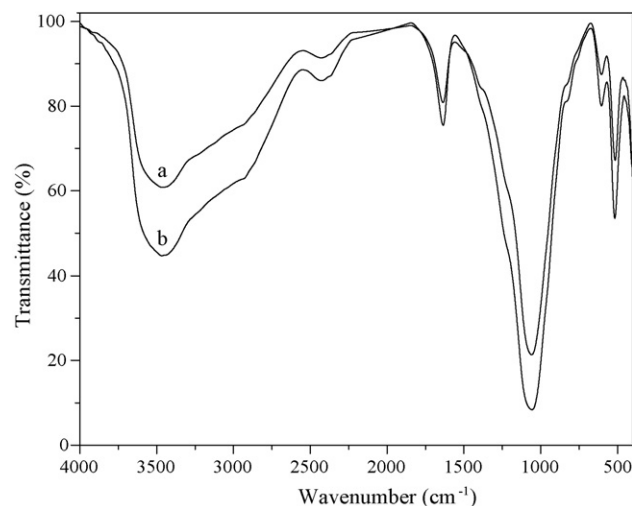


Fig. 4. FTIR spectra of (a) ZrWPCs composite and (b) fluoride-sorbed ZrWPCs composite.

1000–1100 cm⁻¹ represents the presence of PO₄³⁻ groups in the composite [11]. A broad band at 3456 cm⁻¹ indicates the presence of –P–OH groups in the composite. The widening of broad band at 3456 cm⁻¹ in the fluoride-sorbed ZrWPCs composite may be taken as an indicative of the electrostatic attraction between the sorbent and the fluoride [12].

SEM images of ZrWPCs composite are shown in Fig. 5a and b. The fluoride-sorbed ZrWPCs composite is shown in Fig. 5c. The change in the SEM images of the sorbent before and after fluoride treatment indicates the fluoride gets sorbed into the composite. This is further supported by the EDAX analysis. The EDAX spectra of ZrWPCs composite confirm the presence of respective ions in the composite (cf. Fig. 5d). The sorption of fluoride have occurred on ZrWPCs composite which were confirmed by the presence of fluoride, Zr + F and W + F peaks in the EDAX spectra of fluoride treated ZrWPCs composite (cf. Fig. 5e).

The surface morphological changes of ZrWPCs composite were also confirmed by the shifting of pH_{zpc} values. The pH_{zpc} of ZrWP is 2.65 where as for ZrWPCs composite it was shifted to 2.84 which clearly show the occurrence of structural changes in ZrWPCs composite.

3.5. Sorption isotherms

The isotherm is used to characterize the interaction of each fluoride species with the sorbent. This provides a relationship between the concentration of fluoride in the sorption medium and the amount of fluoride sorbed on the solid phase when the two phases are at equilibrium. The most commonly used two isotherms namely Freundlich and Langmuir isotherms have been employed.

3.5.1. Freundlich isotherm

The linear form of Freundlich [18] isotherm is represented by the equation,

$$\log q_e = \log k_F + \frac{1}{n} \log C_e \quad (1)$$

where q_e is the amount of fluoride adsorbed per unit weight of the sorbent (mg g⁻¹), C_e is the equilibrium concentration of fluoride in solution (mg L⁻¹), k_F is a measure of sorption capacity and $1/n$ is the sorption intensity. The linear plot of $\log q_e$ vs. $\log C_e$ indicates the applicability of Freundlich isotherm. The values of $1/n$, n and k_F of ZrWPCs composite are listed in Table 2. The values of $1/n$ lie between 0 and 1 and the n value lies in the range of 1–10 confirm the

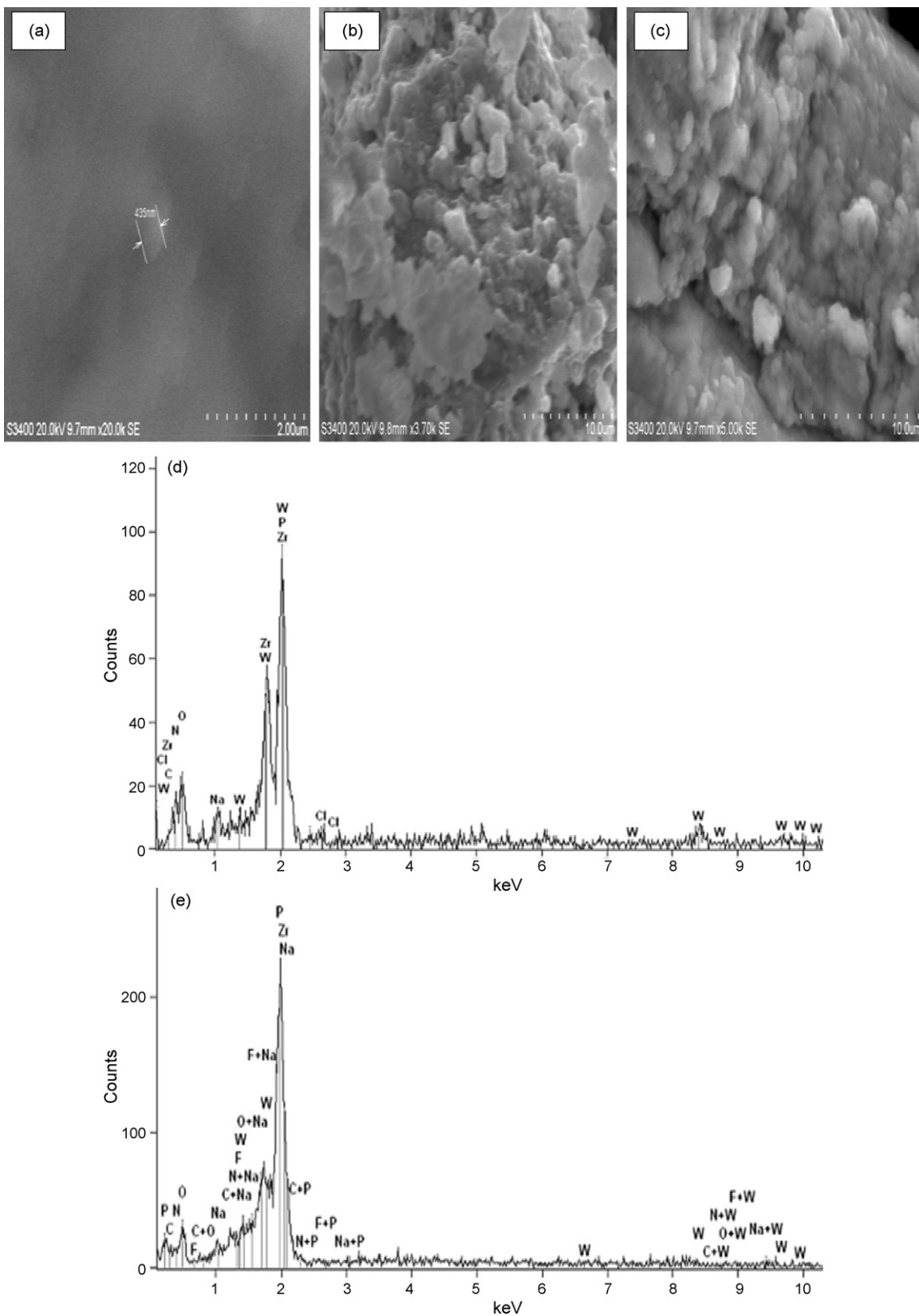


Fig. 5. SEM micrographs of ZrWPCs composite (a) (at 2 μm), (b) (at 10 μm) and (c) fluoride-sorbed ZrWPCs composite (at 10 μm); EDAX spectra of (d) ZrWPCs composite and (e) fluoride treated ZrWPCs composite.

Table 2
Freundlich and Langmuir isotherms of ZrWPCs composite.

Temperature (K)	Freundlich isotherm					Langmuir isotherm				
	1/n	n	k_F (mg g ⁻¹)(L mg ⁻¹) ^{1/n}	r	χ^2	Q^0 (mg g ⁻¹)	b (L g ⁻¹)	R_L	r	χ^2
303	0.928	1.078	0.238	0.999	2.10 E-6	7.634	0.022	0.833	0.990	2.32 E-3
313	0.776	1.289	0.397	0.999	1.60 E-4	8.929	0.036	0.755	0.972	2.80 E-4
323	0.708	1.412	0.532	0.998	1.91 E-4	9.901	0.055	0.669	0.982	3.39 E-4

Table 3
Thermodynamic parameters of ZrWPCs composite.

Thermodynamic parameters	ZrWPCs composite
ΔG° (kJ mol ⁻¹)	
303 K	-9.98
313 K	-9.30
323 K	-8.71
ΔH° (kJ mol ⁻¹)	29.27
ΔS° (kJ mol ⁻¹ K ⁻¹)	0.06

favorable conditions for sorption. With the rise in temperature, the k_F values get increased which indicates that the nature of fluoride uptake by ZrWPCs composite is an endothermic process.

3.5.2. Langmuir isotherm

Langmuir [19] isotherm model can be represented in the form of equation

$$\frac{C_e}{q_e} = \frac{1}{Q^0 b} + \frac{C_e}{Q^0} \tag{2}$$

where Q^0 is the amount of the sorbate sorbed at complete monolayer coverage (mg g⁻¹), which gives the maximum sorption capacity of the sorbent and b (L mg⁻¹) is the Langmuir isotherm constant that relates to the energy of sorption. A linear plot is obtained for the sorbent when C_e/q_e is plotted against C_e which gives Q^0 and b values from the slope and intercept respectively and the calculated results are listed in Table 2. The increase in Q^0 values with respect to temperature indicates the endothermic nature of fluoride sorption.

In order to find out the feasibility of the isotherm, the essential characteristics of the Langmuir isotherm can be expressed in terms of the dimensionless constant separation factor or equilib-

rium parameter [12]

$$R_L = \frac{1}{1 + bC_0} \tag{3}$$

where b is the Langmuir isotherm constant and C_0 is the initial concentration of fluoride (mg L⁻¹). The R_L values lying between 0 and 1 indicate favorable sorption for all the temperatures studied (cf. Table 2).

3.5.3. Chi-square analysis

To identify the suitable isotherm for fluoride sorption onto the composite, the chi-square analysis was carried out. The equivalent mathematical statement for chi-square analysis is

$$\chi^2 = \sum \frac{(q_e - q_{e,m})^2}{q_{e,m}} \tag{4}$$

where $q_{e,m}$ is equilibrium capacity obtained by calculating from the model (mg g⁻¹) and q_e is experimental data on the equilibrium capacity (mg g⁻¹). If data from the model are similar to the experimental data, χ^2 will be a small number, while if they differ, χ^2 will be a bigger number. The results of chi-square analysis are presented in Table 2. As Freundlich isotherm possess lower χ^2 values and hence this isotherm can be considered as the best fitting model for the sorption of fluoride on ZrWPCs composite than Langmuir model.

3.6. Thermodynamic treatment of the sorption process

Thermodynamic parameters associated with the sorption viz., standard free energy change (ΔG°), standard enthalpy change (ΔH°) and standard entropy change (ΔS°) were calculated as follows.

Table 4
Kinetic models of ZrWPCs composite.

Kinetic models	Parameters	303 K				313 K				323 K			
		9 mg L ⁻¹	11 mg L ⁻¹	13 mg L ⁻¹	15 mg L ⁻¹	9 mg L ⁻¹	11 mg L ⁻¹	13 mg L ⁻¹	15 mg L ⁻¹	9 mg L ⁻¹	11 mg L ⁻¹	13 mg L ⁻¹	15 mg L ⁻¹
Pseudo-first-order	k_{ad} (min ⁻¹)	0.143	0.142	0.136	0.127	0.131	0.129	0.128	0.124	0.131	0.129	0.117	0.131
	r	0.991	0.994	0.988	0.986	0.993	0.992	0.985	0.992	0.991	0.987	0.994	0.995
	SD	0.087	0.068	0.096	0.097	0.073	0.071	0.101	0.071	0.077	0.095	0.058	0.059
Pseudo-second-order	q_e (mg g ⁻¹)	1.429	1.689	1.949	2.232	1.639	1.912	2.183	2.494	1.838	2.141	2.404	2.740
	k (g mg ⁻¹ min ⁻¹)	0.270	0.328	0.358	0.306	0.403	0.424	0.403	0.375	0.420	0.394	0.432	0.453
	h (mg g ⁻¹ min ⁻¹)	0.550	0.937	1.361	1.524	1.082	1.550	1.923	2.331	1.420	1.808	2.494	3.401
	r	0.999	0.999	0.999	0.999	0.999	0.999	0.999	0.999	0.999	0.999	0.999	0.999
	SD	0.025	0.018	0.012	0.013	0.012	0.011	0.070	0.062	0.069	0.080	0.046	0.030
Particle diffusion	k_p (min ⁻¹)	0.143	0.144	0.137	0.127	0.131	0.129	0.129	0.125	0.130	0.131	0.118	0.130
	r	0.991	0.995	0.988	0.986	0.993	0.993	0.985	0.992	0.992	0.987	0.994	0.995
	SD	0.201	0.157	0.220	0.222	0.168	0.164	0.233	0.162	0.178	0.219	0.133	0.135
Intraparticle diffusion	k_i (mg g ⁻¹ min ^{-0.5})	0.104	0.100	0.090	0.101	0.081	0.082	0.084	0.092	0.080	0.086	0.080	0.083
	r	0.984	0.958	0.988	0.986	0.986	0.980	0.989	0.987	0.986	0.987	0.986	0.975
	SD	0.025	0.041	0.019	0.023	0.019	0.022	0.017	0.020	0.018	0.019	0.018	0.025

The free energy of sorption process, considering the sorption equilibrium coefficient K_o , is given by the equation

$$\Delta G^\circ = -RT \ln K_o \quad (5)$$

where ΔG° is the standard free energy of sorption (kJ mol^{-1}), T is the temperature in Kelvin and R is the universal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$). The sorption distribution coefficient K_o , was determined from the slope of the plot $\ln(q_e/C_e)$ against C_e at different temperatures and extrapolating to zero C_e according to Khan and Singh method [20].

The sorption distribution coefficient may be expressed in terms of ΔH° and ΔS° as a function of temperature:

$$\ln K_o = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (6)$$

where ΔH° is the standard enthalpy change (kJ mol^{-1}) and ΔS° is the standard entropy change ($\text{kJ mol}^{-1} \text{ K}^{-1}$). The values of ΔH° and ΔS° can be obtained from the respective slope and intercept of the plot of $\ln K_o$ against $1/T$.

The values of thermodynamic parameters are shown in Table 3. The negative values of ΔG° confirm the spontaneous nature of fluoride sorption. The value of ΔH° is positive indicating that the sorption process is endothermic in nature. The positive value of ΔS° indicates the possibility of randomness at the solid/liquid interface during fluoride sorption.

3.7. Sorption kinetic models

The two main types of sorption kinetic models namely reaction-based and diffusion-based models were adopted to fit the experimental data.

3.7.1. Reaction-based models

The most commonly used pseudo-first-order and pseudo-second-order models were employed to explain the solid/liquid sorption.

A simple pseudo-first-order kinetic model [21] is given as

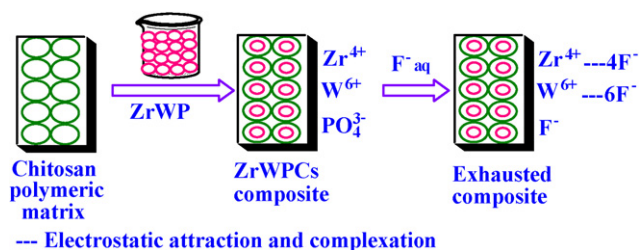
$$\log(q_e - q_t) = \log q_e - \frac{k_{ad}}{2.303} t \quad (7)$$

where q_t is the amount of fluoride on the surface of the composite at time t (mg g^{-1}) and k_{ad} is the equilibrium rate constant of the pseudo-first-order sorption (min^{-1}). The linear plots of $\log(q_e - q_t)$ against t gives straight line indicate the applicability of pseudo-first-order model. The slope of the straight line plot of $\log(q_e - q_t)$ against t at three different temperatures viz., 303, 313 and 323 K give the value of the pseudo-first-order rate constant (k_{ad}) and r are listed in Table 4.

In addition, the pseudo-second-order model is also widely used. There are four types of linear pseudo-second-order kinetic models [22] the most popular linear form is

$$\frac{t}{q_t} = \frac{1}{h} + \frac{t}{q_e} \quad (8)$$

where $q_t = (q_e^2 kt)/(1 + q_e kt)$, amount of fluoride on the surface of the composite at any time, t (mg g^{-1}), k is the pseudo-second-order rate constant ($\text{g mg}^{-1} \text{ min}^{-1}$), q_e is the amount fluoride ion sorbed at equilibrium (mg g^{-1}) and the initial sorption rate, $h = kq_e^2$ ($\text{mg g}^{-1} \text{ min}^{-1}$). The value of q_e (1/slope), k (slope²/intercept) and h (1/intercept) of the pseudo-second-order equation can be found out experimentally by plotting t/q_t against t . The values of q_e , k , h and r of the pseudo-second-order model were obtained from the plots of t/q_t vs. t for fluoride sorption at three different temperatures viz., 303, 313 and 323 K of ZrWPCs composite and are presented in Table 4. The values of q_e increase with the increase in temperature indicating fluoride sorption increases with the rise in



Scheme 1. Mechanism of fluoride removal by ZrWPCs composite.

temperature. The higher correlation coefficient (r) values obtained for pseudo-second-order model than pseudo-first-order indicating the applicability of the pseudo-second-order model for the fluoride sorption onto the composite.

3.7.2. Diffusion-based models

For a solid-liquid sorption process, the solute transfer is usually characterized either by particle diffusion or by intraparticle diffusion control.

A simple equation for the particle diffusion controlled sorption process [12,23] is given as follows,

$$\ln\left(1 - \frac{C_t}{C_e}\right) = -k_p t \quad (9)$$

where k_p is the particle rate constant (min^{-1}). The value of particle rate constant is obtained by the slope of the plot $\ln(1 - C_t/C_e)$ against t .

The intraparticle diffusion model used here refers to the theory proposed by Weber and Morris [24] and its equation is

$$q_t = k_i t^{1/2} \quad (10)$$

where k_i is the intraparticle rate constant ($\text{mg g}^{-1} \text{ min}^{-0.5}$). The slope of the plot of q_t against $t^{1/2}$ will give the value of intraparticle rate constant.

The straight line plots of $\ln(1 - C_t/C_e)$ vs. t and q_t vs. $t^{0.5}$ indicate the applicability of both the particle and intraparticle diffusion models respectively. The k_p , k_i and r values at three different temperatures viz., 303, 313 and 323 K for both the particle and intraparticle diffusion models and are illustrated in Table 4. The r values obtained for both the particle and intraparticle diffusion models are almost comparable and suggest that the fluoride diffusion on ZrWPCs composite follows both the models.

3.7.3. The best-fit model

The assessment of the employed kinetic models for fitting the sorption data was made by standard deviation and the model which possess lower values of SD show better fit to sorption data. The SD values of ZrWPCs composite for all the kinetic models are summarized in Table 4. Smaller SD values were observed for the pseudo-second-order and intraparticle diffusion models indicate that these two models are significant in defining the fluoride sorption process and suggest that the sorption of fluoride ion onto the pores of ZrWPCs composite.

3.8. Sorption mechanism

The possible mechanism for the removal of fluoride by ZrWPCs composite is governed by adsorption/complexation and ion exchange mechanism as shown in Scheme 1. The positive charge of the composite at the surfaces viz., Zr^{4+} and W^{6+} attracts the negatively charged fluoride ions by means of electrostatic attraction as well as complexation [12]. An ion exchange mechanism also involved as the $-\text{PO}_4^{3-}$ group present in ZrWPCs composite is considered as the charge carrier which may gets exchanged for F^- ions.

Table 5

A comparison of the DCs of a few reported sorbents.

Sorbents	Defluoridation capacity (mgF ⁻ kg ⁻¹)	References
ZrWPCs composite	2025	Present study [25]
Nano-hydroxyapatite/chitin composite	2840	
Nano-hydroxyapatite/chitosan composite	1560	[26]
Nano-hydroxyapatite Protonated	1296	[27]
chitosan beads	1664	[6]
Carboxylated chitosan beads	1385	[28]
Raw chitosan bead	52	[6]
Commercial ion exchange resin	97	[4]

Table 6

Field trial results of ZrWPCs composite.

Water quality parameters	Treatment	
	Before	After
F ⁻ (mg L ⁻¹)	2.48	1.38
pH	8.52	7.95
Cl ⁻ (mg L ⁻¹)	390.00	326.00
Total hardness (mg L ⁻¹)	420.00	357.00
Total dissolved solids (mg L ⁻¹)	800.00	600.00

The high DC of ZrWPCs composite may be due to the availability of higher valence ions (Lewis acids) which shows high selectivity towards fluoride ion as it is the hardest Lewis base. At lower pH values where the surface acquires positive charge, the fluoride removal may be due to electrostatic attraction and complexation mechanism and hence observed high DC. However, at high pH values where the surface acquires negative charge, only ion exchange could remove fluoride and hence it recorded lower DC.

A comparison of the DCs of the reported sorbents is given in Table 5. ZrWPCs composite possess an comparable DC with that of the reported sorbents.

3.9. Field study

The ZrWPCs composite used in the present study is also tested with field sample taken from a nearby fluoride endemic village. About 0.1 g of the sorbent was added to 50 mL of fluoride water sample and the contents were shaken with constant time at room temperature. These results are presented in Table 6. It is evident from the result that the sorbent, ZrWPCs composite can be effectively employed for removing the fluoride from water.

4. Conclusions

The defluoridation studies of ZrWPCs composite have been carried out in batch mode. The DC of ZrWPCs composite was influenced by the pH of the medium and decreased in the presence of bicarbonate ions. The sorption of fluoride onto ZrWPCs composite followed Freundlich isotherm. The sorption process was found to be spontaneous and endothermic in nature. The rate of sorption followed pseudo-second-order kinetic model and occurred through intraparticle diffusion. Field studies indicated that ZrWPCs composite could be used as an effective defluoridating agent. ZrWPCs composite could be made into any desired form and used to remove fluoride selectively from water.

Acknowledgement

The corresponding author was grateful to University Grants Commission (No. F.30-56/2004(SR)), New Delhi, India for the provision of financial support to carry out this research work.

References

- [1] J. Fawell, K. Bailey, J. Chilton, E. Dahi, L. Fewtrell, Y. Magara (Eds.), Fluoride in Drinking Water, World Health Organization, IWA Publishing, London, UK, 2006, pp. 41–75.
- [2] S. Ayoob, A.K. Gupta, Fluoride in drinking water: a review on the status and stress effects, *Crit. Rev. Environ. Sci. Technol.* 36 (2006) 433–487.
- [3] S. Ayoob, A.K. Gupta, V.T. Bhat, A conceptual overview on sustainable technologies for the defluoridation of drinking water, *Crit. Rev. Environ. Sci. Technol.* 38 (2008) 401–470.
- [4] S. Meenakshi, N. Viswanathan, Identification of selective ion exchange resin for fluoride sorption, *J. Colloid Interface Sci.* 308 (2007) 438–450.
- [5] Y. Zhao, X. Li, L. Liu, F. Chen, Fluoride removal by Fe(III)-loaded ligand exchange cotton cellulose adsorbent from drinking water, *Carbohydr. Polym.* 72 (2008) 144–150.
- [6] N. Viswanathan, C. Sairam Sundaram, S. Meenakshi, Removal of fluoride from aqueous solution using protonated chitosan beads, *J. Hazard. Mater.* 161 (2009) 423–430.
- [7] B. Zhang, D.M. Poojary, A.C.G. Peng, Synthesis, characterization and amine intercalation behavior of zirconium *N*-(phosphonomethyl)iminodiacetic acid layered compounds, *Chem. Mater.* 8 (1996) 1333–1340.
- [8] C. Ferragina, P. Cafarelli, A. De Stefanis, R. Di Rocco, P. Giannoccaro, Synthesis and chemical–physical characterization of palladium and rhodium new materials derived from octadecyltrimethylammonium cationic surfactant intercalated into zirconium and titanium dihydrogen phosphate, *Mater. Res. Bull.* 36 (2001) 1799–1812.
- [9] P. Jiang, B. Pan, B. Pan, W. Zhang, Q. Zhang, A comparative study on lead sorption by amorphous and crystalline zirconium phosphates, *Colloids Surf., A* 322 (2008) 108–112.
- [10] A.P. Gupta, P.K. Varshney, Studies on tetracycline hydrochloride sorbed zirconium tungstophosphate; La(III)-selective chelating ion exchanger, *React. Funct. Polym.* 31 (1996) 111–116.
- [11] R. Niwas, U. Gupta, A.A. Khan, K.G. Varshney, The adsorption of phosphamidon on the surface of styrene supported zirconium (IV) tungstophosphate: a thermodynamic study, *Colloids Surf., A* 164 (2000) 115–119.
- [12] N. Viswanathan, S. Meenakshi, Enhanced fluoride sorption using La(III) incorporated carboxylated chitosan beads, *J. Colloid Interface Sci.* 322 (2008) 375–383.
- [13] C. Gerente, V.K.C. Lee, P. Le Cloirec, G. McKay, Application of chitosan for the removal of metals from wastewaters by adsorption-mechanisms and models review, *Crit. Rev. Environ. Sci. Technol.* 37 (2007) 41–127.
- [14] J. Zhang, R. Stanforth, Slow adsorption reaction between arsenic species and goethite (α -FeOOH): diffusion or heterogeneous surface reaction control, *Langmuir* 21 (2005) 2895–2901.
- [15] Fluoride Electrode Instruction Manual, Orion Research, USA, 2005.
- [16] APHA, Standard Methods for the Examination of Water and Waste Water, American Public Health Association, Washington, DC, 2005.
- [17] M.V. Lopez-Ramon, F. Stoeckli, C. Moreno-Castilla, F. Carrasco-Marin, On the characterization of acidic and basic surface sites on carbons by various techniques, *Carbon* 37 (1999) 1215–1221.
- [18] H.M.F. Freundlich, Über die adsorption in lösungen, *Z. Phys. Chem.* 57A (1906) 385–470.
- [19] I. Langmuir, The constitution and fundamental properties of solids and liquids, *J. Am. Chem. Soc.* 38 (1916) 2221–2295.
- [20] A.A. Khan, R.P. Singh, Adsorption thermodynamics of carbofuran on Sn (IV) arsenosilicate in H⁺, Na⁺ and Ca²⁺ forms, *Colloids Surf.* 24 (1987) 33–42.
- [21] S. Lagergren, Zur theorie der sogenannten adsorption gelöster stoffe, *K. Sven. Vetenskapsakad. Handl.* 24 (1898) 1–39.
- [22] Y.S. Ho, Second order kinetic model for the sorption of cadmium on to tree fern: a comparison of linear and non linear methods, *Water Res.* 40 (2006) 119–125.
- [23] M. Chanda, K.F. O'Driscoll, G.L. Rempel, Sorption of phenolics onto cross-linked poly (4-vinyl pyridine), *React. Polym.* 1 (1983) 281–293.
- [24] W.J. Weber, J.C. Morris, Equilibria and capacities for adsorption on carbon, *J. Sanitary Eng. Div.* 90 (1964) 79–91.
- [25] C. Sairam Sundaram, N. Viswanathan, S. Meenakshi, Fluoride sorption by nano-hydroxyapatite/chitin composite, *J. Hazard. Mater.* 172 (2009) 147–151.
- [26] C. Sairam Sundaram, N. Viswanathan, S. Meenakshi, Uptake of fluoride by nano-hydroxyapatite/chitosan, a bioinorganic composite, *Bioresour. Technol.* 99 (2008) 8226–8230.
- [27] C. Sairam Sundaram, N. Viswanathan, S. Meenakshi, Defluoridation chemistry of synthetic hydroxyapatite at nano scale: equilibrium and kinetic studies, *J. Hazard. Mater.* 155 (2008) 206–215.
- [28] N. Viswanathan, C. Sairam Sundaram, S. Meenakshi, Sorption behaviour of fluoride on carboxylated cross-linked chitosan beads, *Colloids Surf., B* 68 (2009) 48–54.