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Removal of Fluoride from Aqueous Media by Zirconium Modified Zeolite

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In this study, the fluoride adsorption potential of novel zirconium modified zeolite composite was explored. Batch adsorption experiments were conducted to study and optimize various operational parameters, such as adsorbent dose, contact time, pH, temperature and initial fluoride concentration. It was observed that the zirconium modified zeolite work effectively in neutral solution and showed a maximum adsorption rate of 97.62 % at an initial fluoride concentration of 10 μg/mL, it is much better than raw zeolite of 32.94 % and acid modified zeolite of 57.05 %. The experimental data fitted well into Freundlich adsorption isotherm and follows pseudo-second-order kinetics. Thermodynamic study suggests that fluoride adsorption on zirconium modified zeolite is reasonably spontaneous and an endothermic process. The nature and morphology of sorbents was characterized by using XRD, BET and SEM analysis. From the experimental results, it may be inferred that chemical modification enhances the fluoride removal efficiency of raw zeolite and zirconium modified zeolite works as an effective adsorbent for defluoridation of water.

Keywords: Defluoridation, Adsorption isotherm, Zeolite.

INTRODUCTION

Excessive intake of fluoride, mainly through drinking water, is a serious health hazard affecting humans worldwide[1]. World Health Organization and Ministry of Health in China have recommended a tolerance limit of 1.5 and 1.0 mg L^{-1}, respectively for fluoride in drinking water[2,3]. During recent past, several methods have been tried to remove F^- from water, namely chemical precipitation[4], electro-coagulation[5,6], electro-dialysis[7], reverse osmotic[8], adsorption[3,9], ion exchange[10,11]. Among these methods, adsorption is the most promising method for defluoridation of water due to ease of operation, lower cost and environment friendly. In recent years, researchers have devoted much attention to study the various low cost materials for cost effective defluoridation of water. Many low cost adsorbents have been tried for fluoride removal from water namely quick lime[12], kaolinite[13], laterite[14], spent bleach earth[15], activated alumina[16], montmorillonite[13,17], brick powder[18], fly ash[19], hydrated cement[20], zeolite[21], *etc.*

Since zeolite is a low-cost material with a porous structure and a large surface area widely available and easily processed and modified, it has been further studied in the present work. It has been shown that chemical conditioning using acid improved the surface area and porosity of raw zeolite. Because zeolites have negative surface charges at all pH values[9], they have better adsorption capacity to cations than anions. Nonetheless, their adsorption capacity for anions can be increased by modifying the zeolite surface with multivalent metallic cations such as Fe^{3+}, Al^{3+}, Mg^{2+}, La^{3+}, Mn^{4+} and Zr^{4+}.

Activated alumina has been fully studied[16,22,23], the easy dissolution of aluminum in treated water leads to a secondary pollution. The ability of magnesia to scavenge fluoride is limited because of the alkaline nature of the treated water[24]. Lanthanum oxide incorporated clay shows higher fluoride uptake, however, its cost and the possible toxicity of lanthana limit its use[25]. Manganese oxides have a high specific surface area, a micro-porous structure and a high adsorption capacity towards anions[3,26]. Iron oxide-based materials have been reported as showing good F^- removal performance as well as having favorable characteristics in terms of cost, environmental impact and chemical stability[27,28]. Zirconium oxide has been paid more attention in recent investigations due to its high binding affinity with F^- and acceptable cost[29,30]. To best of our knowledge from reviewing the literature, study on zirconium oxide supported on zeolite adsorbent has not yet been reported.

In this work, a new adsorbent, zirconium modified zeolite, was prepared by coating zirconium oxide on raw zeolite. The main aim of this study is to demonstrate the performance capacity of zirconium modified zeolite to adsorb fluoride from drinking water. A series of experiments such as pH, adsorbent dosage, contact time, temperature and initial fluoride concentration was carried out to investigate their effects on fluoride adsorption capacity of zirconium modified zeolite. The kinetics and isotherms of fluoride adsorption with zirconium modified zeolite were also studied.

EXPERIMENTAL

All chemicals used in the present study were of analytical reagent grade. Raw zeolite was procured from Gongyi Water Supply and Sewerage Equipment Factory in Henan. Zirconium oxychloride was purchased from Kelong Chemical Reagents in Chengdu. Sodium fluoride was purchased from Chengdu Chemical Reagents. A stock solution of fluoride was prepared by dissolving NaF in distilled water and working solution was obtained by appropriate dilutions of the stock solution.

Preparation of zirconium modified zeolite: Raw zeolite was washed with distilled water several times and dried out at room temperature. The desired particle size (mesh 20-40) of raw zeolite was obtained from sieve pumice, which had been grinded previously. The powder was then calcined at 450 °C for 2 h in muffle furnace. The calcined powder was mixed with hydrochloric acid (10 %) for 24 h and the hydrochloric acid level was higher than raw zeolite level about 1 cm. The solids were removed from solution and then dried at 100 °C. The dried mass was calcinated at 450 °C for 2 h to get the acid modified zeolite. 20 g acid modified zeolite was mixed with 300 mL of 0.15M zirconium oxychloride solution and the mixture was shaken for 2 h at 70 °C. After shaking, the above solution was transferred into a 250 mL beaker, the superfluous zirconium oxychloride solution dumped, the liquid level of surplus solution was higher than acid modified zeolite level about 0.5 cm, the remainder solvent was evaporated at 100 °C in oven. Dried mass was calcinated at 450 °C for 2 h. The calcined powder was cooled to room temperature and washed twice with distilled water until neutral. The material was dried out at 65 °C for 2 h and the step of modification was repeated for 2 times to get the zirconium modified zeolite, finally.

Polarography analysis and characterization: The concentration of fluoride ions was analyzed by polarography (JP-303) supplied by Chengdu Instrument Factory. The polarographic condition: the second order derivative linear sweep voltammetric peak currents (ip") was recorded in the potential range from -0.30 V to -1.30 V (*vs*. SCE) at room temperature, scanning rate and standing time was 500 mv s^{-1} and 8s, respectively[31].

The surface structure of raw zeolite, acid modified zeolite and zirconium modified zeolite particles was analyzed using a Hitachi, S300 scanning electron microscope (SEM) with Rigaku: DX-3 X-ray microanalysis. The applied current was 30 mA and the voltage was 15 kV. The scanning range of 2θ was set between 5° and 45°. The mean pore diameter, specific surface area and pore distribution were determined by Brunauer-Emmett-Teller (nitrogen sorption isotherm) methods, using a Micrometrics particle size analyzer (Quantachrome, NOVA2000).

Adsorption studies: 0.25g of sorbent was mixed with 25 mL of solution containing 40 mg L^{-1} as initial fluoride concentration. The mixture was shaken in a thermostatic shaker at a speed of 200 rpm at room temperature for 40 min. The residual F^- concentration in supernatant was analyzed after centrifuging and standing for 24 h. The effect of pH and temperature of the medium, contact time, adsorbent dose and initial fluoride concentrations on fluoride adsorption was studies for optimization.

The adsorption isotherm at pH 7 was studied by varying the initial fluoride concentration from 0 to 5000 mg L^{-1} at three different temperatures (20, 30 and 40 °C) for 60 min and keeping the mass of adsorbent as 0.25 g and the volume of solution as 25 mL. A kinetic study at pH 7 was carried out at different time intervals from 30 to 2160 min with initial fluoride concentration of 10, 20 and 40 mg L^{-1}. The above experiments were carried out at room temperature. The pH of solution was adjusted with 0.1M NaOH and 0.1M HCl.

RESULTS AND DISCUSSION

Characterization of zirconium modified zeolite adsorbents

X-ray diffraction analysis: The results of X-ray diffraction (XRD) spectra demonstrated that the raw zeolite is composed of zeolite (approximately 50 %), quartz, feldspar, $CaCO_3$. As can be seen from Fig. 1, XRD images are observed to be surface morphological change before and after the conditioned with acid. The peak at 2θ diffraction angle of 29.5 and 31.5° is observed due to the coating of ZrO_2.

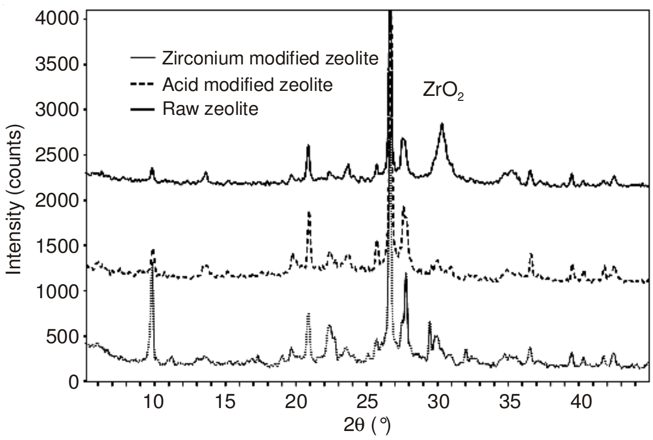

Fig. 1. Power X-ray diffraction patterns of raw zeolite, acid modified zeolite and zirconium modified zeolite

Scanning electron microscopy: As shown in Fig. 2a, raw zeolites has the typical clustered structure. However, the clustered structure has been great changed (Fig. 2b) after acid modification because of acid etching of $CaCO_3$ and impurities. Ordinary zeolites have poor acid accumulator fastnesses which result in the change of its framework. So the irregular second order intrapore could be generated due to acid corrosion of its framework and remove the silicon from framework, selectively. SEM images of zirconium modified zeolite were observed that a mass of irregular flaky ZrO_2 which is with upper crystallinity degree. The flaky ZrO_2 were around by some irregular mesopore and macropore, which could come from intercrystalline pores[32] between the flaky ZrO_2 (Fig. 2c).

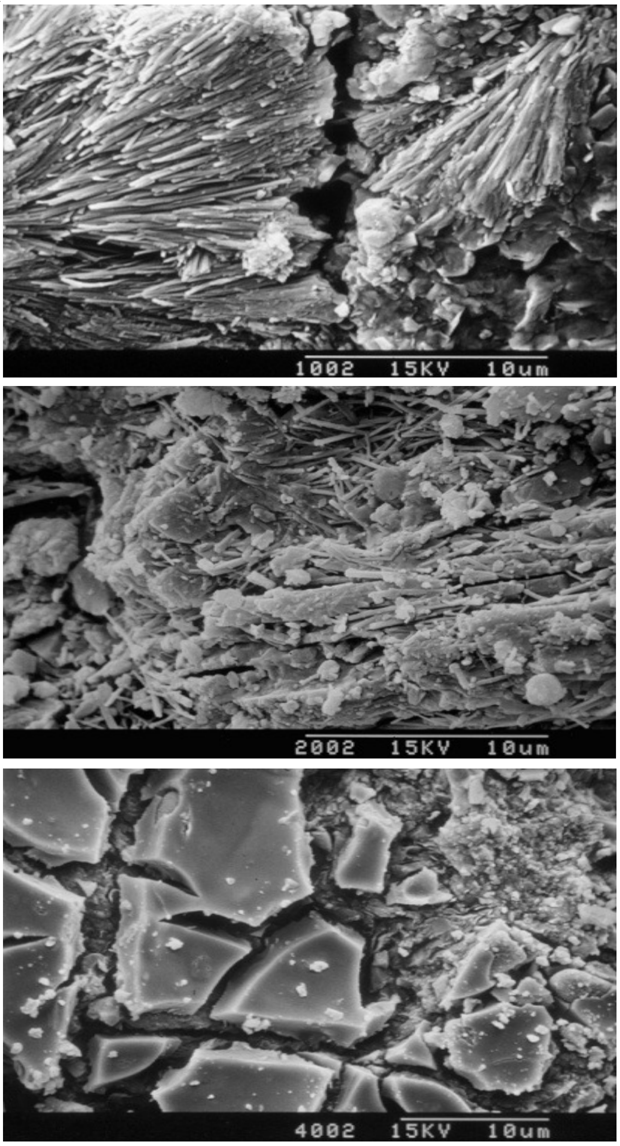

Fig. 2. Scanning electron microscopy photographs: (a) raw zeolite, (b) acid modified zeolite, (c) zirconium modified zeolite

Specific surface area and pore distribution: The BET-specific surface area and mean pore diameter of the raw zeolite, acid modified zeolite and zirconium modified zeolite were determined using the BET isotherm model. The specific surface area of raw zeolite, acid modified zeolite and zirconium modified zeolite were 35.569, 37.965 and 36.499 $m^2 g^{-1}$, respectively. The mean pore diameter of raw zeolite, acid modified zeolite and zirconium modified zeolite were 19.021, 18.987 and 18.744 nm, respectively. The specific surface area of raw zeolite was the smallest, perhaps it is the result of the blockage of its channels by clay, *etc*. However, the acid modified zeolite possesses the largest specific surface area for acid etching. The specific surface area of acid modified zeolite larger than that of zirconium modified zeolite, as the acid modified zeolite was modified with zirconium oxide. Due to modification, some of the main channels of the acid modified zeolite became obstructed by zirconium oxide; Therefore, the diffusion of N_2 into these channels was impeded and resulted in decreasing the specific surface area. The mean pore diameter of the acid modified zeolite decreased when compared with raw zeolite, as the raw zeolite become loose after acid treatment. The pore diameter of raw zeolite and zirconium modified zeolite was in the range of 0-100 and 0-30 nm. The change in pore size distribution reveals that zirconium oxide was reached the internal pore.

Adsorption behavior and possible mechanism of fluoride: The zirconium oxide coated on to the surface of zeolite can form $Zr(OH)_x^{4-x}$ (x = 1-4) in aqueous solution, which further reacts with fluoride ion by replacing hydroxide ions. This exchange of fluoride and hydroxide ions is due to their similar size/comparable ionic radius, while both are also iso-electronic in nature. However, the absorption rate of 32.94 % was observed by using raw zeolite which is due to the anion exchange capacity of raw zeolite.

The surface acquired positive charge at lower pH values and hence the fluoride sorption at this pH level was mainly due to electrostatic attraction between the positive surface and negatively charged fluoride ions and chemisorption dominated. As shown in Fig. 3, fluoride adsorption rate in zirconium modified zeolite decreased when the pH of solution increased from 2 to 6. In alkaline condition, the excessive amount of hydroxyl ions can compete for the active sites on adsorbent, result in the lower sorption capacity for F^-. The weak adsorption of fluoride at pH 12 reveals the aforementioned possible adsorption mechanism. Previous discussions confirm zirconium oxides and hydrous oxides determined the adsorbed amount of fluoride ions. Furthermore, during the adsorption progress, the equilibrium pH markedly increased, the most probable mechanism for F^- adsorption in different acidic condition is mainly as[33]:

$$\text{-ZrOH} + H^+ = \text{-ZrOH}_2^+ \quad (3)$$

$$\text{-ZrOH}_2^+ + F^- = \text{-ZrF} + H_2O \quad (4)$$

$$\text{-ZrF} + OH^- = \text{-ZrOH} + F^- \quad (5)$$

Adsorption of fluoride on zirconium modified zeolite

Effect of pH: The removal of fluoride ions from aqueous fluoride solution was highly dependent on the solution pH in many cases, as it altered the surface charge on the sorbents. The effect of pH on the fluoride adsorption capacity of zirconium modified zeolite was investigated over the pH range of 2-12 (Fig. 3). As seen from the figure, under alkaline conditions, the lowest amounts of fluoride were removed. The maximum adsorption capacity was recorded at pH 2 and the adsorption capacity at pH 7 is second to at pH 2. This figure also showed a gradual decreasing trend when the pH of solution increased from 7 to 12. The pH was optimized to be 7 for further experimental studies. Therefore prior pH adjustment is not required for effective removal of F^- in drinking water purification.

Effect of adsorbent dose: The minimum amount of adsorbent for maximum fluoride removal was determined by studying the effect of variation in adsorbent dose (0.005-0.1 g mL^{-1}) on fluoride removal efficiency (Fig. 4). It was observed that fluoride removal efficiency increased from 6.72 % to 51.10 % with increase in adsorbent dose. This increase in the fluoride removal efficiency with increase in adsorbent dose was obviously owing to the enhancement in the number of active sites available for adsorption of fluoride ions. In addition,

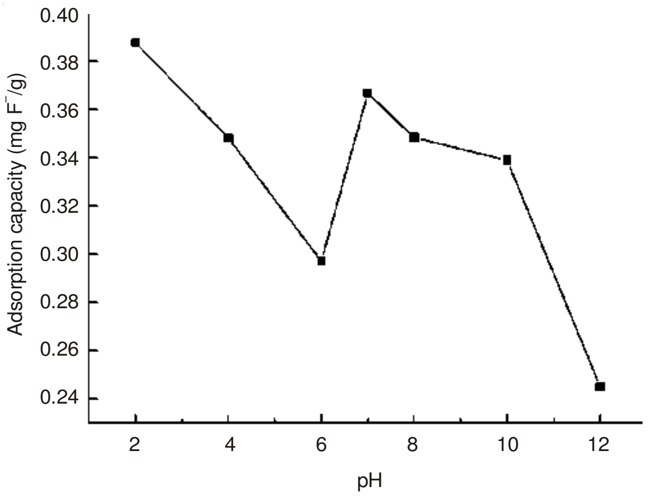

Fig. 3. Adsorption capacity of zirconium modified zeolite at different pH (adsorbent dose: 0.01 g mL^{-1}, initial concentration: 40 mg L^{-1}, contact time: 40 min, temperature: 30 °C)

the rate of fluoride adsorbed to zirconium modified zeolite increased slowly with the increasing in dosage of zirconium modified zeolite from 0.02 to 0.1 g mL^{-1}. Considering adsorption capacity and economy, 0.01 g mL^{-1} of zirconium modified zeolite was fixed as the optimum dose and the rest of the studies were performed at this optimum adsorbent dose.

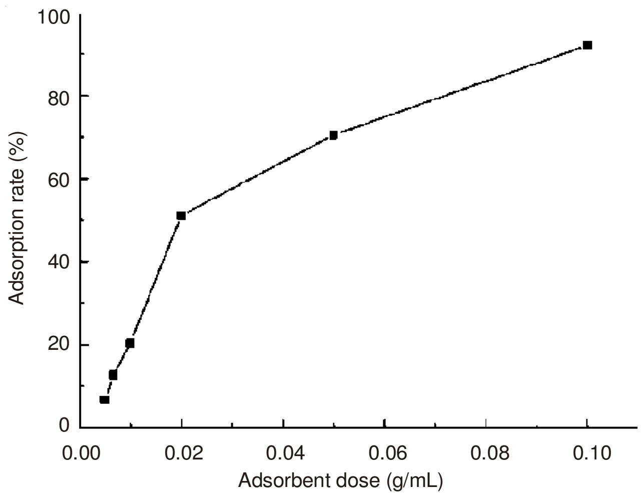

Fig. 4. Fluoride adsorption rate and adsorption capacity of zirconium modified zeolite for different adsorbent dose (contact time: 60 min, initial concentration: 40 mg L^{-1}, pH 7, temperature: 40 °C)

Effect of initial concentration: The effect of initial fluoride concentration on the adsorption capacity and adsorption rate of zirconium modified zeolite was studied (Fig. 5). It was observed that with increase in the initial fluoride concentration, F^- adsorption rate decreases, while the fluoride adsorption capacity increases. This decrease in F^- adsorption rate is obviously due to the availability of more fluoride ions in solution at higher fluoride concentration, which also indicates that the fluoride binding capacity of zirconium modified zeolite was almost exhausted. However, at low fluoride concentration, the ratio of surface active sites to total fluoride is high and therefore the interaction of F^- with the active sites on adsorbent surface was sufficient for efficient fluoride removal. In actual

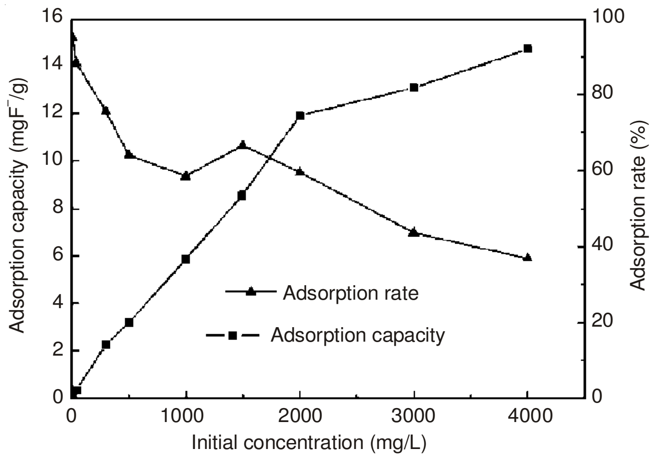

Fig. 5. Fluoride adsorption rate and adsorption capacity of zirconium modified zeolite for different initial concentration (adsorbent dose: 0.01 g mL^{-1}, contact time: 60 min, pH 7, temperature: 40 °C)

water treatment, the initial concentration of fluoride is normally below 40 mg L^{-1}. Therefore, 40 mg L^{-1} were selected for further experiments.

25 mL of 40 mg L^{-1} fluoride solution was mixed with 0.25 g adsorbents in neutral pH, the suspension was shaken for 60 min at 40 °C. At this optimum adsorption condition, the adsorption rate of zirconium modified zeolite is 97.62 %, which it is much better than raw zeolite (32.94 %) and acid modified zeolite (57.05 %).

Adsorption isotherm analysis: The Langmuir and Freundlich equation are generally used to describe the adsorption isotherm, which explain the specific relation between the concentration and amount of adsorbate adsorb on the surface of the adsorbent. Langmuir adsorption model is based on the assumption of surface homogeneity where all adsorption sites are equally available and with a monolayer surface coverage without interaction between adsorbed species[34]. Freundlich isotherm is based on the multilayer adsorption of adsorbate onto the heterogeneous adsorbent surface[35]. The linear equation of Langmuir and Freundlich adsorption isotherm is expressed as follows:

$$\frac{C_e}{q_e} = \frac{1}{k_L q_m} + \frac{1}{q_m} C_e \quad (6)$$

$$\log q_e = -\log k + \frac{1}{n} \log C_e \quad (7)$$

where, q_m is the amount of adsorbate at complete monolayer coverage (mg g^{-1}), which gives the maximum adsorption capacity of the adsorbent. q_e (mg g^{-1}) and C_e (mg L^{-1}) are the equilibrium adsorption capacity and concentration of adsorbate in solution, respectively. k_L (L mg^{-1}) is the equilibrium constant of adsorbent at equilibrium, which indicates the affinity of adsorbate toward adsorbent. The values of q_m and k_L were calculated from the slope and intercept of the linear plots of C_e/q_e *vs*. C_e. n and k (mg$^{1-(1/n)}$ L$^{1/n}$ g^{-1}) are Freundlich constants, which related to adsorption capacity and adsorption intensity, respectively. The values of k and n were obtained from the slope and intercept of the linear plot of log (q_e) *vs*. log (C_e). The isotherm parameters obtained from these models are given in Table-1. The applicability of a particular isotherm model is judged from the regression coefficient value (R).

TABLE-1
SUMMARY OF EQUILIBRIUM ISOTHERM PARAMETERS

Temp. (°C)	Freundlich isotherm			Langmuir isotherm		
	n	k(mg g^{-1}) (L $mg^{-1})^{1/n}$	R	q_m (mg g^{-1})	k_L (L mg^{-1})	R
20	1.435	13.366	0.994	21.739	1.045	0.913
30	1.318	16.331	0.985	23.810	1.235	0.959
40	1.245	21.577	0.994	28.571	0.898	0.987

From the results of Table-1, the Freundlich model fitted well with the isotherm data of fluoride adsorption onto adsorbent. It may be noted that the derived adsorption capacities (q_m = 28.57 mg g^{-1}) at 40 °C for zirconium modified zeolite is greater than the values reported for several other naturally occurring adsorbents *e.g.*, nano-hydroxyapatite/chitin (q_m = 6.993 mg g^{-1}, k_L = 0.116 L mg^{-1})[36], magnesium incorporated bentonite clay (q_m = 2.26 mg g^{-1}, k_L = 0.078 L mg^{-1})[37], aluminum-modified hydroxyapatite (q_m = 26.95 mg g^{-1}, k_L = 0.080 L mg^{-1})[38] and functionalize pumice stone (q_m = 41.65 mg g^{-1}, k_L = 0.078 L mg^{-1})[39,40]. The higher value of k_L (0.898 L mg^{-1}) indicates the strong affinity with F^- of zirconium modified zeolite, the adsorption process proceeds quite rapidly, even at low concentrations and the adsorption equilibrium achieved in a short time. In addition, the n value at different temperatures are higher than unity, which indicates that zirconium modified zeolite is an appropriate adsorbent and beneficial for the adsorption of fluoride from water. The value of q_m was increased with temperature confirms the adsorption process to be endothermic in nature.

Effect of temperature and thermodynamic feasibility of the process: The effect of temperature on adsorption was investigated at three different temperatures (20, 30 and 40 °C) and the results are given in Table-2. The adsorption rate of fluoride and adsorption capacity were found to increase with increase in temperature suggesting the endothermic nature of the sorption process.

TABLE-2
FLUORIDE ADSORPTION RATE AND ADSORPTION CAPACITY OF ZIRCONIUM MODIFIED ZEOLITE AT DIFFERENT TEMPERATURE (ADSORBENT DOSE: 0.01 g mL^{-1}, INITIAL CONCENTRATION 40 mg L^{-1}, pH 7 AND CONTACT TIME: 60 MIN)

Temperature (°C)	20	30	40
Adsorption rate (%)	77.36	82.57	89.16
q_e (× 10^3 mg g^{-1})	309.44	330.28	356.64

In order to evaluate the feasibility of adsorption process, thermodynamic parameters were studied. The standard free energy change ΔG^0 was calculated following eqn. 8, where ΔG^0 is the free energy of sorption (kJ mol^{-1}), T is the temperature in Kelvin (K), R is the universal gas constant (8.314 J mol^{-1} K^{-1}) and K is the sorption equilibrium constant. The sorption equilibrium constant K_0 for the sorption reaction was determined from the slope of the linear plot of ln(q_e/C_e) *vs*. C_e at different temperatures and extrapolating to zero C_e according to method suggested by Khan and Singh[41]. The sorption equilibrium constant K can be expressed in terms of ΔH^0 and ΔS^0 as a function of temperature and is using the eqn. 9, where ΔH^0 is the standard enthalpy change (kJ mol^{-1}) and ΔS^0 is the standard entropy change (kJ mol^{-1} K^{-1}). The values of ΔH^0 and ΔS^0 can be obtained from the slope and intercept of the van't Hoff's plot of ln(K) *vs*. 1/T as shown in Table-3.

TABLE-3
THERMODYNAMIC PARAMETERS FOR SORPTION OF FLUORIDE ON ZIRCONIUM MODIFIED ZEOLITE AT DIFFERENT TEMPERATURES

T (K)	K	ΔG^0 (kJ mol^{-1})	ΔH^0 (kJ mol^{-1})	ΔS^0 (kJ K^{-1} mol^{-1})
293	3.001	–2.676		
303	4.42	–3.744	35.226	0.129
313	7.57	–5.268		

$$\Delta G^0 = -RT \ln K \quad (8)$$

$$\ln K = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad (9)$$

The thermodynamic treatment of the sorption data of the sorbent indicated that ΔG^0 values were negative at all temperatures investigated. The negative values of ΔG^0 confirm the spontaneous nature of sorption of fluoride ion by sorbent. The positive value of ΔS^0 indicates increased randomness at the interface of zirconium modified zeolite solution during the adsorption process. The positive value of ΔH^0 for fluoride sorption confirms the endothermic nature of sorption process. The value of ΔH^0 is greater than 35 kJ mol^{-1} confirmed the hypothesis of chemisorption of fluoride onto zirconium modified zeolite.

Adsorption kinetic studies: The rate of adsorption of fluoride on zirconium modified zeolite was determined by studying the adsorption kinetics at different initial fluoride concentration of 10, 20 and 40 mg L^{-1} at optimum adsorbent dose. As can be seen in Fig. 6, it was observed that fluoride removal increased with the lapse of time and the fluoride adsorption rate was initially rapid after which, the rate slowed down as the equilibrium approached.

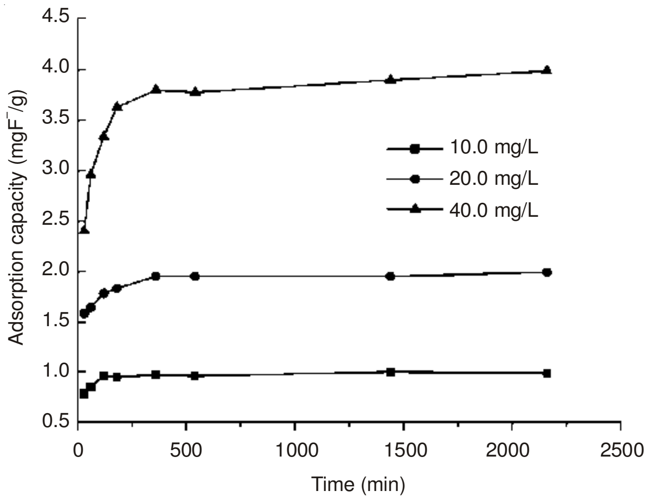

Fig. 6. Kinetics curves on different initial concentration (adsorbent dose: 0.01 g mL^{-1}, pH 7, temperature: 40 °C)

The reaction-based models, which include Bangham, pseudo-first-order[39], pseudo-second-order models[42], were applied to test the fitness of experimental data. These models are represented mathematically as follows:

$$\ln\frac{q_e}{q_e - q_t} = Kt^n \quad (10)$$

$$\log(q_e - q_t) = \log q_e - k_{ad}\frac{t}{2.303} \quad (11)$$

$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{1}{q_e}t \quad (12)$$

where q_e (mg g^{-1}) and q_t (mg g^{-1}) are the adsorption capacity (mg g^{-1}) at equilibrium and time t, respectively; n is the constant of Bangham's equation. K (min^{-n}), k_{ad} (min^{-1}) and k (g mg^{-1} min^{-1}) is the equilibrium rate constant of Bangham sorption, pseudo-first-order sorption and pseudo-second-order sorption. The adsorption kinetic model parameters obtained from the above equations are given in Table-4.

Table-4 clearly shows that the adsorption of fluoride onto the zirconium modified zeolite obeys the pseudo-second-order model ($R^2 \geq 0.995$). Also, the adsorption capacities calculated by the model are close to those results obtained from experiments (Fig. 6). In addition, the fitness of experimental data to the pseudo-second-order model, the basic assumption in the model, implies that the chemisorption plays a major role and likely controls the adsorption process.

To evaluate the rate-limiting of the adsorption of fluoride onto zirconium modified zeolite, the possibility of intra-particle diffusion was explored since the particles were vigorously agitated during the experiment. The data were analyzed by the intra-particle diffusion model[43] and the linear form of the equation is represented by:

$$q_t = k_t t^{0.5} \quad (13)$$

where k_t is the intra-particle rate constant (mg g^{-1} $min^{-0.5}$). Fig. 7 shows a plot of the mass of fluoride adsorbed per unit mass of zirconium modified zeolite *versus* the square root of contact time. The plot should be linear if intraparticle diffusion is involved in the adsorption process. Moreover, the line would pass through the origin if the intraparticle diffusion is the only rate-controlling step[43].

As can be seen from Fig. 7, the data points could be connected by three straight lines. The first linear portion represents the boundary layer diffusion or macropore diffusion, the second linear portion attributes to intra-particle diffusion. The third portion is attributed to the final equilibrium stage, during which intra-particle diffusion started to slow down due to extremely low solute concentrations in the solution. The extrapolations of the first linear portions of the curves do not pass through the origin; This indicates that mechanism of removal of fluoride onto zirconium modified zeolite is complex. The surface adsorption as well as intra-particle diffusion contributes to the rate-determining step.

Effects of coexisting ions and adsorption of fluoride from water samples: Fluoride contaminated ground water usually contains several other ions, which can compete with fluoride during the adsorption process. The effect of coexisting ions and the potential application of zirconium modified zeolite were tested in natural ground water samples collected from Yanan in Sichuan. The pH of this contaminated water was 7.12, compositions of the water samples are showed in Table-5.

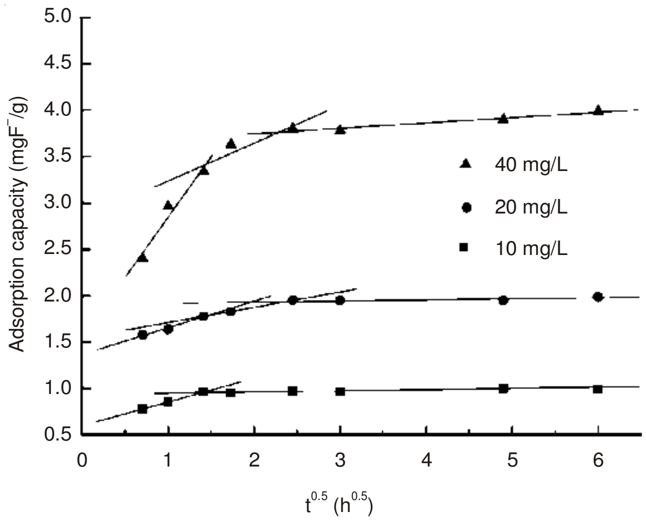

Fig. 7. Intra-particle diffusion rate plot of different initial concentration (adsorbent dose: 0.01 g mL^{-1}, pH 7, temperature: 40 °C)

TABLE-5
CONTENT OF MAIN ION IN WATER SAMPLE

	K^+ + Na^+	Ca^{2+}	Mg^{2+}	Total cation	Cl^-	SO_4^{2-}	HCO_3^-	Total anion
C(μg/mL)	412.20	6.01	3.65	421.9	148.90	33.44	829.80	1021.1

The removal efficiency of fluoride in field water was found to be slightly decreased as compared to synthetic water (Table-6). This may be due to the presence of various competing ions in field water. It also suggests that the common ions in drinking water at its normal content have a slight effect on adsorption capacity and adsorption rate. At an adsorbent dose of 0.01 g L^{-1}, zirconium modified zeolite has reduced the fluoride concentration in ground water from 11.61 to 0.594 mg L^{-1}, which is below WHO maximum permissible limit for fluoride. The results of this study indicated that zirconium modified

TABLE-6
RESULT OF ZIRCONIUM MODIFIED ZEOLITE USED IN NATURAL WATER SAMPLE

Parameters	Distilled water	Natural water samples
C_0 (mg L^{-1})	11.85	11.61
C ($\times 10^{-1}$ mg L^{-1})	4.47	5.94
q_e ($\times 10^{-3}$ mg g^{-1})	114.24	113.27
Adsorption rate (%)	96.24	95.02

TABLE-4
PARAMETERS OF BANGHAM MODEL, PSEUDO-FIRST-ORDER MODEL AND PSEUDO-SECOND-ORDER MODEL

C_0 (mg L^{-1})	Bangham model				Pseudo-first-order model			Pseudo-second-order model		
	q_e (mg g^{-1})	n	K min^{-n}	R^2	q_e (mg g^{-1})	K_{ad} (min^{-1})	R^2	q_e (mg g^{-1})	K (g $mg^{-1}min^{-1}$)	R^2
10	0.985	0.463	0.321	0.835	0.965	0.050	0.817	0.99	1.209	0.998
20	1.998	0.293	0.555	0.935	1.891	0.053	0.583	0.199	0.400	0.998
40	3.919	0.520	0.164	0.896	3.767	0.029	0.884	0.401	0.106	0.998

zeolite is a low-cost and efficient adsorbent that can be used for the elimination of excess fluoride from water.

Conclusion

The chemical modification of raw zeolite with zirconium oxide results in a significant enhancement in its fluoride removal efficiency. It was found that the adsorption conditions (at neutral pH and near room temperature) are mild and no secondary pollution was induced by adsorption process. Adsorption isotherm and adsorption kinetics indicate that the adsorbent has a strong affinity to fluoride and adsorption equilibrium fit with Freundlich isotherm, it is suggested that the adsorption is a chemical adsorption. The ΔG^0 and ΔH^0 values suggest that the adsorption of fluoride by this adsorbent is a spontaneous process and endothermic in nature. Various common ions at their normal content in drinking water have a slightly effect on adsorption rate. The results of this study indicated that zirconium modified zeolite is a low-cost and efficient adsorbent that can be used for the elimination of excess fluoride from water.

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