Biogenic nanozirconium in hydrogel beads for fluoride removal: equilibrium, thermodynamic and kinetic studies

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In the present research work, removal of fluoride from aqueous solution using fenugreek leaf mediated Zr nanoparticle entrapped in calcium alginate beads has been attempted. The adsorption study for removal of fluoride from aqueous solution of defined concentrations has been carried out in batch mode followed by its estimation using ion-chromatography. Synthesized Zr nanoparticles are subjected to various analyses e.g. SEM, TEM, SAED EDAX and FTIR, revealing zirconium an integral component. The adsorption capacity of Zr entrapped calcium alginate beads for fluoride is found to be 90.90 mg/g. The Langmuir isotherm model best fits on equilibrium data since it provides higher R^2 value than Freundlich model similarly, pseudo-second order kinetic model could better explain adsorption kinetic in comparison to pseudo first order model by presenting better correlation coefficient. The overall study suggests that Zr nanoparticles entrapped in alginate beads could be a better candidate for removal of fluoride from aqueous solution.

Fluoride is considered to be essential elements as it is beneficial to human health to the acceptable limit but its high concentration consumption causes deterioration to human health. It is abundantly found in a wide variety of minerals, including fluorspar, rock phosphate, etc [1]. The conventional method for defluoridation of drinking water is liming and the accompanying precipitation of fluorite [2]. Adsorption method is cheap as well as a cost-effective method for the removal of fluoride. The basic principle on which it works is that the fluoride or component to be adsorbed is transported by diffusion from the bulk phase to the solid surface where it is bound at the surface or interface between two phases by either chemical or physical forces [3]. Metal oxides such as titania [4], alumina [5], magnesium-incorporated hydroxyapatite [6] and zirconia (ZrO_2)[7] have been demonstrated to be effective materials for the selective separation of anions from aqueous solutions. The present work explores Zr nanoparticles entrapped in alginate bead as a defluoridating agent.

Experimental Section

Synthesis of Zr nanoparticles and beads preparation

Fenugreek leaves (5 g) was homogenized mechanically in 20 mL of Tris. Cl (20 mM, *p*H 7.5) followed by centrifugation at 10,000 rpm for 5 min at 4°C. The aqueous supernatant was used as a precursor for the synthesis of Zr nanoparticles. Zirconium oxychloride solution (50 mM, 50 mL) was prepared in distilled water, in a clean 250 mL flask and placed it on a magnetic stirrer. The fenugreek extract was added dropwise in the solution followed by its incubation at 37°C at room temperature. The absorption maximum of was determined by measuring the optical density of the colloidal solution from wavelength 350 to 700 nm as described previously using UV-Vis spectrophotometer. Na-alginate solution (5%, 20 mL) was mixed with 10 mL colloidal solution of Zr nanoparticles synthesized using fenugreek leaf extract. This solution was slowly added dropwise in 100 mL, 0.3 M $CaCl_2$ followed by its incubation for 24 hr at room temperature for hardening of beads. Prepared beads were washed thoroughly with distilled water for removal of other contaminants.

Characterization of synthesized nanoparticles

SEM, TEM, SAED, EDAX, and FT-IR studies were carried out to study morphology and chemical constituent of the synthesized nanoparticle. The dried powder of synthesized nanoparticle was subjected to elemental analysis using a scanning electron microscope (Philips, Netherlands) equipped with

Energy Dispersive X-ray System EDAX XL-30, operating at 15-25 KV. A thin film of the sample was prepared on a carbon-coated copper grid and subjected to transmission electron microscope (Techni 20, Philips, Holland) for particle shape and size analysis. The dried powder was used for FT-IR spectrometer (Perkin-Elmer, Spectrum GX, USA) operating at wave number ranging from 400-4000 cm^{-1} with a resolution of 0.15 cm^{-1} to determine the functional groups of the fenugreek leaf extract that might be involved in the particles formation process.

Estimation of fluoride

The concentration of fluoride in the solutions was determined by ion exchange chromatography (Metrohm Eco IC, Switzerland). A calibration curve was obtained using NaF standard solutions with different fluoride concentrations ranging from 0.2 to 2 mg/L.

Adsorption study

The batch study was performed to find out the adsorption capacity of the synthesized nanoparticle. The adsorption experiment was initiated by adding 0.25 to 2g of synthesized nanoparticles in 50 mL of 25 to 200 mg/L fluoride solution. The flask was placed onto a magnetic stirrer until equilibrium time reached. A small fraction of the sample was collected at different time interval followed by its filtration using 0.2 µm syringe filter. The optimization for maximum adsorption of fluoride was evaluated at contact time 5, 10, 15, 30, 45 and 60 min. The percentage sorption of F ions was calculated by the following equation:

$$\text{Sorption } \% = \frac{(C_i - C_t)}{C_i} \times 100 \qquad \dots (1)$$

The adsorption capacity is expressed as the number of F ions adsorbed per gram of adsorbent (mg/g) and was calculated as follows:

$$q_e\left(\frac{mg}{g}\right) = \frac{(C_i - C_t)\text{V}}{\text{M}} \qquad \dots (2)$$

where C_i and C_f are the initial and final concentrations of F ions in the aqueous solution (mg/L), respectively. V is the volume (L) of test solution and M is the mass of Zr nano-adsorbent (g) used. After completion, desorption was carried out by treating Zr nanoparticles with 20 ml of 0.05 M NaOH, 0.1 M NaOH, 0.15 M NaOH, and 0.2 M NaOH followed by extensive washing of beads using deionized water. All the chemicals used in this experiment were procured from Sigma Chemicals Co. (St. Louis, USA) unless mentioned otherwise.

Results and Discussion

UV–Vis spectroscopy

The colloidal solution exhibited absorption maxima at 410 nm. Initially, the colloidal solution appeared colourless but after an incubation period of 48 h, it turned to yellowish green. The building of absorbing maximum at 410 nm clearly indicates the gradual formation of particles during the incubation period. In the study by Joo *et al.*[8], the UV-Vis absorption spectrum of 4 nm sized zirconia nanoparticles exhibited a strong absorption starting at around 270 nm. Prasad *et al.*[9] in their study found absorbance maxima at 420 nm. The maximum absorbance at 410 nm clearly indicates the gradual formation of particles during the incubation period.

TEM and SAED study

The TEM analysis of colloidal solution indicated the formation of polydispersed Zr nanoparticles of size ranges from 62-80 nm (Fig. 1a). The selected area electron diffraction (SAED) pattern of synthesized Zr nanoparticles revealed that materials were crystalline in nature (Fig. 1b).

SEM and EDAX analysis

SEM analysis of beads of calcium alginate containing fenugreek stabilized Zr nanoparticles revealed that the surface of beads was smooth in nature. The image clearly reveals the porosity and surface texture, which provide the adsorbents with large surface areas and high adsorption capacity. Elemental compositions of synthesized nanoparticle after adsorption were determined using EDAX analysis. The analysis revealed the highest proportion of F (41%) in nanoparticles followed by sodium (36%), carbon (17%), oxygen (15%) and Zr (2%) and calcium (4%).

FTIR analysis

FT-IR analysis provides a presumptive idea of interaction between a functional group of chemical constituents of leaf extract and metal ions, leading to the formation and stabilization of Zr nanoparticle. The analysis revealed the presence of various functional groups in the plant extract (Fig. 2), which may possibly influence the reduction process and stabilization of nanoparticles. The shift in peak located around 3438.75 can be assigned as the involvement of
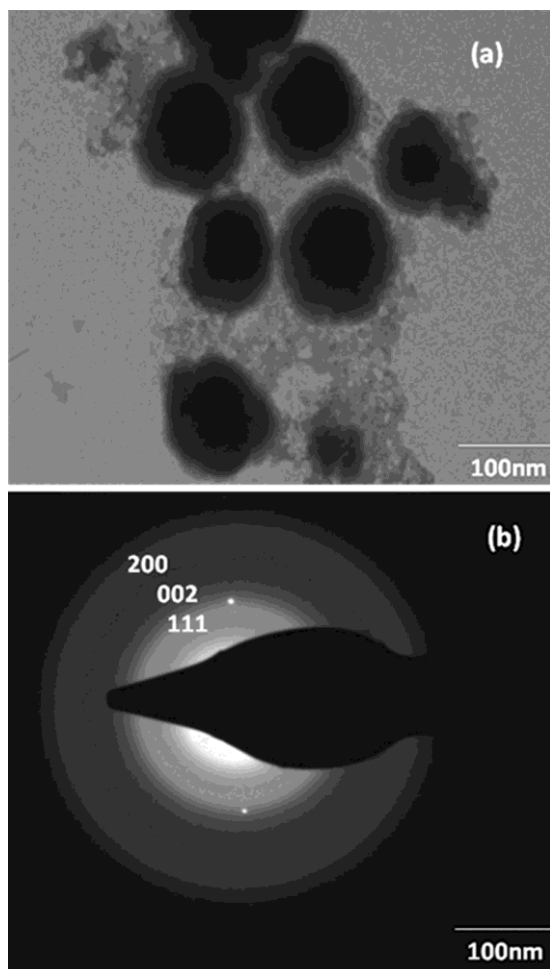
Fig. 1 — (a) TEM image of synthesized nanoparticles and (b) SAED showing diffraction pattern.

the O-H group (of alcohol)[10] in the formation of Zr nanoparticles. The adsorption peaks located at 1631.00 and 1577.01 in a wave range of 1800-1500 can be assigned as peaks due to the presence and involvement of C=O, C=N, and C=C [11]. The peaks around 1300 and 1200 are attributed to the stretching vibration of a single bond between C-O[12]. The peaks around 1200 and 1000 may be due to stretching and vibration between N-H[13].

Effect of *p*H, contact time and biomass doses

The adsorption of F ion was maximum at *p*H 7 where 92.05% of fluoride has been removed from the aqueous solution (Fig. 3a). However, in alkaline condition i.e. at *p*H 9.5, sorption was lower at 72.20%. In earlier studies, neutral *p*H was found to be most favorable for defluoridation as it gave 78.56mg/g of adsorption capacity[14]. The results are found to be similar with many other workers but were not in agreement with Wu and coworkers[15] Bansiwal and colleague [16] and He and coworkers [17]. Effect of contact time on adsorption of F ion was studied with Zr nanoparticles doses of 2g and fluoride solution of 200 mg/L at 28°C (Fig. 3b). The maximum sorption of F ion was observed after mixing sorbate and sorbent for a period of 45 min. The pattern for absorption of F ion at a different dose of Zr indicated a little change in sorption of analyte upon an increase in the amount of biomass beyond 2 g (Fig. 3c). Maximum sorption occurred when 2g of the Zr was subjected to sorption studies. Similarly, an increase in
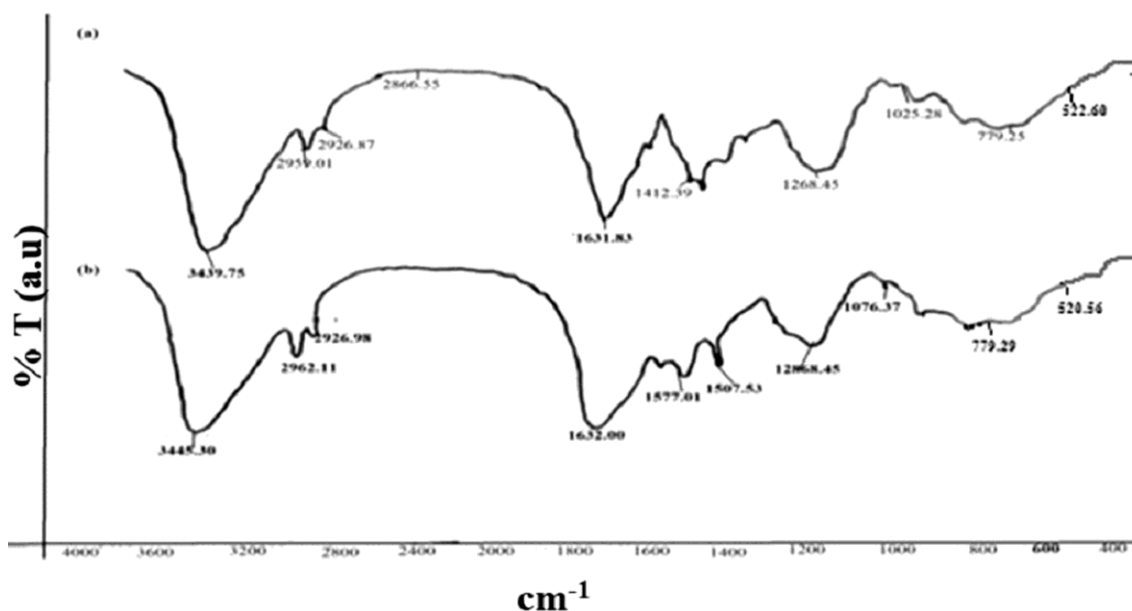

Fig. 2 — FT-IR spectra of untreated extract: (a) and Zr treated fenugreek leaf extract: (b).
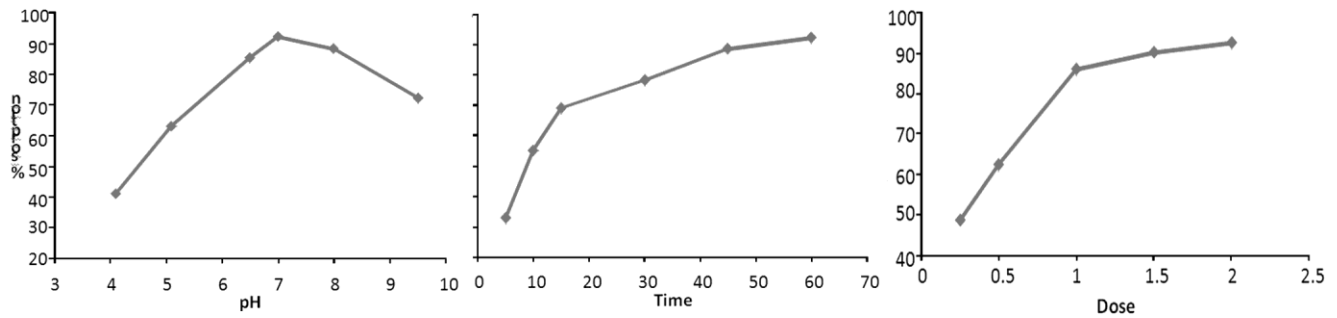
Fig. 3 — Effect of pH (a), effect of contact time (b) on adsorption of fluoride onto Zr nanoparticles (F⁻, 200 mg/L, sorbate concentration: 2g/L at 30°C) composite. Effect of biomass doses (c) for removal efficiency.

F ion concentration to more than 200 mg/L, when biomass doses were 2g, did not enhance overall sorption in batch sorption model.

Adsorption isotherms

The sorption isotherms were investigated using two equilibrium models namely the Langmuir and Freundlich isotherm models. The Langmuir model assumes that the uptake of metal ions on to a solid is a monolayer adsorption process, without any interaction between sorbed ions. A linear form of Langmuir isotherm can be defined according to the following formula:

$$\frac{1}{Q_e} = \frac{1}{K_L Q_m C_e} + \frac{1}{Q_m} \qquad \text{... (3)}$$

where Q_e is the adsorbate concentration on the adsorbent (mg/g), C_e is the equilibrium concentration of adsorbate in the solution (mg/l), Q_m is the monolayer sorption capacity of the adsorbent (mg/g) and K_L is the Langmuir sorption constant (L/mg), relating the free energy of sorption. Langmuir isotherm was obtained by plotting $1/Q_e$ Vs. $1/C_e$ values, which showed a linear relationship between two (Fig. 4a). The coefficients of determination (R^2) were found to be 0.994 for F ion sorption. The maximum sorption capacity (Q_m) of Zr nanoparticles was found to be 90.9mg/g, while K_L value was calculated as 0.003L/mg for F ion sorption. He et al [18] has found the maximum adsorption capacity of 60.65 mg/g at Zr based nanoparticles. The Freundlich model assumes a heterogeneous adsorption surface and active sites with a different energy. This isotherm can be explained by the following formula:

$$Log q_e = Log K_f + \frac{1}{n} Log c_e \qquad \text{... (4)}$$

where K_f is a constant relating the sorption capacity and 1/n is an empirical parameter relating to sorption
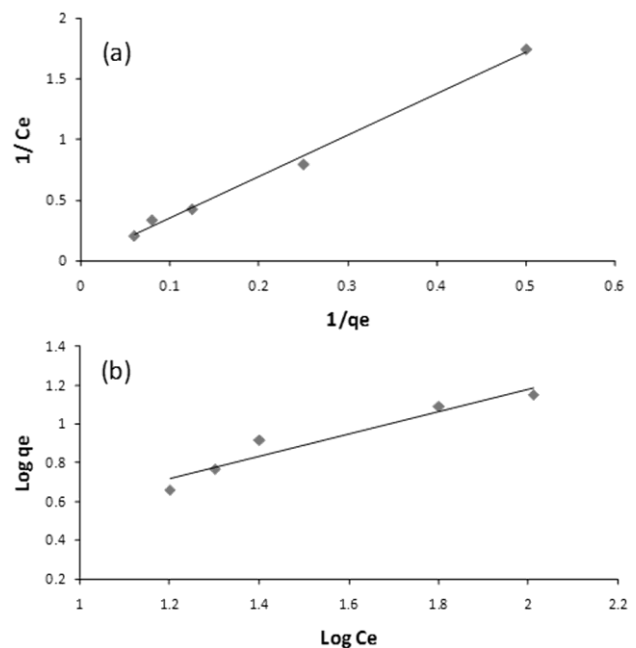

Fig. 4 — Langmuir (a) and Freundlich (b) isotherm for adsorption of fluoride on synthesized fenugreek leaf based nanoparticles

intensity which varies with the heterogeneity of the material. A Freundlich isotherm was obtained by plotting Log q_e Vs. Log C_e values, which showed a linear relationship between two (fig 4b). Values of K_f and $1/n$ were found to be 1.031 and 0.57 for F ion sorption. The 1/n value, between 0 and 1 indicates that the sorption onto the sorbent was favourable at studied conditions with R^2 value 0.925. These results suggested that the Freundlich model was not able to describe the relationship between the amounts of sorbed ions adequately to their equilibrium concentration in the solution. The Langmuir isotherm model best fitted the equilibrium data since it presented a higher R^2 value than the Freundlich model (Table 1).

Adsorption kinetic models

The Pseudo-first order and Pseudo-second order kinetic models were used to analyze the sorption rate

Table 1 — Comperative values of different isotherm parameter

Langmuir isotherm		Freundlich isotherm	
Q_m (mg/g)	90.9	K_f (L/mg)	1.031
R^2 value	0.994	R^2 Value	0.925
K_L (L/mg)	0.003	1/n Value	0.575

F ions on to Zr nanoparticles entrapped beads. The pseudo-first order rate equation is given as:

$$Log(q_e - q_t) = \frac{Log q_e - k_t t}{2.303} \qquad \text{... (5)}$$

where q_e (mg/g) is the amount of fluoride sorbed at equilibrium, q_t is the amount of fluoride sorbed at any time (mg/g) and k_1 is the rate constant of the equation (min^{-1}). The sorption rate constant k_1 can be can be determined experimentally by plotting, log (q_e-q_t) versus t Experimental data were also tested by pseudo-second-order equation:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \left(\frac{1}{q_e}\right) t \qquad \text{... (6)}$$

where k_2 is the equilibrium rate constant (g/mg/min). The values of the correlation coefficient of the pseudo-second-order model (Fig. 5a) was found to be 0.985 which is higher than the pseudo-first-order model i.e. 0.945 (Fig. 5b). Compared to the pseudo-first order equation, the pseudo-second-order model can explain the sorption kinetic behaviour of F ion on to Zr composite with a good correlation coefficient. In the study by Teutli et al.[19] adsorption kinetic data were best fitted on pseudo-second-order kinetic (Table 2).

Adsorption thermodynamics and desorption efficiency

Thermodynamic behavior of the sorption of F ions onto Zr including the change in free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) has been studied. The change in free energy (ΔG°) was calculated from the following equations:

$$\Delta G^o = -RTInK_D \qquad \text{... (7)}$$

where, R is the universal gas constant (8.314 J/mol K), T is temperature (K) and K_D (q_e/C_e) is the distribution coefficient [20]. The enthalpy (ΔH°) and entropy (ΔS°) parameters were estimated from the following equation:

$$InK_D = \frac{\Delta S°}{T} - \frac{\Delta H°}{T} \qquad \text{... (8)}$$

The ΔH° and ΔS° were calculated from the slope and intercept of the plot of ln K_D versus 1/T yields and shown in (Fig. 6). Gibbs free energy change

Table 2 — Kinetic parameter for sorption of F⁻ ion onto Zr nanoparticles composite

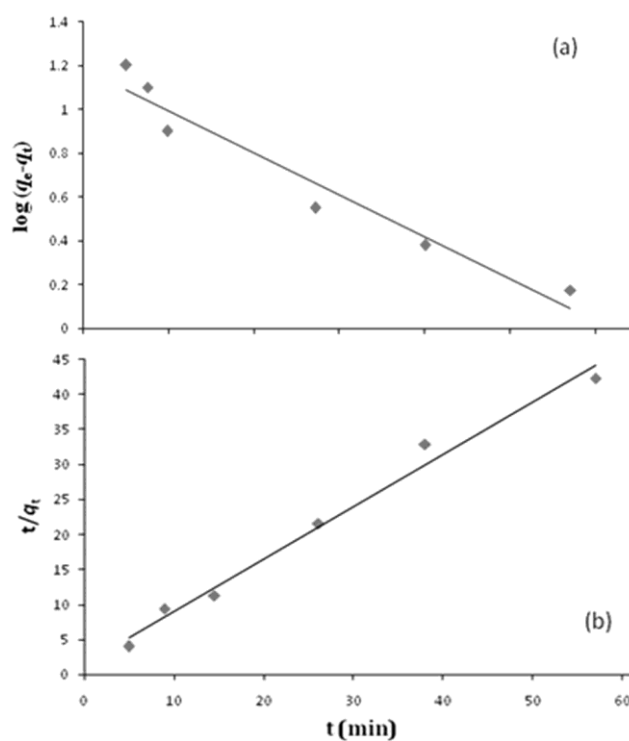| F- Adsorption	Pseudo First Order Reaction	Pseudo Second Order Reaction
Rate constant (min^{-1})	K_1=0.043	K_2=0.34
R^2 value	0.945	0.988

Fig. 5 — Adsorption kinetic models for F⁻ ion uptake (a) pseudo-first-order model for F⁻, (7b) pseudo-second-order model for F⁻ ions.
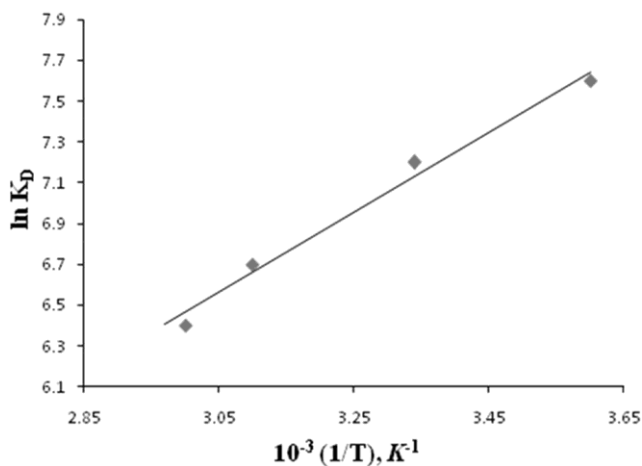

Fig. 6 — Plot of ln K_D Vs. 1/T for the estimation of thermodynamic parameters for sorption of F⁻ ions on to Zr nanoparticles.

($\Delta G°$) was found to be -19.71, -19.01, -17.15 and −17.01 kJ/mol at 20, 30, 40 and 50°C, respectively. The negative $\Delta G°$ values indicated thermodynamically feasible and spontaneous nature of the sorption. The decrease in $\Delta G°$ values with increase in temperature suggested a lesser feasibility of sorption at high temperatures. The enthalpy of biosorption $\Delta H°$ parameter was found to be −28.41 kJ/mol for F ion sorption. The negative $\Delta H°$ indicates the exothermic nature of sorption at 20 to 50°C [21]. The enthalpy or the heat of sorption ranging from 2.1 to 20.9 KJ/mol corresponds to physical sorption whereas ranging from 20.9 to 418 KJ/mol is regarded as chemical sorption. Therefore the $\Delta H°$ value suggests that the sorption process of F ion occurred due to chemisorptions. The negative $\Delta S°$ (−33.12 J/mol) value suggested a decrease in the randomness at the solid/solution interface during the sorption process. The highest recovery was found to be 98.96, 98.65, 98.29, 97.96, 97.61, 97.36, 97.08, 96.89, 96.32 and 95.81% in 10 cycles of sorption and desorption process using 0.1 M NaOH.

Higher concentration of NaOH for stripping F ions from Zr nanoparticles showed similar results suggesting that the optimum strength of NaOH solution for desorption was 0.1 M.

Conclusion

Leaf extract of fenugreek was used for the synthesis of Zr nanoparticles. The colloidal solution of organically capped, polydispersed Zr nanoparticles of 62-80 nm showed UV-Vis absorption maximum at 410 nm. FT-IR analysis indicated the involvement of functional groups (−OH, −NH, −C=O, −C=N −C=C) during synthesis processes. EDAX analysis revealed the presence of fluoride onto Zr nanoparticles entrapped in calcium alginate beads after adsorption study. The sorption capacity of synthesized green Zr nanoparticles composite was 90.90 mg/g at optimal experimental conditions. The sorption pattern fitted well with the Langmuir model and followed pseudo-second-order kinetics. The negative $\Delta G°$ values indicated thermodynamically feasible and spontaneous nature of the sorption. . The negative $\Delta H°$ indicates the exothermic nature of sorption. $\Delta H°$ value suggests that the sorption process of F ion occurred due to

chemisorptions. Desorption and reuse of Zr nanoparticles for fluoride removal further suggests its potential use as a filtration system for removal of fluoride contamination from aqueous solution. This low cost composite can be used for the removal of fluoride from contaminated water.

Acknowledgement

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