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NOVEL HYBRID SORBENT FOR THE REMOVAL OF FLUORIDE FROM DRINKING WATER

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Abstract - A novel zirconium(IV)-ethylenediamine (ZrEDA) hybrid material was prepared by using sol-gel method. The material was characterized by FTIR, SEM, and XRD. This hybrid material was tested for removal of fluoride from aqueous solution with variation of solution parameters. The extent of fluoride removal was more than 99% and fluoride adsorption equilibrium was attained in 14 minutes time period. The adsorption follows a pseudo second order kinetics with theoretical adsorption capacity ($q_{e,cal}$) and experimental adsorption capacity ($q_{e,exp}$) values found to be very close to each other. The adsorption isotherms were also evaluated and compared for six different error functions. The value of thermodynamic parameter ΔH indicated an endothermic adsorption process and the negative value of ΔG shows the feasibility and spontaneity of material-anion interaction. The adsorbed fluoride could easily be desorbed from the material by using 0.1 M NaOH solution. Further, the regenerated material was tested up to 10th consecutive cycles of operation without significance loss of adsorption efficiency.

Keywords: fluoride; adsorption; zirconium; hybrid material

1. Introduction

In recent years considerable attention has been devoted to develop cost effective new adsorbents for the removal of fluoride from drinking water and waste water (Sujana et al., 2009). Fluoride is a persistent, non-degradable pollutant. Presence of fluoride in drinking water in exceeding limits at various places all over the world has been reported by various researchers (Ayoob & Gupta, 2009). Fluoride could disperse to the environment through various mediums such as water, food, and several other engineering processes (Thakre et al., 2010; Alagumuthu & Rajan, 2010). According to the World Health Organization (WHO), the maximum allowable concentration limit of fluoride in drinking water is 1.5 mg L⁻¹ (Kemer et al., 2009). Long term ingestion of fluoride rich drinking water causes various serious health disorders (Reardon and Wang, 2000). Among various defluoridation techniques available for removal of fluoride from drinking water, adsorption is found to be most effective, economic and environment friendly one. A number of adsorbent materials and related technology have been developed for the effective removal of fluoride (Sujana et al., 2009). Materials containing rare earth elements are projected as potential adsorbents mainly due to their high electro-negativity and strong affinity towards fluoride (Alagumuthu & Rajan, 2010).

Among various rare earths, zirconium is an interesting element having high affinity towards fluoride. Zirconium is generally non-toxic as an element or in compound and the oral toxicity is reported to be quite low. Therefore, in this communication we are reporting synthesis, characterization and fluoride adsorption

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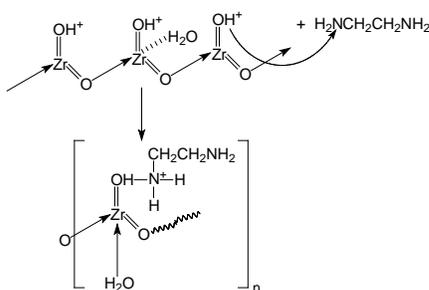
characteristics of a new zirconium-ethylenediamine (ZrEDA) hybrid sorbent. The investigation primarily focuses on isotherm, kinetics and thermodynamics of adsorption processes. The mechanism of fluoride removal was also purposed to emphasize more upon material characteristics. Reusability and sustainability of the material was also evaluated by desorption studies.

2. Materials and methods

Zirconium oxychloride (Aldrich) (Zr) and ethylenediamine (Aldrich) (EDA) were used for the synthesis of ZrEDA. Aqueous solution of zirconium oxychloride (0.1M) was mixed with aqueous solution of ethylenediamine (0.1M) in different volume ratios (v/v) with variation of pH of the medium. The white gel material was allowed to dry at 50°C in an oven for 24 hours. The material characterization was done using various instrumentation techniques. The extent of fluoride removal was studied using batch experiment technique with variation in experiments were conducted at variable dose, initial concentration, agitation time, pH and temperature.

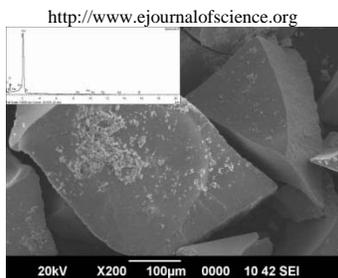
3. Result and Discussions

A proposed mechanism of formation of hybrid material due to the combination of zirconium oxychloride and ethylenediamine is presented by scheme-1.



(Scheme-1): The proton shifting mechanism in the formation of ZrEDA.

Analysis of FTIR spectrum of hybrid material indicates presence of hydroxyl group (3500-3200 cm^{-1}) and formation of weak hydrogen bond between protonated nitrogen and fluoride (1620 cm^{-1}). Further, thermogram of hybrid material shows a sharp deflection in the range 430-475°C indicating decomposition of attached organic molecules in the matrix. The scanning electron micrograph and energy dispersive spectrum (EDS) of fluoride adsorbed hybrid material (ZrEDAF) confirms the elemental composition as C, O, Zr, and F (Fig.1). The XRD spectrum confirms the amorphous characteristics of the material. The specific surface area, micropore volume and average micropore diameter of the hybrid material was determined to be 196.5 $\text{m}^2 \text{g}^{-1}$, 0.39 $\text{cm}^3 \text{g}^{-1}$ and 5.75 nm, respectively.



(Fig.1). Scanning electron micrograph (embedded with energy dispersive spectrum) of ZrEDAF.

It is shown that almost 99.2% of fluoride (from a 10 mg L⁻¹ solution) could be successfully removed by using 1.0 g of adsorbent at natural pH (pH = 7.0) of the medium. It was observed that the adsorption equilibrium point was reached in just 14 minutes. However, the reduction of amount of fluoride removal in an acidic pH (pH < 3.0) range, the amount of removal of fluoride is quite less (< 21%) and this is attributed to the formation of weakly ionized hydrofluoric acid species. The sorption kinetic studied at fixed temperature of 25°C, initial fluoride concentration of 10 mg L⁻¹ and adsorbent dose of 1.0 g L⁻¹ favours pseudo-second order kinetic equation with almost equal values for experimental adsorption capacity ($q_{e,exp}$) and calculated adsorption capacity ($q_{e,cal}$). The value of adsorption intensity (1/n) in Freundlich adsorption equation was found to be 0.625 (obtained by linear method) indicates that nearly 62.5% of active adsorption sites contain equal energy for adsorption process.

The effect of temperature upon adsorption process was studied with variation of temperature of the medium from 10 to 50°C. Various thermodynamic parameters such as ΔG , ΔS and ΔH were also calculated. It was observed that the percentage of fluoride removal by the adsorbent material increases with increase in temperature of the medium. The feasibility of adsorbent-fluoride interaction process is represented by the thermodynamic equation:

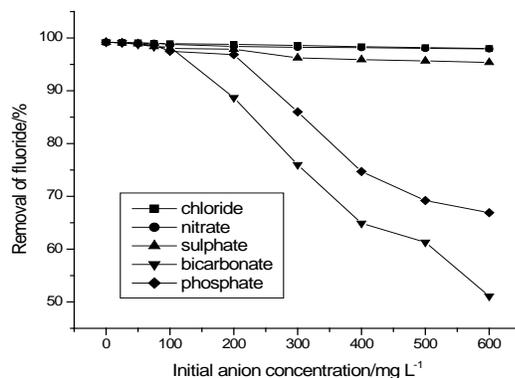
$$\Delta G^\circ = -RT \ln K_D \text{ -----(1)}$$

where ΔG° is the change in free energy, T is the absolute temperature, R is the universal gas constant (8.314 J mol⁻¹ K⁻¹), and K_D is the equilibrium constant. Negative values of ΔG° at all temperatures indicated the spontaneous nature of the adsorption process. The values of the enthalpy change (ΔH°) and the entropy change (ΔS°) associated with the processes were evaluated using the relationship:

$$\ln K_D = \Delta S^\circ/R - \Delta H^\circ/RT \text{ -----(2)}$$

The positive value of ΔH° indicates that the process is endothermic in nature. The value of ΔS° was found to be 0.369 kJ mol⁻¹ K⁻¹ indicating a relatively ordered state.

Drinking water contains many other anions such as sulphate, chloride, nitrate, phosphate, bicarbonate, etc., which may compete with fluoride for selective adsorption processes. The effect of various diverse ions/competing co-ions upon adsorption of fluoride is presented graphically in Fig.2.



(Fig.2). Effect of co-ions upon removal of fluoride from solution; amount of adsorbent: 1.0 g L⁻¹; concentration of fluoride: 10 mg L⁻¹; time of contact: 30 min; temperature: (25±2) °C.

The result indicates that NO₃⁻, Cl⁻, SO₄²⁻ had little effect upon adsorption processes. However, presence of phosphate and bicarbonate in the medium reduces the adsorption capacity. Attempting to regenerate and reuse the hybrid material in a batch cyclic operation carried up to 10th continuous cycle. The result shows minor reduction (from 99.0% to 96%) of adsorption capacity of hybrid material. Desorption of fluoride using very low concentration of NaOH (0.001M) was quite successful and almost 80% fluoride could be easily eluted from the hybrid material.

A mechanism of fluoride adsorption by the hybrid material (presented here as MOH) was also proposed based on pH and zeta potential measurement studies. Fluoride could be removed due to an electrostatic attraction process or an ion-exchange process as outlined below:

- (i) $\text{MOH} + \text{H}_3\text{O}^+ + \text{F}^- \rightarrow \text{MOH}_2^+ + \text{F}^- + \text{H}_2\text{O}$ (electrostatic attraction)
- (ii) Ion-exchange reaction between positively charged metal centre and fluoride:
 $\text{MOH} + \text{H}_3\text{O}^+ + \text{F}^- \rightarrow \text{M}^+ + \text{F}^- + 2\text{H}_2\text{O}$ (ion-exchange)

4. Conclusion

A new hybrid sorbent ZrEDA was developed from combination of zirconium and ethylenediamine specifically for the removal of fluoride. Maximum fluoride (almost 99%) could be removed at solution pH 7.0, indicating the efficiency of hybrid material for fluoride decontamination from drinking water. The adsorption process followed a pseudo-second order kinetic model. The material shows efficiency in presence of diverse anions. The simple regeneration procedure and reusability of the material shows the wide scope of utility of the material for sustainable use.

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