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Guar Gum Hydrogel Beads for Defluoridation from Aqueous Solution: Kinetic and Thermodynamic Study

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ABSTRACT

In the present research work, batch adsorption study was carried out to optimize the fluoride removal capacity of guar gum hydrogel beads from aqueous solution. The adsorption capacity was found to be 71.2 mg/g. The FTIR spectrum revealed the presence of functional groups that might be involved in fluoride adsorption. Adsorption of fluoride onto bio-sorbent was investigated as a function of pH, adsorbent dosage and time. The experimental equilibrium sorption data well fitted to the Langmuir mo del and the sorption kinetics for the bio-sorbent was found to follow second order rate expression. The negative values of ΔG° suggest that the sorption of fluoride onto the bio-sorbent was spontaneous and exothermic due to the negative value of ΔH°. The negative ΔS° value for the guar gum was found to be decreasing in randomness at the solid-liquid intersection.

INTRODUCTION

Fluoride in drinking water can be beneficial as it plays an important role in mineralization of bones and teeth but its excess uptake causes incurable dental and skeletal fluorosis. The main source of fluoride in groundwater is weathering and leaching of rocks containing minerals such as fluorite, fluorapatite, cryolite etc. (Carrillo-Rivera et al. 2002). According to World Health Organization (WHO) norms, the upper limit of fluoride concentration in drinking water is 1.5 mg/L. It is estimated that more than 200 million people worldwide depend on groundwater that contains a high concentration of fluoride. According to WHO guideline, the permissible limit for fluoride in drinking water is 1.5 mg/L. Various defluoridation technologies have been developed to reduce the fluoride concentration in water such as adsorption, ion exchange and precipitation to reduce fluoride level in the water. Among these methods, adsorption technique seems to be a promising technique for fluoride removal, because of ease of operation and selectivity of many natural adsorbents from various plant extracts and animal sources that have been tried as defluoridation agents. Seeds of the drumstick (Parlikar & Mokashi 2013), biomass of white rot fungus (Amin et al. 2015), tamarind seeds (Murugan & Subramanian 2006), leaf ash of *Syzygium cumini* (Tirkey et al. 2018) eggshell powder (Kashi et al. 2015), tea waste loaded to Al-Fe (Cai et al. 2015), porous starch loaded with common metal (Xu et al. 2017) and *Aloe vera* extract (Prasad et al. 2014) are few among them. Guar gum is obtained from the beans of the *Cyamopsis tetragonoloba* plant. Chemically, it is an exopolysaccharide composed of galactose and mannose (Khan et al. 2017). Guar gum has been used as an adsorbent for Hg (Singh et al. 2015), Cr (Maity & Ray 2016), and Pb (Pandey & Ramontja) ions removal. The present study explores the utility of guar gum for the removal of fluoride from aqueous solution.

MATERIALS AND METHODS

Guar beans were collected from the plant *Cyamopsis tetragonoloba* and left under the sun to dry for 3 to 4 days. The dried seeds were then crushed into a fine powder. The sodium salt of gum was made by mixing 10 g of powder into 100 mL, 1 M NaOH. Unreacted excess NaOH was removed by washing with 10 volume of double-distilled water. Ionotropic gelation method was carried out for beads preparation. Hydrogel beads were prepared by dropwise addition of 1% sodium salt of gum into 200 mL of 0.2 M $CaCl_2$ solution. The FTIR analysis was performed with attenuated total reflectance Fourier transform spectrometer at wave number ranging from 400-4000 cm^{-1} with a resolution of 4 cm^{-1} to determine the chemical constituent of guar gum powder that might be helpful for fluoride removal from aqueous solution. Adsorption experiments were carried out with 50 mL of 100 mg/L fluoride solution on a magnetic stirrer at 28°C for 60 min. The adsorbent of 2 g was added to the fluoride solution. Adsorption experiments were carried out with 50 mL of 100 mg/L fluoride solution on a magnetic stirrer at 28°C for 60 min. The adsorbent of 2 g was added to the fluoride solution. The adsorption of fluoride onto adsorbent was studied under different conditions including pH, temperature, contact time and biomass doses. In kinetic studies, the initial fluoride concentration was set to 100 mg/L, and the samples were analysed at certain time intervals. Also, the effect of the temperature was observed by conducting the experiments at five different temperatures (28, 36, 42, 48 and 52°C) in order to obtain thermodynamic parameters. The concentration of fluoride in the solutions was determined by ion exchange chromatography (Metrohm Eco IC). A calibration curve was obtained using NaF standard solutions with different fluoride concentrations ranging from 2.5 to 10 mg/L.

The percentage sorption of F ions was calculated by the following equation:

$$\text{Sorption } \% = \frac{C_i - C_f}{C_i} \times 100 \quad \ldots(1)$$

The amount of fluoride adsorbed was calculated from the following equation:

$$q_e = \frac{(C_i - C_f)\ V}{M} \quad \ldots(2)$$

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 nano-adsorbent (g) used.

RESULTS AND DISCUSSION

The FT-IR spectrum revealed the presence of carboxylic, hydroxyl and methyl groups. Fig. 1 shows the spectrum of guar gum powder. The peak located around wave number 3400 can be assigned as the involvement of the OH group. The adsorption peaks located in a wave range of 1800-1500 can be assigned as peaks due to the presence and involvement of C=C. The peak at 1,601 cm^{-1} is due to the asymmetrical -COO- stretching vibration (Helm & Naumann 1995) (Kishor et al. 2007).

Effect of pH on Adsorption

The adsorption data obtained for the effect of different pH values from 4 to 9 on defluoridation are shown in Fig. 2(a). The maximum adsorption capacity of 97.2% was observed at a pH value of 7, however, the adsorption capacity declined with the increase of pH value. The favourable neutral pH range observed for this study was found to be similar and reported by Hamamoto & Kishimoto (2017), Sujana et al. (1998) and Das et al. (2003). Many researchers have also found that the acidic pH also has good removal capacity for fluoride as reported by Wu et al. (2007) and He et al. (2018).

Effect of Contact Time

The effect of contact time on adsorption of F ion was investigated by performing an experiment by varying contact

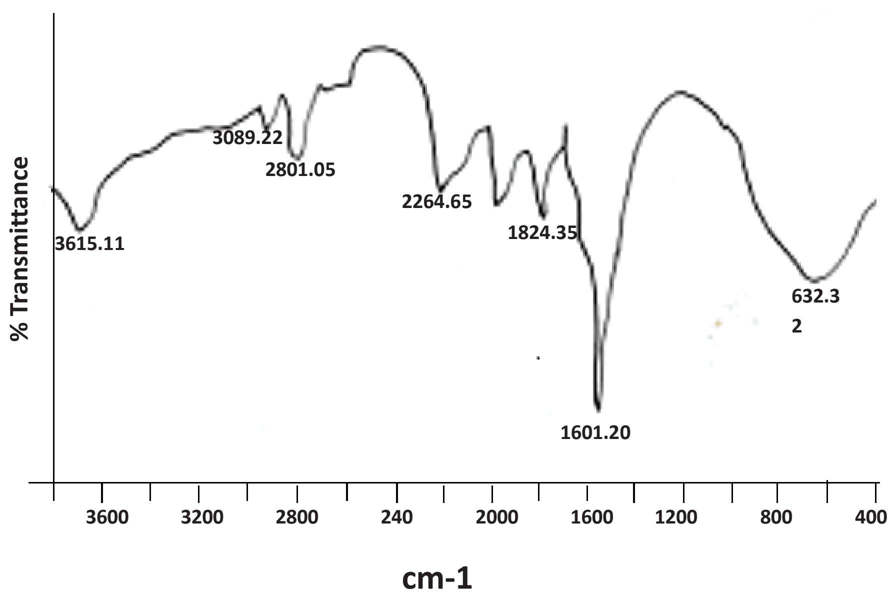

Fig. 1: FT-IR spectra of fluoride adsorbed Guar gum hydrogel beads.

time from 5 to 60 min using the adsorbent dose 2 g/L with an initial concentration of fluoride solution of 100 mg/L at 28°C. The effect of contact time on fluoride removal efficiency is shown in Fig. (2b). The maximum adsorption capacity for fluoride on equilibrium time was found to be 98%. It was also found that further increase in contact time showed very less change in the result, which concluded that 60 min was equilibrium contact time for fluoride removal.

Effect of Biomass Dosage and Fluoride

The pattern for adsorption of F ion at different doses of adsorbent indicated a little change in sorption of fluoride upon an increase in the amount of biomass beyond 2 g (Fig. 3a). Maximum sorption occurred when 2 g of the adsorbate was subjected to sorption studies. Similarly, an increase in F ion concentration to more than 200 mg/L, when biomass doses were 2 g, did not enhance overall sorption in batch sorption model (Fig. 3b).

Adsorption Isotherms

The adsorption isotherm for fluoride removal by guar gum was determined by Langmuir and Freundlich model. The Langmuir model works on the hypothetical assumptions of monolayer surface interaction whereas the Freundlich model applicable to both monolayer as well as multilayer adsorption. A linear form of Langmuir isotherm can be defined according to the following formula:

$$\frac{1}{Q_e} = \frac{1}{K_{LQ_m Ce}} = \frac{1}{Q_m} \qquad \ldots(3)$$

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/Qe Vs. $1/C_e$ values, which showed a linear relationship between the two (Fig. 4a). The coefficients of determination (R^2) were found to be 0.998 for F ion sorption. The maximum sorption capacity (Q_m) was found to be 71.2 mg/g, while K_L value was calculated as 0.017 L/mg for F ion sorption.

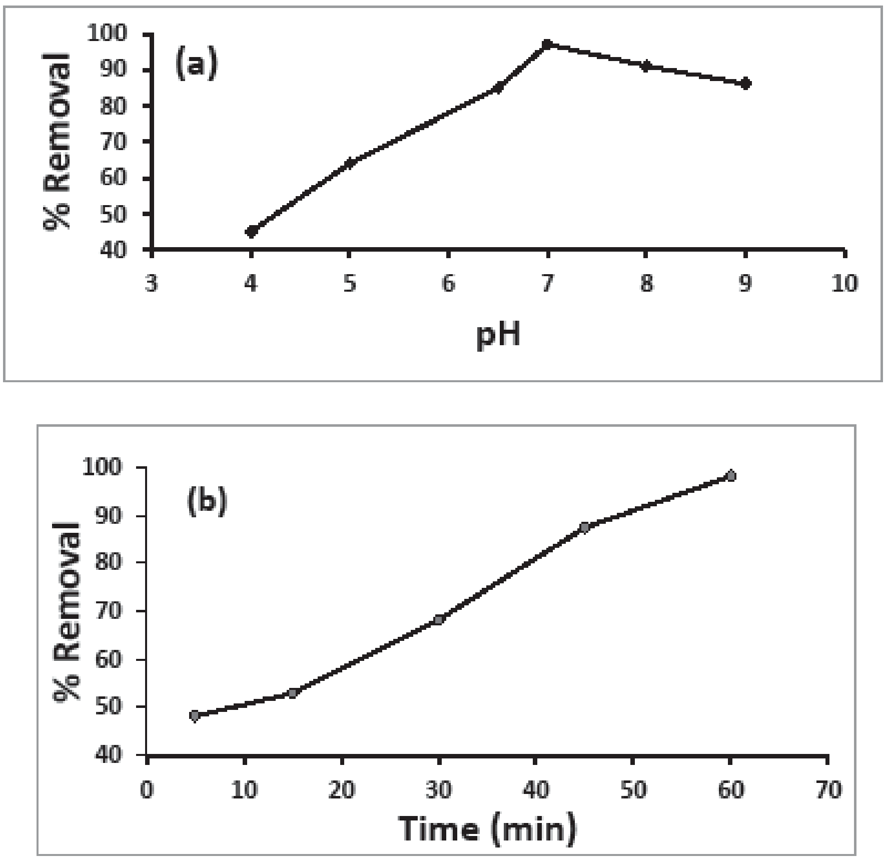

Fig. 2: Effect of pH (a), effect of contact time (b) on adsorption of fluoride onto Guar gum hydrogel.

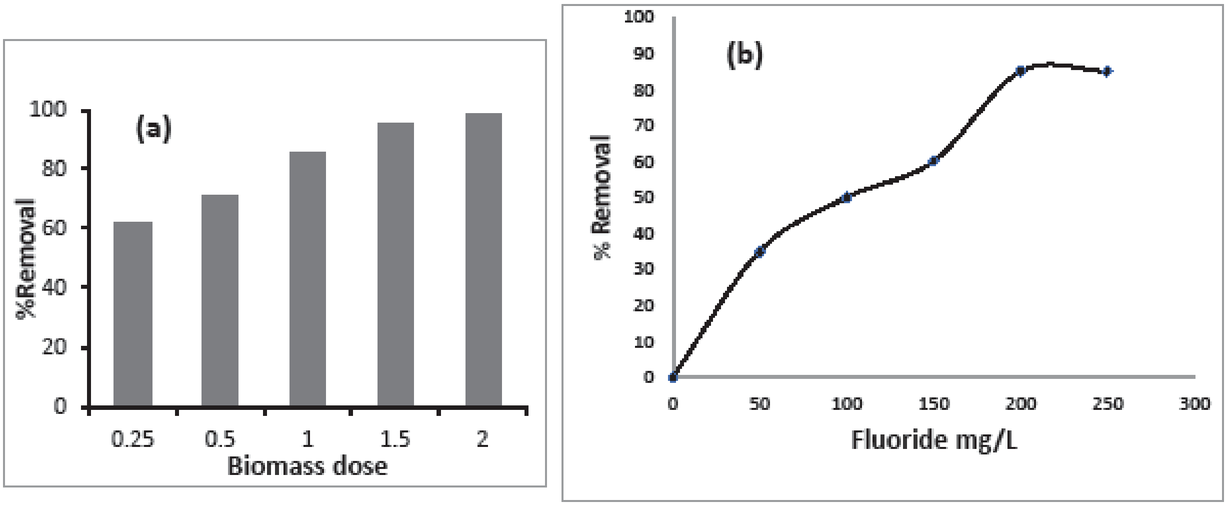

Fig. 3: Effect of biomass doses (a) (2g/L at 30°C) for removal efficiency & effect of adsorbate concentration (F^-, 200 mg/L).

Another study by Ghosh et al. (2014) reported a maximum adsorption capacity of 19.5 mg/g.

The Freundlich model assumes a heterogeneous adsorption surface and active sites with a different energy. This isotherm can be explained by the following formula:

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

Where, K_f is a constant relating the sorption capacity and 1/n is an empirical parameter relating to sorption intensity, which varies with the heterogeneity of the material. The Freundlich isotherm was obtained by plotting Log q_e Vs. Log C_e values, which showed a linear relationship between the two (Fig. 4b). Values of K_f and n were found to be 1.28 and 2.51 for F ion sorption respectively. The R^2 value was found to be 0.803. These results suggested that the Langmuir isotherm model best fitted the equilibrium data since it presented a higher R^2 value than the Freundlich model.

Adsorption Kinetic Models

Pseudo-first order and Pseudo-second order kinetic models were used to analyse the sorption rate of F ions on guar gum. The linear form of the equation is given as:

$$\log\left(q_e - q_t\right) = \frac{\log q_e - k_t t}{2.303} \qquad \ldots (5)$$

Where, q_e (mg/g) are the amount of fluoride adsorbed at equilibrium, q_t (mg/g) is the amount of fluoride adsorbed at any time and k_1 is the rate constant of the equation (min^{-1}). The linear graph obtained by plotting log (q_e-q_t) versus t and the values for rate constant can be calculated by the slope of the plot (Fig. 5a). The sorption kinetics was also

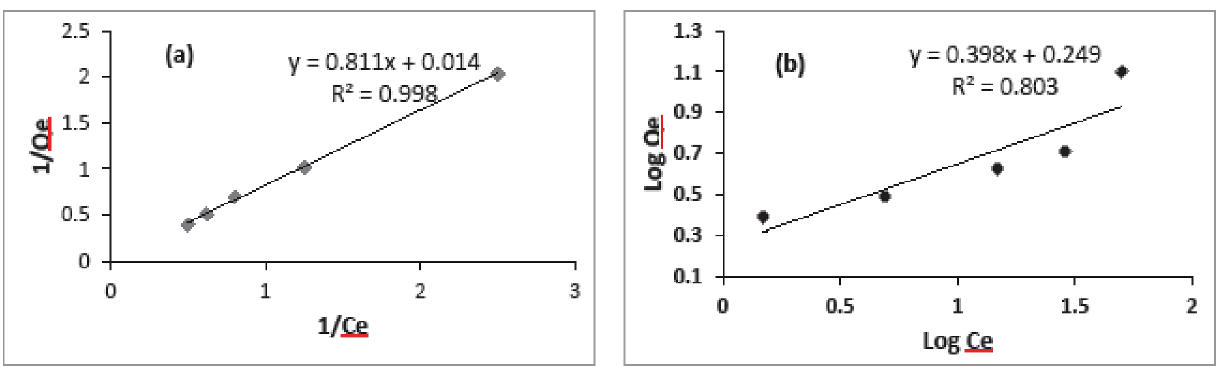

Fig. 4: Langmuir (a) and Freundlich (b) isotherm for adsorption of fluoride on prepared beads.

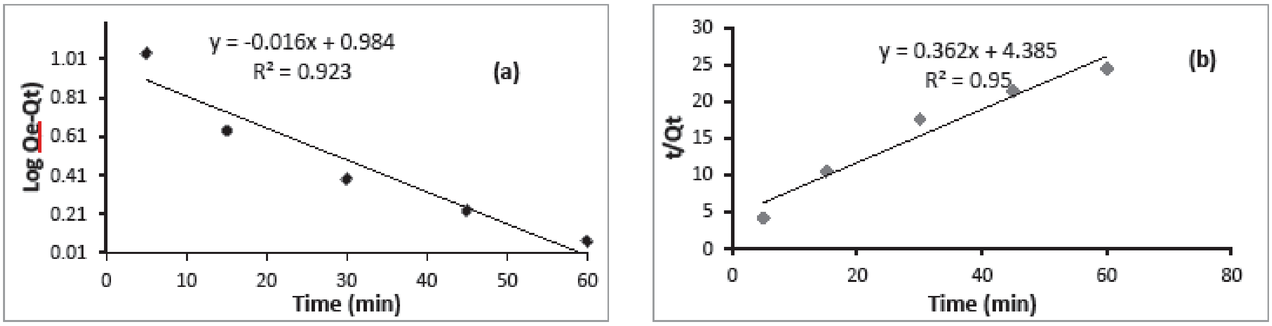

Fig. 5: Adsorption kinetic models for F⁻ ion uptake pseudo-first-order model for F⁻(a) and pseudo-second-order model for F⁻ ions (9b).

studied by pseudo-second-order model. The linear form of pseudo-second-order equation is given as:

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

Where, k_2 is the equilibrium rate constant (g/mg/min). If the pseudo-second-order kinetic equation is applicable, the plot of t/qt against t should give a linear relationship, from which q_e and k_2 can be determined from the slope and intercept of the plot (Fig. 5b). The values of the correlation coefficient of the pseudo-second-order model were found to be 0.95 which is higher than the pseudo-first-order model, i.e. 0.92. Compared to the pseudo-first-order equation, the pseudo-second-order model can explain the sorption kinetic behavior of F ion with a good correlation coefficient. In the study by Teutli-Sequeira et al. (2014) adsorption kinetic data were best fitted on pseudo-second-order kinetic.

Thermodynamic Studies

Thermodynamic parameters of an adsorption process are important to determine the nature of adsorption. Gibb's free energy change, ΔG°, is the fundamental criterion of spontaneity. Reactions occur spontaneously at a given temperature if ΔG° is a negative value. The thermodynamic parameters of Gibb's free energy change, Δ*G* for the adsorption processes are calculated using the equation (7).

$$\Delta G^\circ = -RT \ln K_D \qquad \ldots(7)$$

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 (Alagumuthu & Rajan 2010). The enthalpy (ΔH°) and entropy (ΔS°) parameters were estimated from the following equation:

$$\ln K_D = \left(\frac{\Delta S^o}{T}\right) - \left(\frac{\Delta H^o}{RT}\right) \qquad \ldots(8)$$

The negative ΔG° values indicated the thermodynamically feasible and spontaneous nature of the sorption. The increase in the negative value of ΔG° with an increase in temperature suggested lesser feasibility of sorption at high temperatures. In most of the cases, adsorption of fluoride is

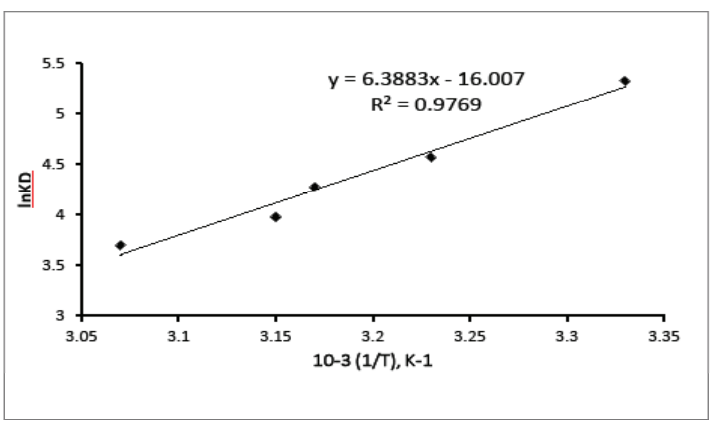

Fig. 6: Plot of ln KD Vs. 1/T for the estimation of thermodynamic parameters for sorption of F⁻ ions on to guar gum hydrogel beads.

found to have a negative value of ΔG^o which confirmed the spontaneous nature of adsorption (Gopal & Elango 2007, Gao et al. 2009, Boparai et al. 2011, Swain et al. 2011, Jin et al. 2015). The ΔH and ΔS were calculated from the slope and intercept of the plot of ln K_D versus 1/T (Fig. 6) and found to be -52.29 and -133.09 respectively. The negative H° indicates the exothermic nature of sorption (Chaudhry et al. 2017). 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 (Prasad et al. 2014). Therefore, the $\Delta H°$ value suggests that the sorption process of F ion occurred due to chemisorption. The negative $\Delta S°$ value suggested a decrease in the randomness at the solid-liquid interface during the sorption process.

CONCLUSIONS

The removal capacity of guar gum powder fluoride was found to be 98% with 71.2 mg/g at optimal experimental condition. The negative values of $\Delta G°$ and $\Delta H°$ indicate the spontaneous and exothermic nature of adsorption respectively. $\Delta H°$ value suggests that the adsorption process occurred due to chemisorption. The negative value of $\Delta S°$ suggests the decrease in randomness at the solid-liquid interface. Guar gum is eco-friendly low-cost biosorbent that has been used for removal of other metals as well as dye from solution but to the best of our knowledge this is for the first time that guar gum based hydrogel beads is used for removal of fluoride.

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