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Defluoridation of Drinking Water Using Calcium Modified Chitosan

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Fluoride in water has become a major environmental and health issue now a day. A new adsorbent chitosan calcium compound was prepared and used for defluoridation purpose. Defluoridation capacity of the adsorbent was studied by batch technique. Adsorption of fluoride was studied as a function of contact time, pH, initial fluoride concentration and adsorbent dose. The equilibrium sorption data were fitted to Freundlich, Langmuir and Temkin isotherms. The kinetics of sorption was found to follow pseudo second order and particle diffusion model. Result shows that the chitosan calcium adsorbent can be used for defluoridation of water without causing any harm to environment.

Keywords: Fluoride, Adsorption, Chitosan, Batch technique.

INTRODUCTION

Water is essential for existence of life on earth, but in present era we are in search of safe and clean drinking water due to tremendous increase in pollution of water bodies. Both inorganic and organic pollutants are equally responsible for water pollution. Among inorganic pollutants, fluoride is one of the significant contributors of water pollution. According to World Health Organization (WHO), the permissible limit of fluoride in water is 1.5 mg/L [1].

Higher concentration of fluoride in groundwater is geogenic, which happens when ground water comes in contact with the rocks rich in fluoride bearing minerals like topaz, fluorite, fluorapatite, cryolite and phosphorite [2], but fluoride in surface water is anthropogenic due to industrial and mining activities. Fluoride is actually toxic waste from aluminium, steel and fertilizer industries [3]. Silico fluorides are toxic hazardous waste products of these industries, which are captured by wet scrubbers and discharged in water bodies. High concentration of fluoride in water has many adverse effects on human health in terms of dental and skeletal fluorosis [4]. Therefore defluoridation of water having high concentration of fluoride is essential for us.

Fluoride from water can be removed by various methods such as reverse osmosis [5], by using chemicals like aluminum sulphate, magnesium or calcium phosphate [6] or by percolation through a bed of material, such as activated carbon [7], activated alumina [8], lignite [9], activated magnesia [10], granular calcite [11] or ion exchange resins [12,13], but these methods are costly, time consuming and pH sensitive. Adsorption is one of the most efficient methods for the removal of fluoride from water [14].

In the current study, chitosan calcium compound was prepared and used to remove fluoride from water. Chitosan has naturally activating capability without virulent side effect on human body and environment. The influence of adsorption time, initial pH and initial concentration of fluoride was evaluated and equilibrium data was fitted with isotherms and kinetic models.

EXPERIMENTAL

Preparation of chitosan calcium compound: For synthesis of chitosan calcium compound, a known amount of commercial chitosan powder was dissolved in HCl by flocculating it for appropriate time. The composite adsorbent of chitosan and metal was prepared by adding a known amount of metal to the solution and stirring for appropriate time. The solution mixture was then neutralized by adding base solution. The precipitate was filtered, dried in hot plate and kept in oven overnight. Oven dried modified chitosan was powdered with the help of mechanical grinder.

Preparation of stock solution: Fluoride stock solution was prepared by dissolving a known quantity of analytical-grade sodium fluoride in distilled water. The solutions used for the study were obtained by dilution of the stock solution to the required concentrations. Concentration of fluoride was then determined by ion selective electrode. All adsorption experiments were carried out at room temperature (25 °C). Solutions were placed in plastic flasks.

Batch study: Batch sorption experiments were conducted in order to study the effect of different controlling parameters like pH, initial fluoride concentration, contact time and compound dose on fluoride removal capacity of chitosan calcium compound. After adding required quantity of adsorbent dose, fluoride solutions were kept for a specified contact time. The supernatant of sample was filtered through Whatmann filter paper and analyzed for residual fluoride concentration.

Analysis: A fluoride-selective electrode (Orion Model 720 Aplus) equipped with combination pH/ISE meter (Orion Model, 720 Aplus) was employed for the measurement of fluoride ion concentration. The method of direct potentiometry was used, where the concentration can be read directly. The fluoride ion selective electrode was calibrated prior to each experiment in order to determine the slope and intercept of the electrode. The pH was measured with pH glass electrode. The meter was calibrated whenever the measurements were made by using pH calibration buffers. The adsorption capacity q_e and removal efficiency E of fluoride were calculated with the following equations [15]:

$$q_e = (C_0 - C_e)V/m \qquad (1)$$

$$E = [(C_0 - C_e)/C_0] \times 100 \qquad (2)$$

RESULTS AND DISCUSSION

Effect of pH: The pH of the aqueous solution plays an important role in adsorption process. The effect of pH (3-12) on removal of fluoride for a constant adsorbent dose, fixed standing time and fluoride concentration was studied (Fig. 1). It was found that pH had a marked effect on the fluoride uptake in this experiment. The percentage adsorption was found to decrease with an increase in pH from 3 to 5 and then increased with a further increase in pH 5 to 7 and again it decreased when pH increased up to 12. The adsorbent showed maximum defluoridation capacity of 7.725 mg of fluoride per kg at pH 3. Therefore the optimum pH for the removal of fluoride was found to be 3. This result may be due to the fact that at lower pH value higher concentration of hydrogen ion is available that neutralizes the negative charges present at the surface of the adsorbent, which helps in diffusion of the negatively charged fluoride ions on to the increased active surface of adsorbent. Similar result was obtained by Dave and Machhar [16]. Defluoridation capacity of the adsorbent decreases in alkaline medium may be due to competition of fluoride ion and hydroxyl ions for active sites of adsorbent [17].

Time dependence studies for fluoride binding: The variation in removal percentage of fluoride with time was studied using the solution of fluoride with initial concentration of 2 mg/L, adsorbent dose 5 g at pH 3 (Fig. 2). The time was varied from 1 to 5 h. On increasing the contact time, the percentage removal was found to gradually increase till 3 h, which may be due to larger availability of vacant active site of adsorbent. Further increase in time does not show any marked effect on the removal of fluoride as the active sites of adsorbent may get saturated with adsorbate ions with the progress of experiment. Hence the optimum contact time for fluoride removal was 3 h at pH 3 for chitosan calcium compound.

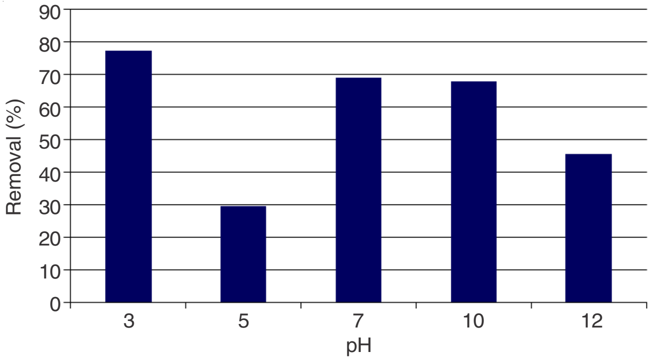

Fig. 1. Effect of pH on removal of fluoride

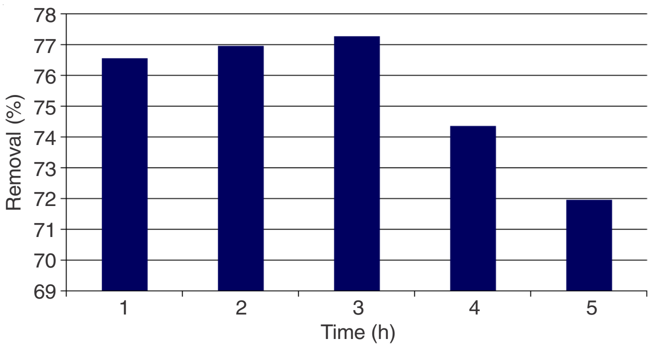

Fig. 2. Effect of contact time on removal of fluoride

Effect of adsorbent dosage on fluoride adsorption: To achieve the maximum adsorption capacity of fluoride for chitosan calcium compound, the experiment was conducted under optimum conditions *i.e.* fixed contact time of 3 h, initial concentration of fluoride 2 mg/L at pH 3.To study the effect of adsorbent dose on the percentage removal of fluoride, 0.5 to 5 g of adsorbent was added to 25 mL of sodium fluoride solution of initial concentration of 2 mg/L. The adsorption was found to increase from 57.05 to 77.25 % with increasing adsorbent dose from 0.5 to 5 g due to increase in adsorbent/fluoride ratio. Further increase in dosage showed no further increase in the percentage removal of fluoride (Fig. 3). Hence the adsorption studies were made by keeping the sorbent mass as 5 g and the volume of solution 25 mL at pH 3.

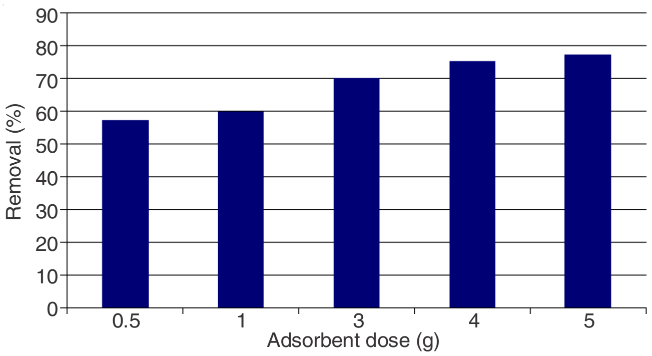

Fig. 3. Effect of adsorbent dose on removal of fluoride

Effect of initial fluoride concentration: The effect of fluoride concentration on adsorption was studied for chitosan calcium compound by varying fluoride concentration from 0.5 to 2.5 mg/L at pH 3 under optimum condition of adsorbent dose and contact time. The result indicate that the percentage removal gradually increased with increasing initial concentration of fluoride from 0.5 to 2.0 mg/L then it decreases with increase in fluoride concentration up to 2.5 mg/L (Fig. 4). The percentage removal was 65.4-77.25 % from 0.5-2.0 mg/L of fluoride solution. At higher fluoride concentration active sites of the adsorbent may get saturated which may be responsible for decrease in adsorption capacity of adsorbent for fluoride concentration more than 2 mg/L.

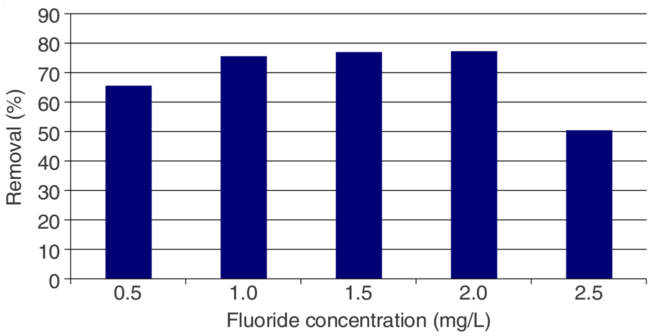

Fig. 4. Effect of fluoride concentration on removal of fluoride

Adsorption isotherm: The adsorbate quantity taken up by an adsorbent is a function of the characteristics and concentration of adsorbate as well as the temperature. Usually the quantity of adsorbed material is determined as a function of the concentration at a constant temperature and the function obtained in this way is known as adsorption isotherm. Fluoride ion distribution between the liquid and solid phase help to determine the position of equilibrium in the adsorption and it can be expressed by the Freundlich, Langmuir and Temkin isotherms.

Freundlich isotherm: Freundlich model indicates the heterogeneity of adsorbent surface [18] and it is given by:

$$q_e = K_F C_e^{1/n} \quad (3)$$

The linearized equation of Freundlich model (1906) is given by:

$$\log q_e = \log K_F + 1/n \log C_e \quad (4)$$

where K_F and n are Freundlich constants related to adsorption capacity and adsorption intensity, respectively, which are obtained from the intercept and slope of the plot between log q_e and log C_e. If n = 1 then the partition between the two phases are independent of the concentration. If value of 1/n is below one it indicates a normal adsorption. On the other hand, 1/n being above one indicates cooperative adsorption [19]. The values of Freundlich constants are shown in Table-1, which shows that the value of 1/n is less than one for the adsorption process indicating the normal adsorption of fluoride ions on chitosan calcium compound.

Langmuir isotherm: This Langmuir adsorption isotherm quantitatively describes the formation of a monolayer of adsorbate on the outer surface of the adsorbent having a finite number of identical sites and after the formation of such a monolayer no further adsorption occurs on the surface of adsorbent. Thereby, the Langmuir represents the equilibrium distribution of ions between the solid and liquid phases [20,21]. The model assumes uniform energies of adsorption onto the surface and no transmigration of adsorbate in the plane of the surface. Based upon these assumptions, Langmuir represented the following equation:

$$q_e = (Q_0 K_L C_e)/(1 + K_L C_e) \quad (5)$$

The linearized equation of Langmuir isotherm [22] is given by:

$$C_e/q_e = 1/(Q_0 K_L) + C_e/Q_0 \quad (6)$$

where, C_e and q_e are the free and adsorbed concentrations of fluoride ion, respectively at equilibrium; Q_0 and K_L are the Langmuir constants representing the adsorption capacity and energy, respectively. The linear plots of C_e/q_e *versus* C_e is shown in Fig. 5. The linearity of the plot indicates to the formation of monolayer coverage on the surface of the adsorbent by the fluoride ion [23].

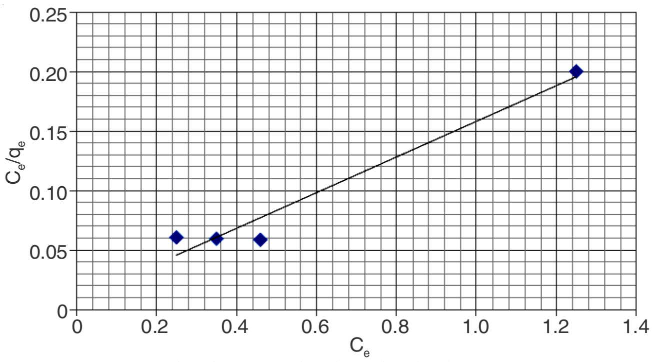

Fig. 5. Langmuir adsorption isotherm

The essential characteristics of Langmuir equation can be shown by dimensionless factor R_L, which is given by:

$$R_L = 1/(1 + K_L C_0) \quad (7)$$

where C_0 is the highest initial concentration of fluoride (mg/L). The value of R_L is given in Table-1 which is less than one indicating favourable adsorption of fluoride on adsorbent.

Temkin isotherm: Temkin isotherm [24] is given by following equation:

$$q_e = (RT)/b_T \ln(A_T C_e) \quad (8)$$

Linear form of Temkin isotherm is given by

$$q_e = B_T \ln A_T + B_T \ln C_e \quad (9)$$

where $B_T = RT/b_T$; A_T = Temkin isotherm equilibrium binding constant, b_T = Temkin isotherm constant, R = universal gas constant (8.314 J/mol/K), T = Absolute temperature, B = Constant related to heat of sorption (J/mol).

This isotherm assumes that the heat of adsorption of all molecules in layer would decrease linearly rather than

TABLE-1
FREUNDLICH, LANGMUIR AND TEMKIN ISOTHERM CONSTANTS

Freundlich constants					Langmuir constants					Temkin constants		
1/n	n	K_F	R^2	χ^2	Q_0	K_L	R_L	R^2	χ^2	A_T	B_T	R^2
0.49	2.04	4.79	0.831	0.32	6.67	18.86	0.025	0.96	0.25	7.62	13.9	0.99

logarithmic with coverage of appropriate concentration range due to interaction between adsorbent and adsorbate [24,25]. Above equation shows that it is derived on the basis of uniform distribution of binding energies. The constants of this model were determined from the slope and intercept of the plot between adsorbed quantity q_e and ln C_e (Fig. 6) and shown in Table-1. These values indicating a physical adsorption process.

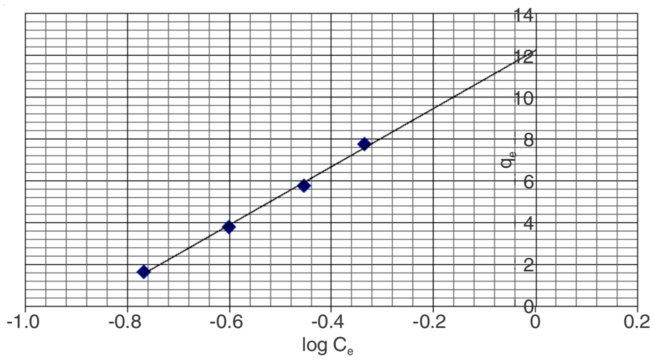

Fig. 6. Temkin isotherm

Results shows that Freundlich, Langmuir and Temkin isotherm correlation coefficient R^2 value are 0.831, 0.96 and 0.99, respectively (Table-1). R^2 value for Freundlich isotherm is lesser than the R^2 value of Langmuir and Temkin isotherm for chitosan calcium compound, so the results indicate that Langmuir and Temkin adsorption isotherm fit reasonably well with the experimental data.

Chi-square analysis: To identify the suitable isotherm for fluoride sorption onto the adsorbent, the chi-square analysis was carried out. The mathematical equation for chi-square analysis is

$$\chi^2 = \Sigma(q_e - q_{em})^2/q_{em} \quad (10)$$

where q_{em} is equilibrium capacity obtained by calculating from the model and q_e is experimental data on the equilibrium capacity. Small value of χ^2 is the indication of the fact that the data from the model are similar to the experimental data. The results of chi-square analysis are given in Table-1. As Langmuir isotherm possess lower χ^2 values and hence this isotherm can be considered as the best fitting model for the sorption of fluoride on chitosan calcium adsorbent than Freundlich model.

Kinetics study: The removal of fluoride from aqueous solution by chitosan calcium adsorbent may be presented by reaction based model as pseudo first-order [22] and pseudo second-order model [26] and diffusion based model as particle diffusion [27,28] and intraparticle diffusion kinetic models [22].

Reaction based model: Pseudo first order rate equation describes the adsorption rate on the basis of adsorption capacity and it is widely used for adsorption of pollutants from aqueous solution. Pseudo second order model predicts the behaviour of adsorption over the range of concentration taken for study and represents chemisorption.

Table-2 presents the kinetics equation and constant value for fluoride adsorption on adsorbent, from which it is clear that the experimental values of q_e determined in this work is very close to the theoretical one in case of second order kinetics and the accuracy is better for second order kinetics as R^2 value is near to unity ($R^2 = 0.99$). Therefore fluoride–adsorbent interaction showed good fit with pseudo-second order rate equation (Fig. 7) and this indicated the chemisorption nature of adsorption here.

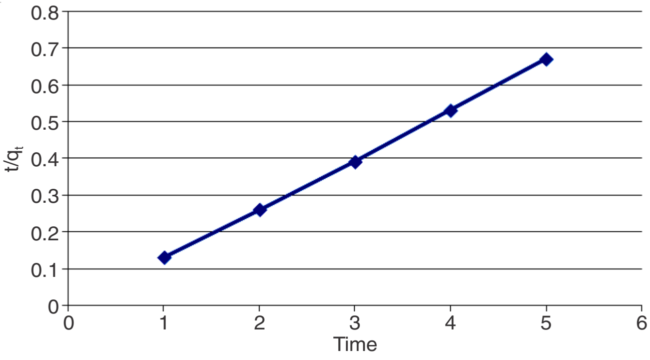

Fig. 7. Plot of second order model for fluoride absorption

Best-fit model: The kinetic model which fits best with the sorption data was determined by standard deviation (SD). The model shows lower value of SD better fit to sorption data. The SD values of chitosan calcium compound for both the kinetic models are summarized in Table-2. Smaller SD values were observed for the pseudo-second-order model indicates that this model is significant in defining the fluoride adsorption process on chitosan calcium adsorbent.

Diffusion based model: 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 [27,28] is given as follows:

$$\ln(1 - C_t/C_e) = -k_p t \quad (11)$$

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.

Intraparticle diffusion plot is used to identify the mechanism involved in the adsorption process and is given by:

$$q_t = k_{diff}\, t^{1/2} + C \quad (12)$$

The slope of the plot gives the value of intraparticle diffusion constant k_{diff} whereas intercept of the plot shows the boundary

TABLE-2
COMPARISON OF FIRST AND SECOND-ORDER KINETICS CONSTANTS

Kinetics	Equation	Linear form	R^2	Constant	Value
Pseudo first order	$\frac{dq_t}{dt} = k(q_e - q_t)$	$\log(q_e - q_t) = \log(q_e) - \frac{k}{2.303}t$	0.85	K q_e (calculated) SD	0.17 1.14 3.39
Pseudo second order	$\frac{dq_t}{dt} = k(q_e - q_t)^2$	$\frac{t}{q_t} = \left(\frac{1}{kq_e^2}\right) + \left(\frac{1}{q_e}\right)t$	0.99	K q_e (calculated) SD	2.04 7.40 0.13

TABLE-3
COMPARISON OF PARTICLE AND INTRA-PARTICLE DIFFUSION CONSTANTS

Diffusion model	Linear form	R^2	Constant	Value
Particle diffusion	$\ln(1\text{-}C_t/C_e) = -k_pt$	0.85	k_p	0.016
Intraparticle diffusion	$q_t = k_{diff}\,t^{1/2} + C$	0.83	k_{diff}	0.244
			C	7.950

layer effect. Large value of intercept as shown in Table-3 is an indication of greater contribution of the surface sorption in rate controlling step. The linear plot for intraparticle diffusion did not pass through the origin which shows that rate limiting process is not only governed by intraparticle diffusion but some other mechanism is also involved along with it.

The straight line plots of $\ln(1–C_t/C_e)$ *vs.* t (Fig. 8) and q_t *vs.* $t^{0.5}$ (Fig. 9) indicate the applicability of both the particle and intraparticle diffusion models, respectively. The k_p, k_{diff} and R^2 values for both the particle and intraparticle diffusion models are illustrated in Table-3. The R^2 values obtained for both the particle and intraparticle diffusion models are almost comparable and suggest that the fluoride diffusion on chitosan calcium compound follows both the models.

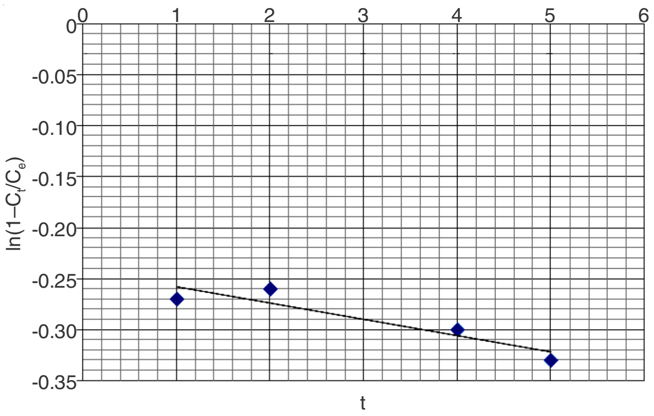

Fig. 8. Particle diffusion model

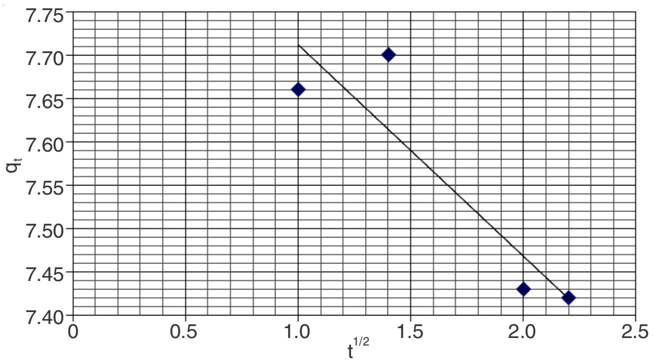

Fig. 9. Intraparticle diffusion model

Conclusion

The present study showed that the chitosan calcium compound is helpful in reducing fluoride concentration in water. With increasing fluoride concentration the fluoride removal efficiency of adsorbent increases initially. The maximum efficiency for fluoride removal by this adsorbent is 77.25 % at pH 3, contact time 3 h and 2.0 mg/L concentration of fluoride. For chitosan calcium compound Freundlich, Langmuir and Temkin adsorption isotherms were studied. The R^2 value for Langmuir adsorption isotherm for chitosan calcium compound suggested that the adsorption process was monolayer and adsorption of each molecule had equal activation energy. The value of separation factor R_L below one indicates the favourable adsorption of fluoride on chitosan calcium compound. Higher regression coefficient of Temkin isotherm may be because of linear dependence of heat of adsorption over appropriate concentration range. Fluoride adsorbent interaction was best fitted with pseudo second order indicating the chemisorptions nature of adsorption of fluoride on chitosan calcium adsorbent. The regression coefficient values obtained for both the particle and intraparticle diffusion models were almost analogous which shows that adsorption here can be explained with these models. Result obtained from this study showed that chitosan calcium adsorbent can be used as environment friendly adsorbent for removal of fluoride from water.

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