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ORIGINAL ARTICLE

Isotherm Studies of Equilibrium Sorption of Fluoride onto Calcium Alginate Beads

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ABSTRACT

The continued consumption of fluoride (in excess to 1.5 mg/L) and the resultant disease of fluorosis is one of the incurable diseases which have been known in India for a long time. In this paper it is attempted to develop a fluoride-biosorbents system in the term of calcium alginate beads (CAB) as adsorbent and then fluoride (f-adsorption) investigation was carried out using aqueous solutions of different concentration of adsorbate (fluoride) during the study period. The efficiency of adsorbents has been investigated by performing laboratory batch experiment studies. Based on the facts that the analysis of the equilibrium data is important to establish the equation, several isotherm equations have been used for the equilibrium modeling of adsorption systems and accordingly the sorption data have been subjected to different sorption isotherms in the present study. Here we reports that the loading capacity increases by increasing initial fluoride concentration levels and the uptake capacity of adsorbent increased at optimum set of parameters and the percentage removal of fluoride decreases from 78% to 59% with increase in fluoride concentration from 1 to 10mg/L as the initial fluoride concentration increased from 1-10mg/L. Though regression values of the Langmuir and Freundlich isotherms (R^2=0.975) for CAB is good enough but it is highest for Langmuir isotherm (R^2=0.996) suggesting the best fit of this model to experimental data. Similarly based on the coefficients of the Temkin isotherm model with R^2 value as 0.984 for CAB suggests there is good fit of Tempkin isotherm than that of the Dubinin-Raduskevich (D–R) isotherm model with regression R^2 value (R^2=0.925) for adsorbent CAB.

Key words: *Calcium alginate beads as CAB, Biosorbents, Defluoridation, Adsorbate, Removal efficiency.*

INTRODUCTION

Increasing population, urbanization and high industrialization in developing countries like India are creating hazardous environmental problems of enormous dimensions. Fluoride contamination of drinking water is one of such problem around the globe. The occurrence of fluoride in water is a result of the earth's crust being rich in fluoride bearing minerals and through contamination by application of pesticides, phosphate fertilizers, sewage sludge, or by runoff water has become a major public health issue. Intake of drinking water is considered as the major contribution to the fluoride entering the human body. India is one among the 23 Nations worldwide, where human health problems have been reported due to the range of fluoride beyond permissible level (1.5mg/L maximum tolerance limit WHO 1984) in drinking water. An estimated 62 million people in India in 17 out of 28 states are affected with dental, skeletal and/or non skeletal fluorosis. Drinking water in India indicated that over 43.5 million people living in 1.42 lakh habitations spread over 200 districts are at health risks due to water quality problems and fluoride was identified as one of the major contaminants (UNICEF 1999; Sushella, 1993, 2007). Fresh water resources constitute the most important resources to sustain quality life and therefore, potable water supply in terms of quality and quantity is of vital importance (Baghvand *et al.*, 2006). Defluoridation technique has been developed but still many areas are in urgent need of attention from the higher authorities (Ministry of Rural Development, 1993). Keeping the view in mind fluoride (*f*-adsorption) investigation was carried out by developing a fluoride-biosorbents system calcium alginate beads (CAB) as adsorbent using aqueous solutions of different concentration of adsorbate (fluoride) during the study period. Based on the facts that the analysis of the equilibrium data is important to establish the equation, several isotherm equations have been used for the equilibrium modeling of adsorption systems and accordingly the sorption data have been subjected to different sorption isotherms in the present study

MATERIAL AND METHODS

All the reagents used were of analytical grade and sodium alginate, calcium chloride used for preparation of calcium alginate beads whereas, sodium fluoride used as a source of fluoride were procured from Loba Chemie Mumbai. Total ionic strength adjustment buffer (TISAB) used to eliminate the interference effect of complexing ions from fluoride solution was obtained from Thermo Electron Corporation, USA. Milli-Q water was used in all the experimental work throughout the study period.

ADSORBENT DEVELOPMENT

A transparent and viscous 2% solution of sodium alginate was prepared in Milli-Q water. Sodium alginate solution was added drop wise at approximately one drop per second by a syringe to a beaker containing the chilled calcium chloride solution, and it was stirred gently at approximately 60 rpm to allow the spheres to form. The spheres that were formed were left stirring for 3 hr. Then, the spheres were separated from the solution and washed 5 times with deionised water. Finally, the spheres were dried in an oven at 35°C.

BATCH STUDY

The efficiency of adsorbents is investigated by performing laboratory batch experiment studies. Specific amount of adsorbent were taken in 100 ml aqueous solution of fluoride ions at selected pH 6.5, adsorbent dose 0.7gm/dl, and a varying initial fluoride ion concentration from 1 to 10 mg/L and stirred at 40 rpm for optimum time period of 80 min. At the end of pre-determined time the solution was filtered and the filtrate was analyzed for residual fluoride was monitored by ion selective electrode using ELICO (LI-126) Hyderabad (A.P.) India.

RESULTS AND DISCUSSION

1. EFFECT OF INITIAL FLUORIDE ION CONCENTRATION

The results obtained during the study period show that the loading capacity increases by increasing initial fluoride concentration levels and the uptake capacity of adsorbent increased from 0.097mg/gm to 0.737mg/gm at optimum set of parameters as the initial fluoride concentration increased from 1-10mg/L (Figure 1a). This remarkable property can be explained by the fact that at higher concentrations the less accessible sites of the adsorbents are more likely to adsorb fluoride. This is obvious from the fact that a higher initial fluoride concentration provides an important driving force to overcome all of mass transfer resistance of the fluoride as pollutant between the aqueous and solid phases thus increased the uptake**.** Furthermore the increase of loading capacity of adsorbents with increasing initial fluoride concentration may be due to the higher interaction between fluoride and newly developed adsorbent. The percentage removal of fluoride decreases from 78% to 59% with increase in fluoride concentration from 1 to 10mg/L (Figure 1b).

2. ADSORPTION ISOTHERM STUDIES

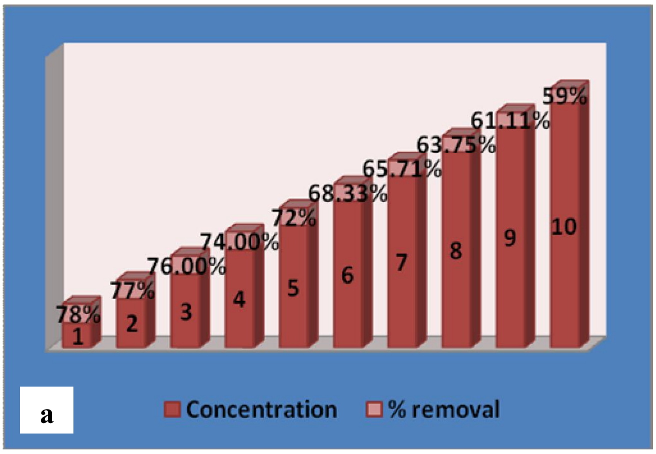
Adsorption isotherms are important for the description of how adsorbate will interact with an adsorbent and are critical in optimizing the use of adsorbent. Thus, the correlation of equilibrium data using either a theoretical or empirical equation is essential for adsorption data interpretation and prediction. Several mathematical models can be used to describe experimental data of adsorption isotherms. Four famous isotherm equations, the Langmuir, Freundlich, Temkin and D-R isotherm equilibrium models were used for the present analysis of the calcium alginate beads (CAB)-fluoride sorption system.

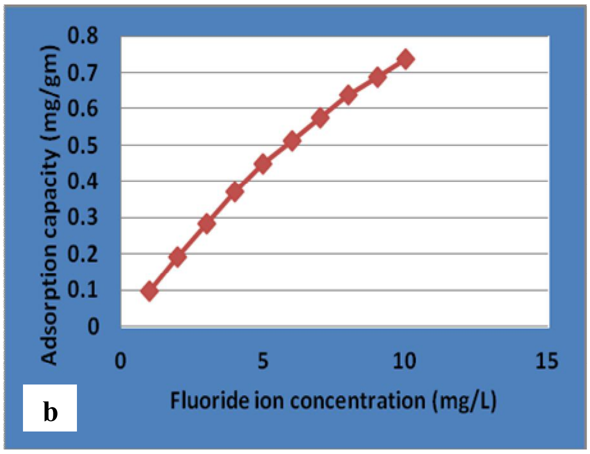
2.1. Langmuir isotherm:

Langmuir's model assumes monolayer adsorption of adsorbate on definite sites on surface of adsorbent having same adsorption energy at all the sites. The rearranged Langmuir's adsorption isotherm equation can be given as $\frac{C_e}{q_e} = \frac{1}{bq_m} + \frac{C_e}{q_m}$ where, q_e= amount of adsorbate, adsorbed at equilibrium (mg/g), q_m= theoretical maximum adsorption capacity of the adsorbents (mg/g), C_e = equilibrium concentration of the adsorbate in solution (mgL^{-1}), b=constant related to the adsorption energy (L/g).

From the data obtained during the study period reveals the linear plot of C_e/q_e *Vs* q_e (Figure 3) which indicates that adsorption follows the Langmuir adsorption model. The value indicate that the adsorption pattern for fluoride ions on test adsorbent CAB followed the Langmuir isotherm (R^2 = 0.996). Analyzed and calculated data also confirm with a support of the statement that the maximum adsorption capacity value of q_m is 1.127 and Langmuir constant b as 0.4507 for CAB (Table 1 and Figure 2a). Based on the coefficients of the Langmuir isotherm model, R_L values for fluoride adsorption onto CAB on the set optimum parameters were less than 1 and greater than zero at all initial concentrations of fluoride indicating favorable adsorption.

Fig 1(a-b): Effect of fluoride concentration on adsorption capacity and % removal efficiency of CAB





2.2. Freundlich isotherm:

The Freundlich adsorption equation is perhaps the most widely used mathematical description of adsorption in aqueous systems and related constants are the characteristics of the system indicating the adsorption capacity and adsorption intensity. The Freundlich equation is an empirical expression that encompasses the heterogeneity of the surface and the exponential distribution of sites and their energies. For linearization of the data, the Freundlich equation is written in logarithmic form as:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e$$

The plot of logarithmic value of fluoride removal per unit weight (*log* q_e) and equilibrium concentration of fluoride(*log* C_e) gives the linear plot for fluoride adsorption as the R^2 values is 0.975 for CAB confirms the good fit of Freundlich adsorption isotherm (Figure 4). The slope representing *1/n* and intercept representing *log* K_f are the Freundlich empirical parameters for the specific adsorbents. K_f is related to the adsorption capacity, and the exponent *1/n* is related to surface heterogeneity and adsorption intensity .The value of *n* lying between1 to 10 indicates favorable adsorption. In the present study the value of Kf and n was obtained for fluoride adsorption is in the order 0.32 and 1.485 thus indicating favorable adsorption (Table 1 and Figure 2b). Though R^2values of the Langmuir and Freundlich isotherms for CAB is good enough but it is highest for Langmuir isotherm suggesting the best fit of this model to experimental data. This suggest that the fluoride ion are adsorbed forming a monolayer onto adsorbent and the ions did not compete each other.

2.3. Tempkin isotherm:

Tempkin considered the effects of some indirect sorbate/adsorbent interactions on adsorption isotherms and suggested that because of these interactions the heat of adsorption of all the molecules in the layer would decrease linearly with coverage. The model is given by the equation: $q_e = B \ln A + B \ln \; C_e$ where A =Temkin isotherm equilibrium binding constant (L/g) corresponding to maximum binding energy, B = Constant related to heat of sorption (J/mol). Based on the coefficients of the Temkin isotherm model, the parameter A (5.5506), B (0.2255) with R^2 value as 0.984 for CAB suggests there is good fit of Tempkin isotherm for adsorbent CAB (Table 1 and Figure 2c).

2.4. D-R isotherm:

D-R isotherm is widely used to determine the physical or chemical adsorption phenomenon and related to heterogeneity of energies over the surface. The Dubinin-Raduskevich (D–R) isotherm model does not assume a homogenous surface or a constant adsorption potential and is expressed as $\ln q_e = \ln q_m - \beta \xi^2$ where q_m is the theoretical saturation capacity (mg/g), β a constant related to the mean free energy of adsorption per mole of the adsorbate (mol²/kJ²), ξ is the Polanyi potential. D-R isotherm parameters suggesting that this model also fits the experimental results obtained during the study period. For this isotherm model the value of q_m (0.6014) followed by β (1.117), *Es* (0.669) showing the regression R^2 value as 0.925 for CAB (Table 1 and Figure 2d).

Fig. 2(a-d): Adsorption isotherms for adsorbent CAB

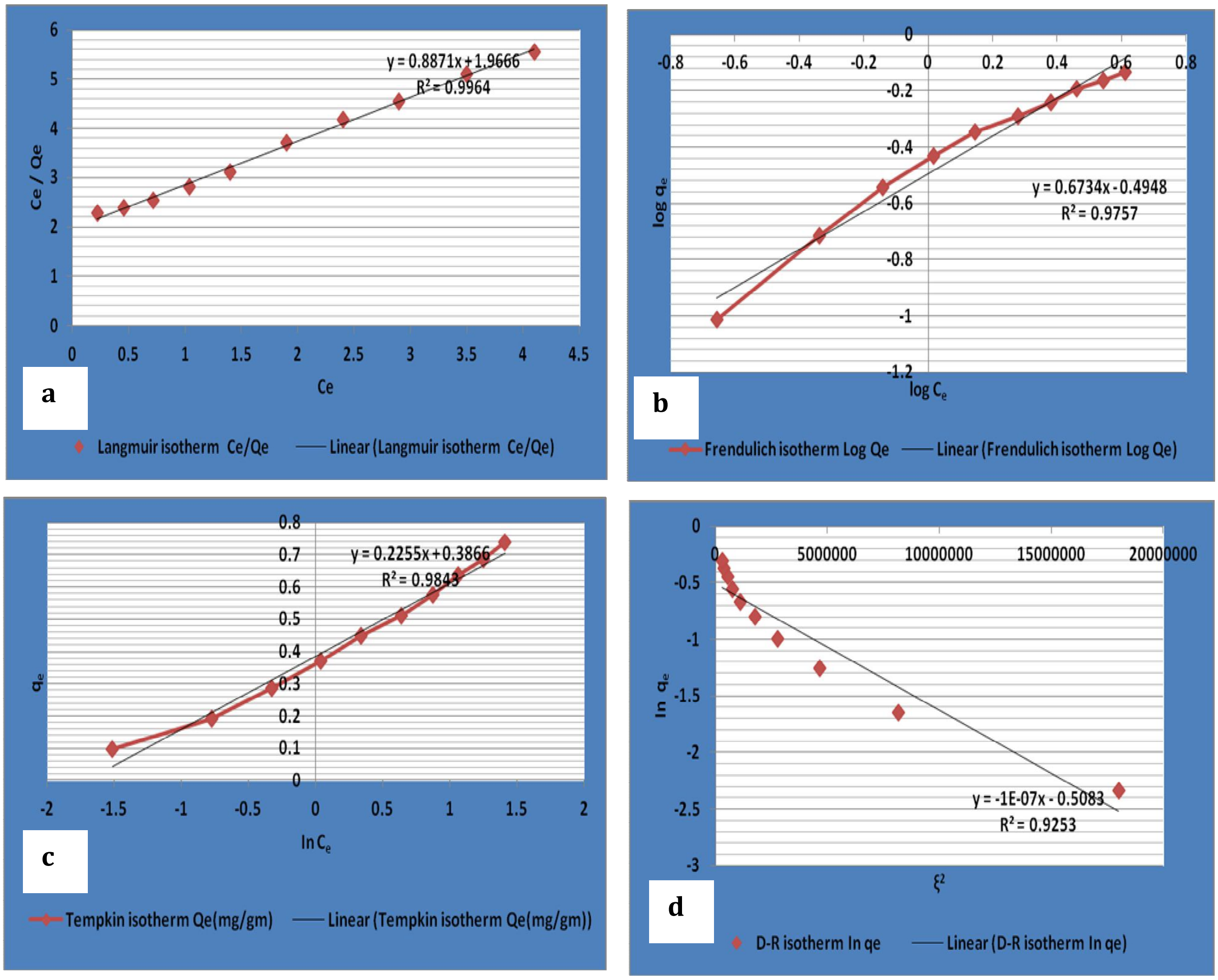


Table 1: Adsorption isotherm constants of defluoridation by adsorbent CAB

Langmuir isotherm constants		Freundlich isotherm constants		Tempkin isotherm constants		D-R isotherm constants	
q_m (mg/g)	1.127	K_f	0.32	**A**(L/g)	5.5506	q_m(mg/g)	0.6014
b (L/mg)	0.4507	**n**	1.485	**B**(mg/g)	0.2255	β(mol^2/kJ^2)	1.117
R^2	0.996	R^2	0.975	R^2	0.984	**Es**	0.669
-	-	-	-	-	-	R^2	0.925

Table 2: Initial F ion Concentration

Initial F ion concentration (mg/L)	Dimension less factor R
1	0.689
2	0.525
3	0.425
4	0.356
5	0.307
6	0.269
7	0.24
8	0.217
9	0.197
10	0.181

CONCLUSION

Biosorption is an alternative promising technique for adsorbing fluoride by using biopolymers like alginate as sorbent having several functional groups which are expected to display different affinities to various ions. Biosorption method has proven its high efficiency for removing fluoride from water as it requires a short time of treatment. These biomaterials have been recognized as potential alternatives to conventional technologies for removing fluoride from water. It may be concluded that biosorption technique utilizing biocomposites in terms of calcium alginate beads may be used as cost effective, efficient, alternative green method compared to traditional, more costly, chemical and physical remediation and decontamination techniques.

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