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EQUILIBRIUM ANALYSIS FOR BATCH STUDIES OF ADSORPTION OF FLUORIDE IN WATER USING ACTIVATED ALUMINA R AND D 651-X

WAHEED S. DESHMUKH* **and S. J. ATTAR**

Department of Chemical Engineering, Bharti Vidyapeeth, Deemed University,
PUNE – 400441, (M. S.) INDIA

ABSTRACT

Fluoride is one of the accumulative toxin. The batch adsorption studies were undertaken to asses the suitability of commercial available adsorbent activated alumina. From the earlier work, it was evident that the large surface area, higher acidity and good mechanical properties are requisites for the choice of suitable adsorbent. The most promising adsorbent used for defluoridation purpose is activated alumina. Among the various types of activated alumina, the type of activated alumina chosen for present study is UCIL R and D 651-X. To test its performance for defluoridation, the static studies have aimed at investigation of rate at which adsorption occurs under the varying condition of the major parameters of adsorption, viz. pH, dose of adsorbent, rate of stirring, contact time and initial adsorbate concentration on fluoride removal efficiency were studied and optimized by batch procedure, in which mixture of known concentration of fluoride solution continuously agitated and samples were taken at appropriate times, have been used in all experiments. The optimum sorbent dose was found 3.5g/L by varying the dose of adsorbent from 0 to 5 g; equilibrium was achieved in 100 min for the optimum pH. It has been observed that the optimum pH range for adsorption is between 6 to 7, by varying pH from 2 to10 and enhanced adsorption was obtained at pH 6.5. Maximum fluoride removal was observed to be 96% at optimum conditions. Freundlich as well as Langmuir isotherms were plotted and constants of isotherms were determined.

Key words : Fluoride ion, Adsorption, Activated alumina, Freundlich isotherm, Langmuir isotherm

INTRODUCTION

Fluorine the most electronegative of all elements, has not only notable chemical properties but also physiological properties of great importance to human health and well being. Fluorine is the most highly reactive element of halogen family. The chemical

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* Author for correspondence; E-mail:awasdk@gmail.com; Phone +91-7258-224244, Fax:+91-710-4236458

activity of the fluoride ion makes it physiologically more active than any other elemental ion. Fluoride is a salt of element fluorine. Small amount of it is found in seawater, bone, teeth and in ground water mainly as fluoride ion. Most of the fluorides associated with monovalent cations such NaF and KF, are water soluble, while that one formed with divalent cations such as CaF_2 and PbF_2 are generally insoluble. With low concentration of fluoride ion, enzymatic processes may be either inhibited or stimulated and interactions with other organic and inorganic body components may occur that are of great importance for humans.

Fluoride has a dual significance. If its content is less, then it may result in problems, like dental caries. World Health Organization (WHO) recommended it in the range of 0.1-0.5 ppm. The standard of United States of America is between 0.6-1.5 ppm. Thus, the requirement of fluorine varies among countries and depends on the geography and the age of people involved. An intake of more than 6 mg of fluoride per day results in fluorosis. The influence of water quantity on the incidence of fluorosis and the effect of Ca^{2+} and Mg^{2+} and alkinity was studied by Bhargava and Killedar[1]. The occurrence of high fluoride concentration beyond permissible limit in ground water is a problem faced by many countries notably India, Srilanka, Pakistan, China and parts of east Africa. Fluoride epidemic has been reported in as many as 19 states of India and Union territories. India is among 23 nations in the world, where the fluoride contaminated ground water is creating the health problems. The state of art report of UNICEF confirms the fluoride problem in 177 districts of 20 states of India. The high fluoride levels in the drinking water have increased the importance of defluoridation studies. The magnitude of the problem is sinking in an effort are being made towards defluoridation of drinking water, combating the debilitating fluorosis and taking steps to prevent and control the disease. Defluoridation is the process of removal of fluoride ion in drinking water.

Several methods have been suggested from time to time for removing excess fluorides from water; these are adsorption, ion exchange, precipitation and membrane separation. Nalgonda technique developed by NEERI is commonly preferred at all levels because of its low price and ease of handling. Adsorption is the process considered to be efficient to defluoridate the water. Researches were carried on different adsorbents, viz, activated carbon, processed bone char powder, activated bauxite, fly ash, granular calcite, alum, lime etc.[1-3]. Some of researchers also tried for the adsorbent prepared from the natural materials such as dry powder, holly oke, neem bark powder, activated cotton, jute carbon, leaf powder adsorbents[4,5].

The different methods so far tried for removal of excess fluoride from water can be broadly classified into four categories. (a) Adsorptive methods (b) Ion exchange methods (c) Precipitation methods and (d) Miscellaneous Methods. Some defluoridation techniques developed to control fluoride in water are reverse osmosis, adsorption method using sunflower plant baggase ash, burnt bone powder etc. as the adsorbent. However, due to high cost or lower efficiency, or non-applicability on mass scale, these techniques are not much in use.

The present work includes the defluoridations using activated alumina as an adsorbent by batch adsorption technique. (R and D 651-X) i.e. one of the type of commercial activated alumina.

EXPERIMENTAL

Materials and methods

All reagents used are of AR grade. Fluoride stock solution was prepared by dissolving 221 mg anhydrous sodium fluoride in 1000 mL distilled water in volumetric flask. Fluoride standard solution was prepared by diluting 100 mL stock solution to 1000 mL distilled water in volumetric flask. This 1 mL solution has 0.1 mg of fluoride.

Dosing of adsorbent was done in wet basis through 5% slurry prepared in distilled water. The characteristics of activated alumina used are given in the Table 1.

Table 1 : Specification of activated alumina (R and D 651-X)

S. No.	Description
Size	1/16” Extrudates
Pore volume	0.65 c. c. /g
Pore volume distribution	About 60% pores between 29-100 A units
Bulk density	0.5 Kg/Litre
Crushing strength	3.5 Kgs Dwl
Surface area	About 220 m^2/g
Attrition loss	Less than 5%
Phase of alumina	Gamma

Equipment

Fluoride ion was estimated by fluoride ion meter as per standard methods. pH meter (Hanna Portable). Batch adsorption studies were conducted using jar test apparatus

(Scientific Corporation, India) equipped with stirring paddles with provision for controlling mixing speed.

RESULTS AND DISCUSSION

In order to apply the adsorption technique successfully, it is necessary to determine the optimum conditions of the important parameters, which affect the extent of adsorption. Knowledge of the optimal conditions would herald a better design and modeling process. Thus, the effect of some parameters like pH, contact time, dose of adsorbent, initial concentration of fluoride ion and stirring rate was considered to determine extent of adsorption. Adsorption studies were performed by batch technique to obtain the equilibrium data and rate of adsorption. Experiment were carried out by taking suitable adsorbent dose with 100 mL of solution containing known concentration of fluoride ion. Initially, the stirring rate maintained was 30 rpm. Sample containing fluoride ions were maintained at a desired pH by adding 0.5N HNO_3 or 0.1M NaOH. All the experiment were conducted at room temperature (29 ± 0.5ºC).

Effect of pH

The pH has a very significant role on the adsorption of fluoride as it affects the solubility of fluoride ion to a great extent. The pH of the aqueous solution is the controlling factor in the adsorption process and hence, it becomes necessary to determine pH values, where maximum adsorption will take place. pH was adjusted either by adding HNO_3 or 0.1M NaOH. The role of hydrogen ion was studied by taking 100 mL of solution having initial concentration 5 mg/L with dose of adsorbent 2 g/L by keeping contact time of 60 minutes; pH was maintained in the range of 2 to 10 and the stirring rate was maintained at 30 rpm.

It was observed (Fig. 1) that the percentage of fluoride removal increased in the solution for pH from 4 to 7. Further increasing pH from 6 to 7, pH reaches to its maximum value and then it decreases. Result shows that the adsorption reached maximum at normal water pH of 7. Hence the optimum pH 6.5 was maintained for further studies. In their study, Choi and Chen[5] reported that at pH > 7, silicates and hydroxyl ions appeared to compete more strongly with fluoride ions for alumina exchange sites. At pH < 7, the soluble alumino–fluoro complexes are formed resulting in the presence of aluminum ions in the treated water.

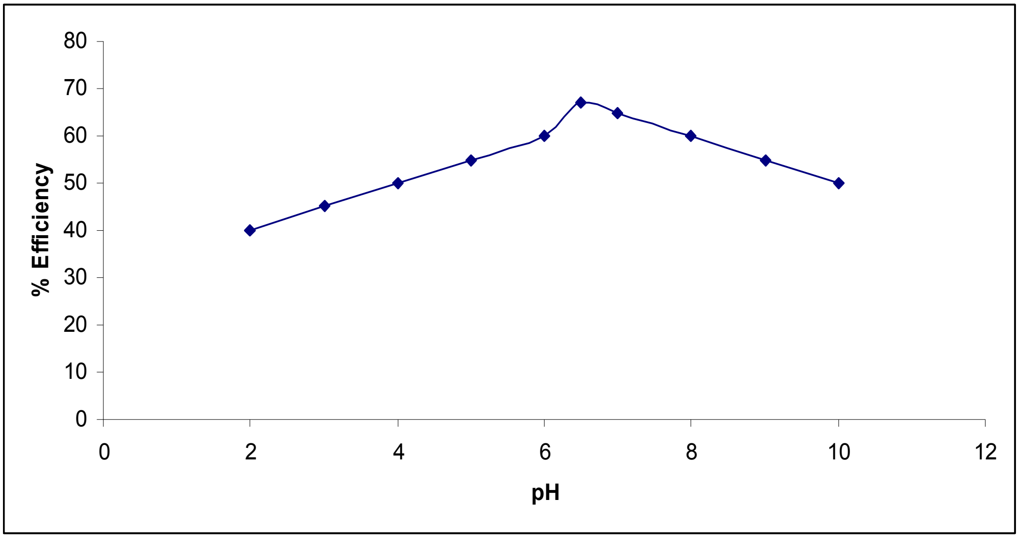

Fig. 1: Effect of pH on % removal of fluoride ion. (Adsorbent dose : 2g /l, volume : 100 mL, initial adsorbate concentration : 5 mg/L, contact time : 60 min, stirring rate : 30 rpm.)

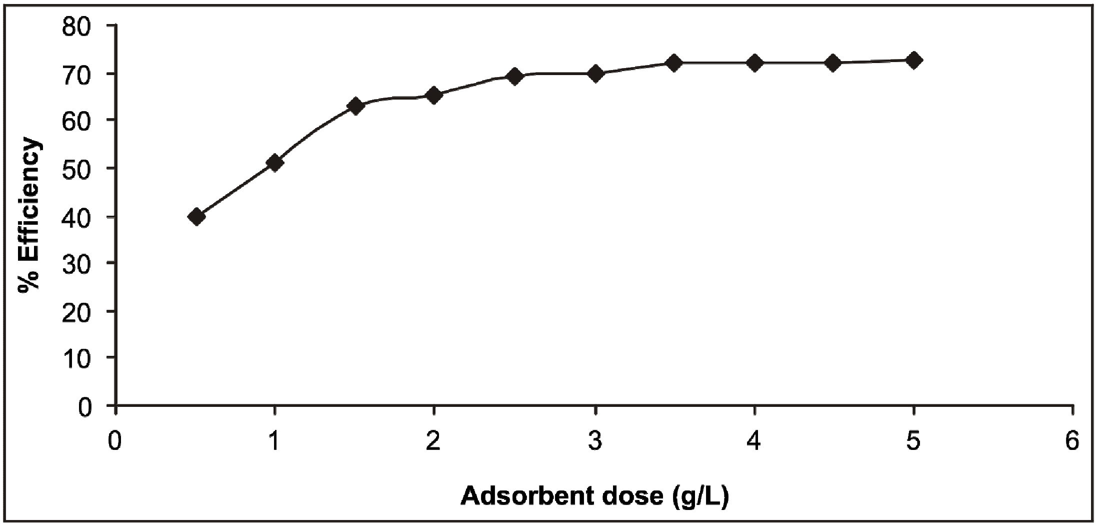

Fig. 2 : Effect of adsorbent dose on % removal of fluoride ion. (pH : 6.5, volume : 100 mL, initial adsorbate concentration : 5 mg/L, contact time : 60 min, stirring rate : 30 rpm.)

Hence, it is preferable to carry out defluoridation at normal water pH, to avoid aluminum dissolution and moreover no acid/alkali treatment is required after treatment. It has been observed by Jamode et al.[4,5] that lower pH yields the maximum efficiency for fluoride removal using biosorbent.. This may be due to neutralization of the negative charges at the surface of biosorbent by greater hydrogen concentration at lower pH values. This reduces hindrance to diffusion of negatively charged fluoride ions on to the increased active surface of treated biosorbent. Similar results were observed using fish bone charcoal[1, 6].

The effect of adsorbent dose on the removal of fluoride ion was studied by keeping fluoride ion concentration constant. The response of adsorbent dose on the removal of fluoride shows that an increase in the adsorption occurs with the corresponding increase in the dose of adsorbent. The increase in the removal efficiency with the simultaneous increase in adsorbent dose is due to increase in the surface area and hence, more active sites are available for adsorption of fluoride. The adsorbent dose was varied in the rage of 0.5 to 5.0 g/L, by maintaining optimum pH 6.5, contact time 1 hour, with a stirring rate of 30 rpm. The result shows that the maximum dose of adsorbent was observed 3.5 g/L, for initial concentration of 5 mg/L, which gives 70% fluoride ion removal efficiency. For further study, the optimum dose was considered as 3.5 g/L

Effect of stirring rate

Studies were conducted to find the effect of stirring rate on the fluoride removal efficiency. For this study, the stirring rate was varied between 20 to 60 rpm at the optimum values of pH and dose of adsorbent, with a contact time of 1 hour and initial concentration of 5 mg/L.

The influence of rate of stirring on the extent of adsorption is shown in Fig. 3

It reveals that the fluoride removal is a function of stirring rate. At a given time, fluoride removal increases as the rate of stirring was increased[6,7]. The removal was 70% at 30 rpm and it attains 85% at the stirring rate of 50 rpm. The percentage adsorption is less at lower stirring rate and increases with the stirring rate up to 50 rpm and thereafter remains more or less constant. The reason for the increase in the efficiency may be due to increase in the contact between adsorbate and adsorbent at higher speeds. Further increase in the rpm beyond 50 does not show any increase in the adsorption and hence, 50 rpm was considered the optimum stirring rate.

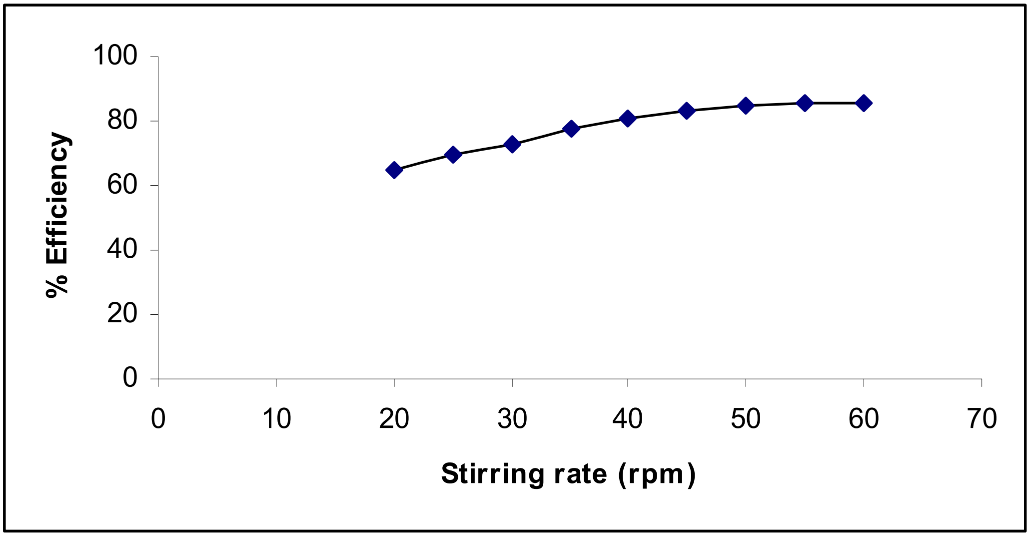

Fig. 3: Effect of stirring rate on % removal of fluoride ion (Adsorbent dose : 3.5 g /L, volume : 100 mL, initial adsorbate concentration : 5mg/L, contact time : 60 min, pH = 6.5)

Effect of contact time

Studies on effect of contact time on the fluoride removal efficiency was carried by varying it from 30 to 120 minutes keeping pH 6.5, dose 3.5 g/L and initial concentration of solution 5 mg/L. Rate of stirring was maintained to its optimum value of 50 rpm.

Fig. 4 shows the progression of adsorption reaction and percentage removal of fluoride for different contact times. It is found that removal of fluoride ions increases with increase in contact time to some extent; however, further increase in the contact time does not increase the uptake due to deposition of fluoride ions on the vacant sites of adsorbent. Preliminary investigation shows that the rate of adsorption is quite high and most of adsorption takes place within first hour. Typically 85% of adsorption occurs during the first hour and it increases up to 100 minutes and remains constant. For further optimization of other parameters this contact time was considered as the equilibrium time. The changes in the extent of adsorption might be due to the fact that initially all the adsorbent sites were open and the solute concentration was high. Later, the fluoride uptake by the adsorbent decreased significantly, due to decrease in the active sites. It indicates that the possible monolayer of fluoride ions on the outer surface, pores of the adsorbent and pore diffusion on to inner surface of adsorbent particles through the film due to continuous mixing maintained during the experiment[8].

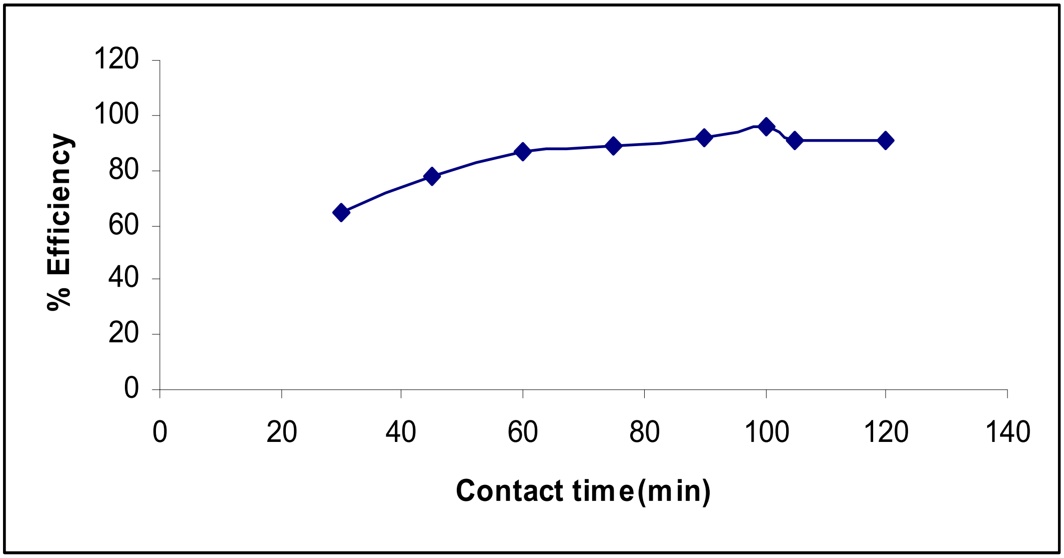

Fig. 4 : Effect of contact time on % removal of fluoride ion (Adsorbent dose : 3.5 g/L, volume : 100 mL, initial adsorbate concentration : 5 mg/L, stirring rate : 50 rpm, pH 6.5)

Effect of initial fluoride ion concentration

The effect of initial concentration on adsorption capacity of the activated alumina R and D 651-X was studied by keeping pH, contact time, rate of stirring, dose of adsorbent and contact time at their optimum values of 6.5, 50 min., 3.5 g/L and 100 mins respectively, by varying the initial concentration from 5 mg/L to 20 mg/L.

The results (Fig 5.) indicate that the percentage of removal of fluoride ion decreased as the initial concentration of fluoride ion increases. The percent removal efficiency was observed at 96.1% at initial fluoride concentration of 5 mg/L and it goes decreasing up to 70% at initial fluoride ion concentration of 20 mg/L.

This is due to the fact that capacity of adsorbent materials gets exhausted sharply with the increase in the initial fluoride ion concentration.

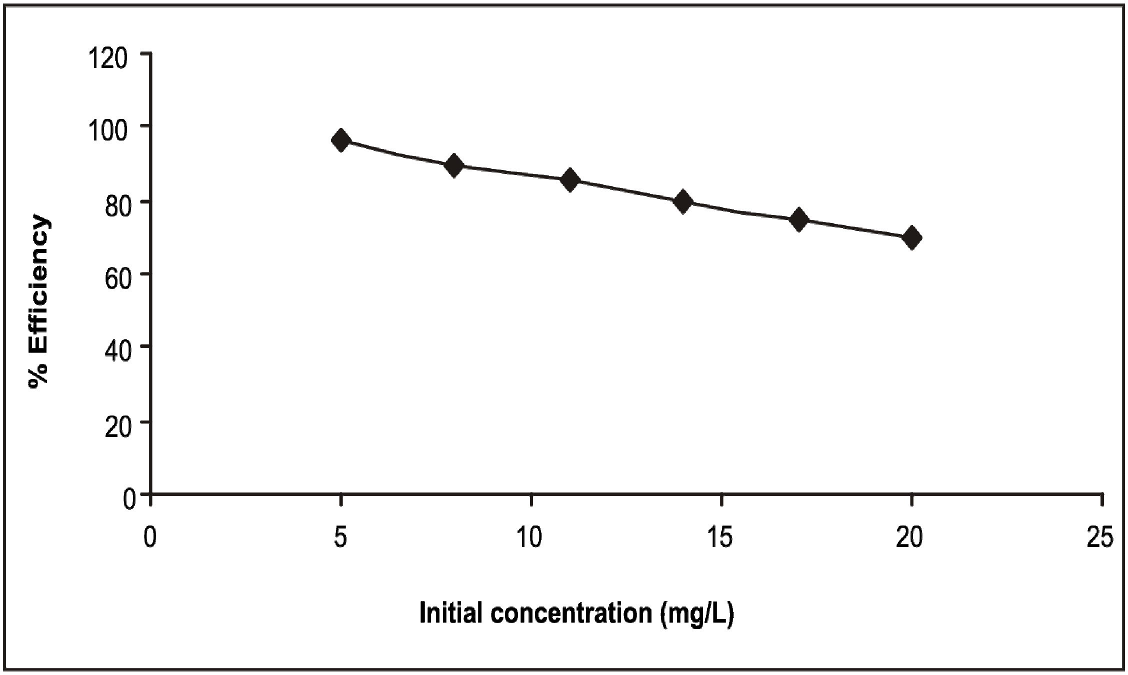

Fig. 5: Effect of initial concentration on % removal of fluoride ion (Adsorbent dose: 3.5 g/L, volume : 100 mL, initial stirring rate : 50 rpm, pH 6.5, contact time : 100 min.)

Sorption mechanism

Adsorption of the solute involves the establishment of equilibrium between the amount adsorbed on the surface and the concentration of substance in solution. The variation of extent of adsorption with concentration of solute is usually represented by the Freundlich and Langmuir adsorption isotherms. Adsorption isotherms help in determining the feasibility of activated alumina[9]. Freundlich and Langmuir isotherms were plotted to provide deep insight to the adsorption of fluoride on activated carbon.

Freundlich isotherm

The isotherm provides the detail idea about the effectiveness of the adsorbent and the maximum amount of adsorbate will get adsorbed by adsorbent. The Freundlich equation is basically empirical but is often useful as a means for data description. The general form of Freundlich isotherm is given in the following equation:

$$q_e = K_f C_e^{1/n} \quad \ldots(1)$$

The linearised form of Freundlich isotherm is given by the following equation –

$$\text{Log}\,(q_e) = \log K_f + 1/n \log C_e \quad \ldots(2)$$

Where

$\log(q_e)$ is the amount of fluoride ions adsorbed per unit weight of adsorbent (mg/g)

C_e is the equilibrium concentration in solution (mg/L)

K_f and 1/n are the Freundlich constants.

Freundlich isotherm (Fig. 6) was plotted with log q_e vs. log C_e. From the graph, the value of K_f was obtained as 0.064 and 1/n = 0.485 and thus, Freundlich isotherm is,

$$q_e = 0.064\, C_e^{0.485}$$

A smaller value of 1/n, points out a better adsorption mechanism and formation of relatively stronger bond between adsorbate and adsorbent.

If 1/n < 1, bond energies with surface density, if 1/n > 1, bond energies decrease with surface density and if 1/n = 1 all surface sites are opening in order to generate the equilibrium data C_e (mg/L). The different adsorbent doses are applied to confirm the applicability of Freundlich isotherm.

Langmuir isotherm

Langmuir isotherm is based on the assumption that point of valance exists on the surface of the adsorbent and that each of these site is capable of adsorbing one molecule. It is assumed that the adsorption sites have equal affinities for molecules of adsorbate and that the presence of adsorbed molecules at one site will not affect the adsorption of molecules at an adjacent site. The Langmuir equation is commonly written as

$$Q_e = Q_0\, bC_e/(1 + bC_e) \quad \ldots(3)$$

where q_e is the amount adsorbed (mg/g) and C_e is the equilibrium concentration of adsorbate (mg/L), Q_0 and b are Langmuir constants related to capacity and energy of adsorption respectively. Thus from Fig. 7, the Langmuir equation for defluoridation using activated alumina (R and D 651-X) is –

$$q_e = 0.156\, C_e / (1 + 0.14\, C_e)$$

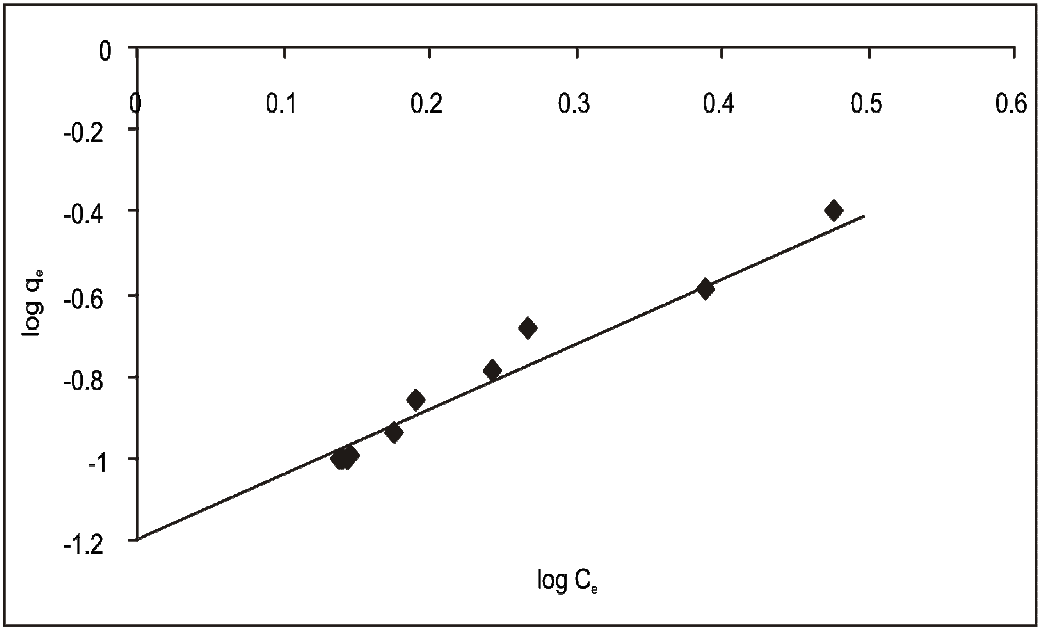

Fig. 6 : Freundlich isotherm

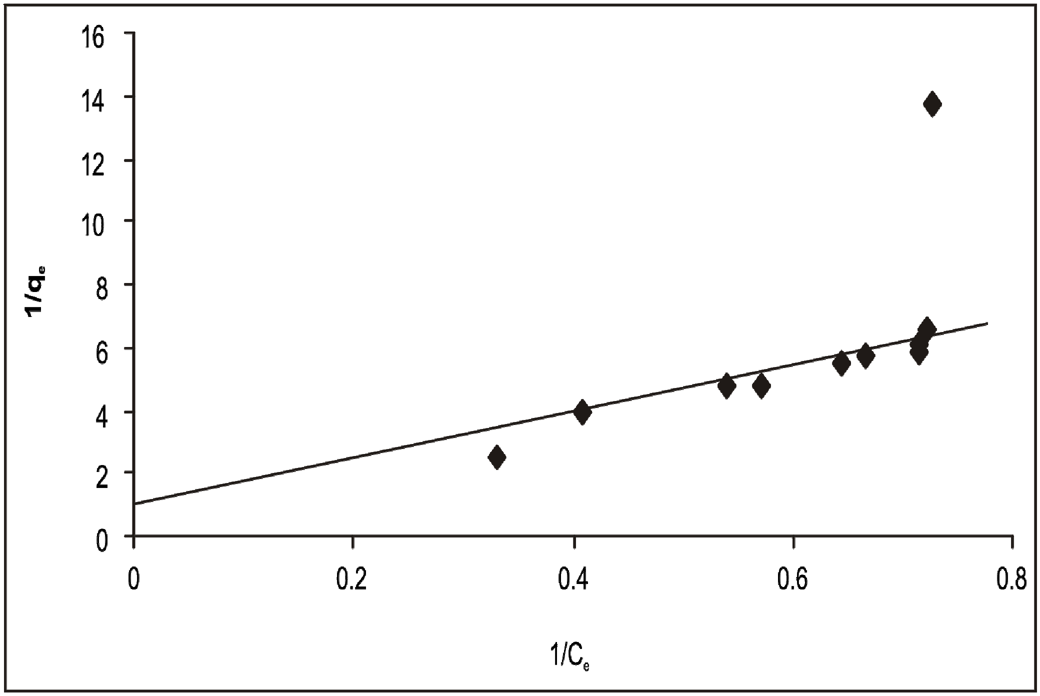

Fig. 7: Langmuir isotherm

CONCLUSIONS

Based on these studies, it is concluded that activated alumina R and D 651-X has shown promising results for the removal of fluoride. The uptake of fluoride is possible in the range of pH 2 to 10. The adsorption reached maximum at normal water pH of 7. Hence, it is preferable to carry out defluoridation at normal water pH, to avoid aluminum dissolution. From the present study it observed that fluoride removal for adsorbent increases with time attaining equilibrium within 1 to 1.5 hour. The percentage of fluoride removal was found to be function of adsorbent dose and contact time at a given initial solute concentration. It increases with time and adsorbent dose, but declines with higher initial solute concentration with time and adsorbent dose. The present study on defluoridation using activated alumina (R and D 651-X) follows Freundlich as well as Langmuir adsorption isotherm.

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