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FLUORIDE REMOVAL USING ACTIVATED ALUMINA: A CASE STUDY OF BHOOMA CHOTA WATER

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ABSTRACT

The adsorption of fluoride, from a fluoride contaminated ground water sample from the village, Bhooma Chota, District Sikar, in the Sate of Rajasthan, India has been studied using activated alumina grade DF-101. The fluoride absorption capacity (q_t) has been fitted into the psuedo first order adsorption, pseudo second order adsorption, Elovich and intraparticle diffusion models. It has been found that the kinetic data fits best in the pseudo second order rate equation giving very high correlation coefficient (R^2= 0.991). The modelled fluoride absorption capacity (q_t) has been calculated from the various equations using the constants derived from the least square regression plots. The calculated q_t values, model the experimental data very well, for the pseudo second order and Elovich equations, as is evident from the sum of square error calculations. Fluoride removal is through a combination of surface absorption and intraparticle diffusion. A study of fluoride removal process with increasing dosage of activated alumina reveal that though the percentage of fluoride removal increases with activated alumina, the adsorption capacity at equilibrium decreases. The minimum dosage of activated alumina which causes the maximum percentage removal of fluoride from water, while at the same time brings forth its highest equilibrium absorption capacity has been determined.

KEYWORDS: **Activated alumina, fluoride adsorption**

RESUMO

A adsorção de fluoreto a partir de água contaminada do villarejo Bhooma Chota, Distrito de Sikar, Estado de Rajasthan, Índia foi estudada usando alumina ativada, grau DF-101. A capacidade de absorção do fluoreto (q_t) foi analizada com vários modelos. Os resultados experimentais concordaram melhor com a equação de pseudo-segunda ordem (R^2=0.991). A remoção do fluoreto acontece através de uma combinação de absorção na superfície e difusão intraparticular. A dosagem mínima de alumina ativada para a melhor remoção de fluoreto foi determinada.

PALAVRAS CHAVE: **Alumina ativada, Adsorção de fluoreto**

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INTRODUCTION

Ground water is the major source of drinking water in India [1]. In most cases particularly in rural areas it is not treated before being used for drinking purposes. Fluoride is a major contaminant of ground water in India, particularly in the western desert state of Rajasthan [2]. Drinking water containing fluoride beyond the permissible limit of 1.5 ppm for prolonged periods causes Fluorosis [3]. The first signs of Fluorosis are yellowing and damage to the tooth enamel, followed by pain in knees, ankles and other joints. People afflicted with Fluorosis are unable to bend and do physical labour as it effects the muscles also [3]. It has been reported earlier that the ground water of the Sikar District of Rajasthan contains fluoride beyond permissible limits [4 (a-c)]. Children with mottled teeth, the first signs of Fluorosis are a common sight. There are unusually high incidences of the middle age population suffer from pains in joints, and stiffening of spine [5].

Activated alumina is known to absorb fluoride from water [6(a-l)]. Different grades of activated alumina are available from different manufactures [6f]. Domestic Defluoridation units have been distributed in Rajasthan India [7], using indigenously manufactured activated alumina grade DF-101 [8 (a-c)].

In the process of designing and fabricating simple domestic defluoridation filters of our own design, we decided at first to test the efficacy of DF-101 grade activated alumina to remove fluoride from locally available fluoride contaminated ground water and in this paper we report the case study of kinetics of fluoride adsorption from the ground water of a nearby village called Bhooma Chota in the Lakshmangarh Tehsil of Sikar District in Rajasthan, India.

EXPERIMENTAL

Fluoride was measured using a Fluoride ion meter and Fluoride combination electrode (Orion-Thermo Scientific, USA) using TISAB buffer. Activated alumina grade DF-101 was procured from M/S Bhargava Industries, Surat, Gujrat, India. All shaker experiments were done in duplicate. 100 ml of Bhooma Chota Middle tube Well water was shaken with fixed quantity of Activated alumina grade DF-101 at 180 rpm, at ambient temperature (20 deg °C) for a specified times. The activated alumina was filtered from water using a Whatman 42 filter paper and the residual fluoride was measured immediately.

RESULTS AND DISCUSSION

Bhooma Chota (Lat. 27.78 Long. 74.93 and altitude 354 m from msl,) is a big village with an area 1,089 hectares and population of 1,600 (2001 census). It has a dry, extreme climate (max. summer temp 48°C and minimum winter temp of 0°C) with an average annual rainfall 494 mm. The area has no mentionable natural resources. The region is arid, semi desert like with coarse sandy soil and little or no moisture content. There are frequent dust storms in summer. There are three deep tube wells (originally dug wells) which supply piped water supply to all houses. Of these, the tube well located at the centre of the village meets the domestic and drinking water needs of two third of the households. All people from the village are show signs of dental Fluorosis (fig. 1).

Water samples were collected on 15th January 2011 from the tubewell located at the centre of the village in Bhooma Chota (depth 102 m) and analyzed using standard procedures and the results of the analysis are as follows pH 8.9, TDS 1500 ppm (TDS meter), chloride 298 ppm (argentometric), carbonate 90 ppm, bicarbonate 1784 ppm (titrimetric H_2SO_4), Ca hardness 14 ppm (EDTA, P and R indicator), Mg hardness 43 ppm (EDTA, difference), sulphate 1.5 ppm (colorimetric), nitrate 100 ppm (phenol disulphonic acid), Na^+ 350 ppm (flame photometer), K^+ 13 ppm (flame photometer), fluoride 2.41 ppm (ISE). Notice the particularly high concentration of bicarbonates which are known to interfere with the fluoride adsorption capacity of activated alumina [6b,] [9].

The manufacturer's specifications for activated alumina (DF-101) balls are given in table 1.

The absorption capacities at equilibrium and at time t, q_e and q_t (mg/gm) are defined as $q_e = \frac{(C_0 - Ce)V}{W}$ (1)

and

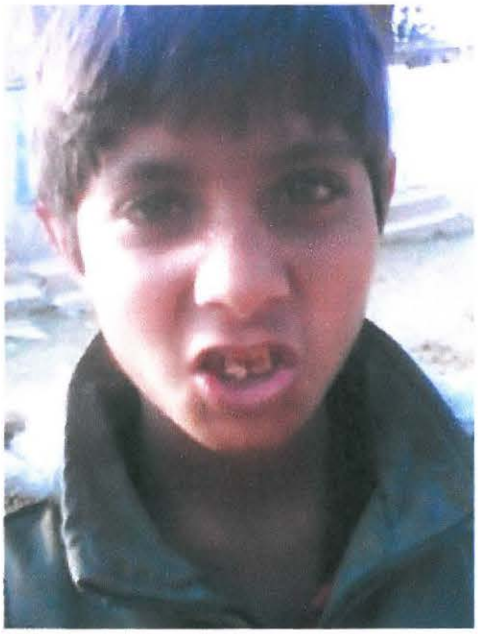

Fig. 1. Photograph of a Boy from village Bhooma Chota Showing Symptoms of Dental Fluorosis.

Table 1. Characteristics of Activated Alumina (DF-101) Balls (Manufactures Specifications)

a) Physical Properties

Parameters	**Values**
Sizes	0.40 -1.2 mm
Surface Area, m^2/g	360
Total Pore Volume, cc/g	0.50
Packed Bulk Density, gm/cc	0.769
Abrasion loss, wt %	0.5
Static Adsorption @60% R.H at 30^0C	22
LOI (250-1000°C)	6.5

b) Chemical Properties

Constituents	% Wt
Al_2O_3	92.5
SiO_2	0.025
Fe_2O_3	0.025
Na_2O	0.30

$$q_t = \frac{(C_0 - C_t)V}{W} \tag{2}$$

$$\%removal = \frac{(C_0 - C_t)}{C_i} \times 100 \tag{3}$$

Where

C_o = initial concentration of fluoride in water (mg/l)

C_e= equilibrium concentration of fluoride in water (mg/l)

C_t= concentration of fluoride in water (mg/l) at time t

V = volume of solution (L)

W= weight of Activated Alumina used (g)

Taking C_o=2.41 ppm and C_e= 0.27 ppm yields $q_e = 0.214$ mg/gm.

The time profile of percentage removal of fluoride from ground water has been determined from the average of two experiments is shown in Fig. (2). A plot of the fluoride removal versus time plot is smooth and continuous leading to saturation indicating the possible monolayer coverage of fluoride ions on the surface of the activated alumina. Fluoride removal is 88% at saturation level.

The kinetics of fluoride adsorption from ground water on AA has been analyzed by using different kinetic adsorption models and is discussed below.

Pseudo First Order Rate Equation

The experimental data has been fitted into the Lagergen's [10] pseudo first order rate equation

$$\log(q_e - q_t) = \log q_e - \frac{K}{2.303} t \tag{4}$$

where K, is the pseudo first order rate constant (min^{-1})

If the adsorption process is to follow the Lagergen's equation, a plot of $\log(q_e - q_t)$ vs. t should yield a straight line. We find that a linear plot is obtained (fig.3) (R^2=0.9547). Notice however that there is considerable deviation of the experimental data from the best fit regression line. We obtained the value of pseudo first order rate constant K= 0.029 min^{-1} and thereby calculated the theoretical value of q_e= 0.1557 mg/gm which considerably differs from the experimental value mentioned above.

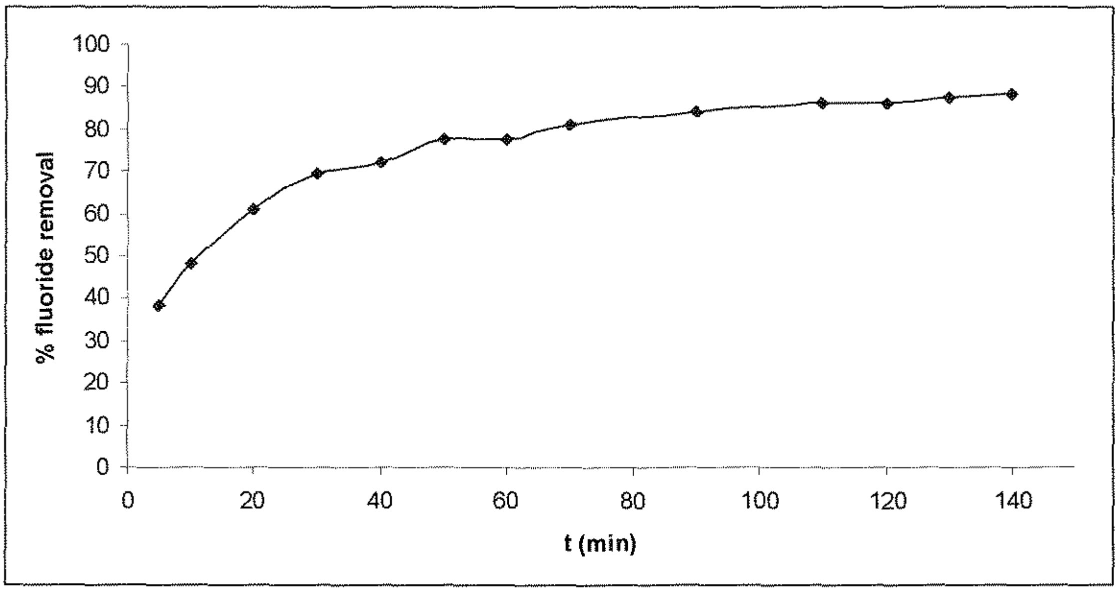

Fig.2.Experimental time profile of percentage removal of fluoride by AA from ground water.

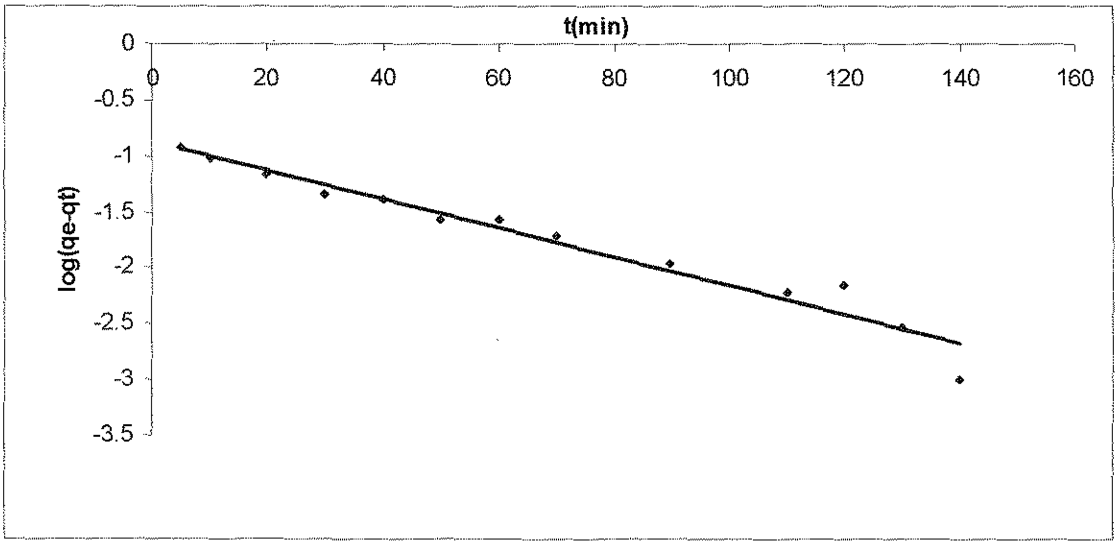

Fig. 3. Pseudo first order adsorption kinetics of fluoride on AA from ground water.

Pseudo Second Order Rate Equation

We tested experimental data with the Ho [11a,b] second order rate equation

$$\frac{t}{q_t} = \frac{1}{h} + \frac{t}{q_e} \tag{5}$$

Where $h = K(q_e)^2$ (6)

If the adsorption process is to follow the pseudo second order rate equation, a plot of t/q_t vs. t should yield a straight line. We find that a linear plot is obtained (fig. 4) (R^2=0.9991). Notice that the t/q_t vs. t plot shows an excellent agreement with experimental data. The pseudo second order rate constant was found to be K= 0.4305 gm mg^{-1} min^{-1}. The calculated q_e = 0.226 mg/gm value agrees well the experimental value obtained.

Elovich Equation

The Elovich equation [12] as simplified by Chien and Clayton [13] and with the boundary conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$ [14] is

$$q_t = \frac{1}{\beta}(\ln \alpha\beta) + \frac{1}{\beta}(\ln t) \tag{7}$$

where α and β are constants. While α is the initial adsorption rate, β is related to the extent of surface coverage and the activation energy for chemisorption. This equation was used to fit the experimental data and if the equation is valid then a plot of q_t vs. lnt should yield a straight line. It was found that the straight line (fig. 5) had a R^2 = 0.9887. The Elovich constants α and β values were found to be 0.102 mg g^{-1} min^{-1} and 27.77 g/mg. The R^2 values are lower than pseudo second order model discussed earlier.

Weber and Morris Intraparticle Diffusion Model

A simplified form of Weber and Morris Intraparticle Diffusion Model [15] requires that

$$q_t = Kt^{0.5} \tag{8}$$

where K is the intraparticle diffusion rate constant (mg g^{-1} $min^{-1/2}$) .

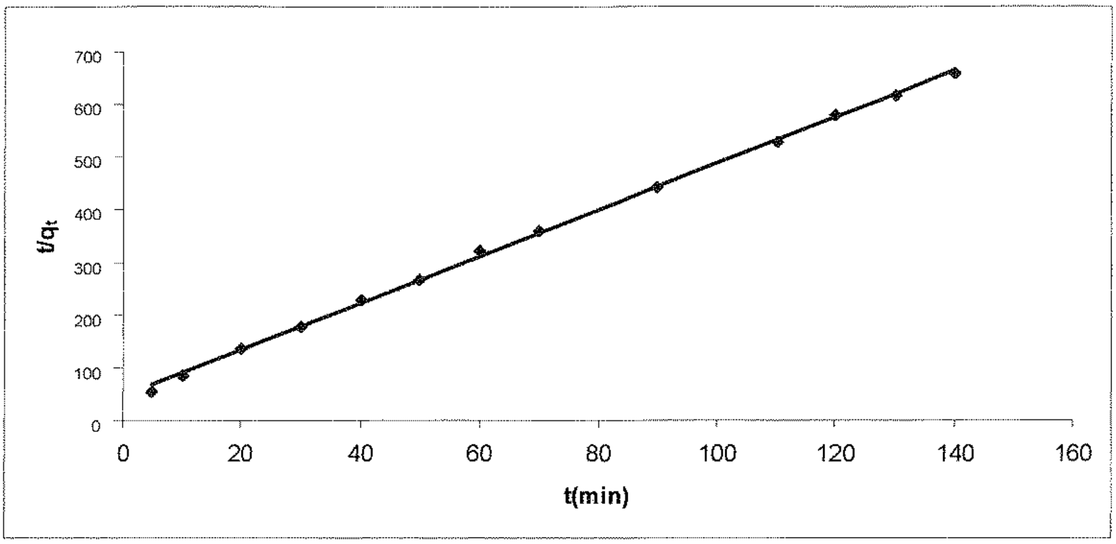

Fig. 4. Pseudo second order adsorption kinetics of fluoride on AA from ground water.

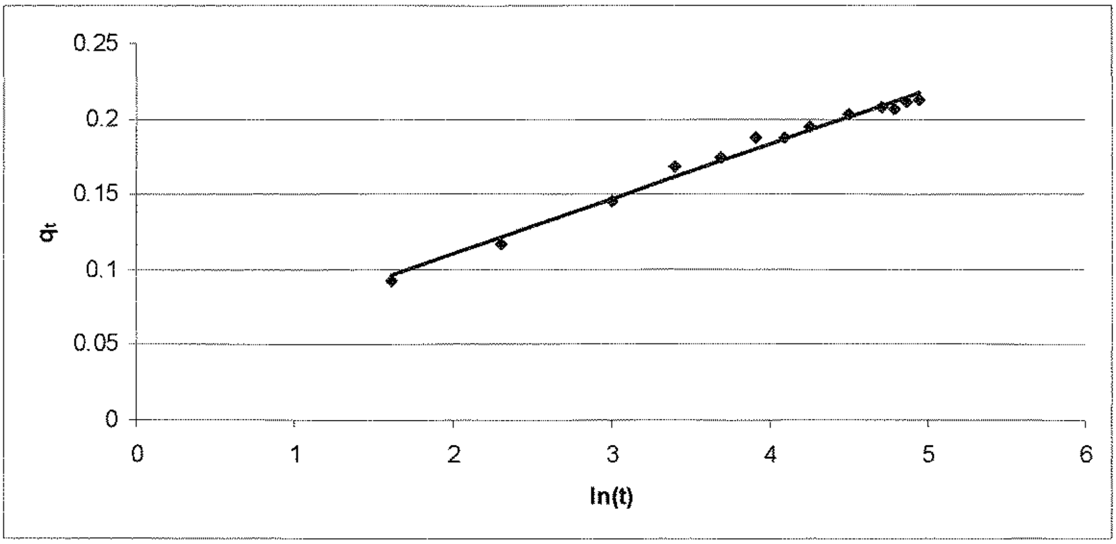

Fig. 5. Elovich adsorption kinetics of fluoride on AA from ground water.

If a plot of q_t vs. t $^{0.5}$ should pass through the origin then intraparticle diffusion is the only rate limiting step. Larger the values of C intercept, greater the contribution of the surface adsorption in the rate controlling step. On plotting the experimental data it was observed that (fig. 6) there are three distinct regions in the plot. There is a linear portion region, followed by a curved potion and finally the plateau like equilibrium portion. Notice that the linear portion starts from 5 to 30 min. Before this period nearly 40% of the fluoride is adsorbed (fig. 2). This is when the fluoride ions gets adsorbed on the most readily available adsorption sites on AA. The second stage (linear portion of the curve) is intraparticle diffusion rate controlled. The R^2 value for the initial linear portion of the curve (5 to 35 min) is 0.9986, C intercept is 0.0428 mg gm^{-1} and the intra particle rate constant value is 0.023 mg $gm^{-1/2}$ $min^{-1/2}$ (fig. 7). Though we obtain a linear relationship, the fact that the line does not pass through the origin indicates that intraparticle diffusion is not the sole mechanism contributing to the rate determining step during the time period of 5min to 30 min. In the equilibrium portion of the curve intraparticle diffusion is very slow because of the low equilibrium concentration of fluoride remaining in the solute. Such multistage adsorption phenomena with lines of different slopes have been earlier observed [6k, 16].

Modelling of Experimental q_t

The time profile of fluoride adsorption capacity of AA from ground water has been modelled using the constants determined from the four different models and the results are shown in fig. (8). A sum of squared errors (eqn. 8)

$$SSE = \sum \left(qt(\exp) - qt(calc)\right)^2 \qquad (8)$$

has been calculated for q_t of all the models (Table 2). Notice that the modelled q_t values obtained from the Elovich Equation (R^2=0.9887) has the least value of the sum of square errors, (0.000372). However, the pseudo second order kinetic model (R^2=0.9991) has a SSE= 0.00048. The difference between the squared sum of errors between the two models is marginal. On the basis of R^2 values the pseudo second order kinetic model is the most applicable to describe the kinetic behaviour the adsorption process during the

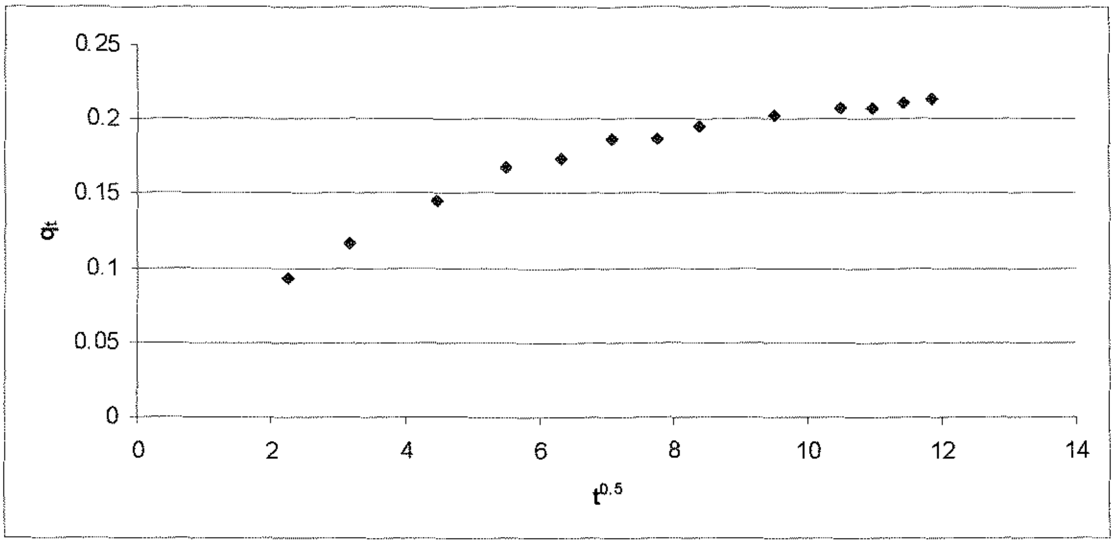

Fig. 6. Weber and Morris adsorption kinetics of fluoride on AA from ground water

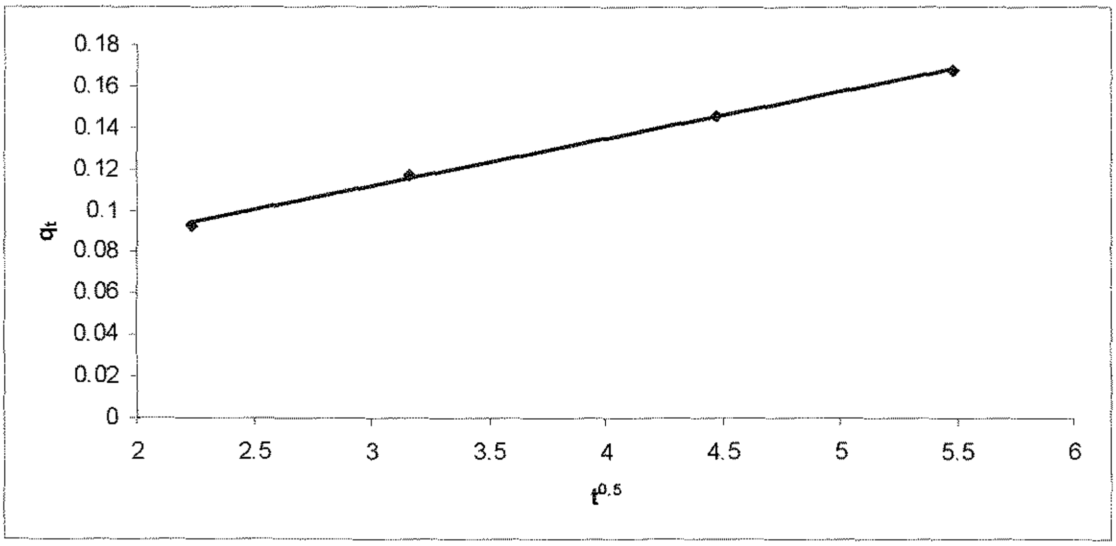

Fig. 7. Intraparticle adsorption kinetics of fluoride on AA from ground water (initial part of Weber and Morris Plot.

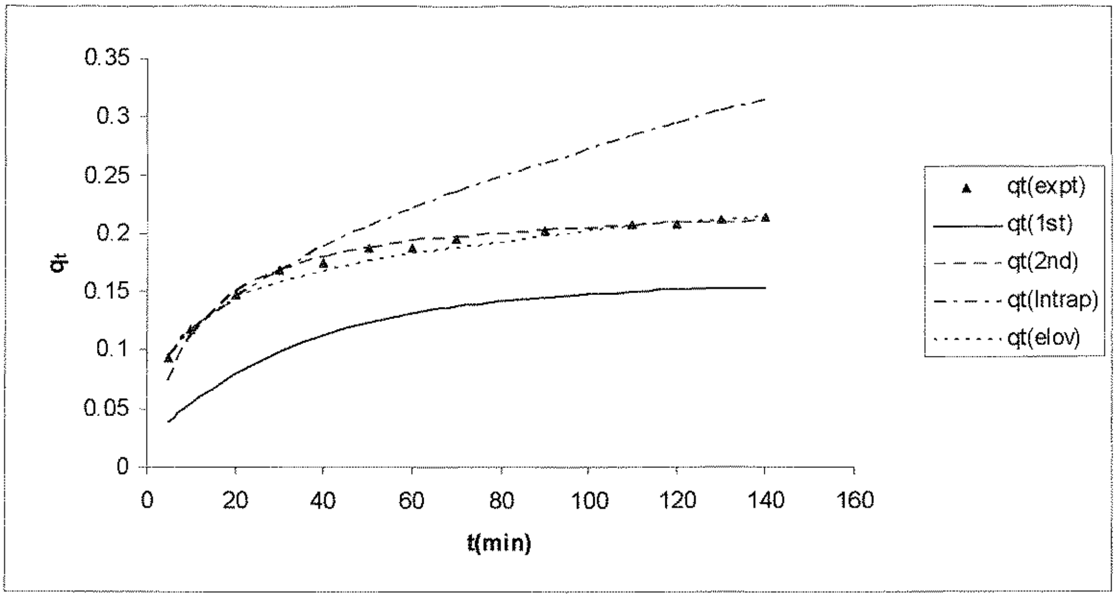

Fig. 8.Modelled and Experimental time profiles of adsorption capacity of AA for fluoride from ground water.

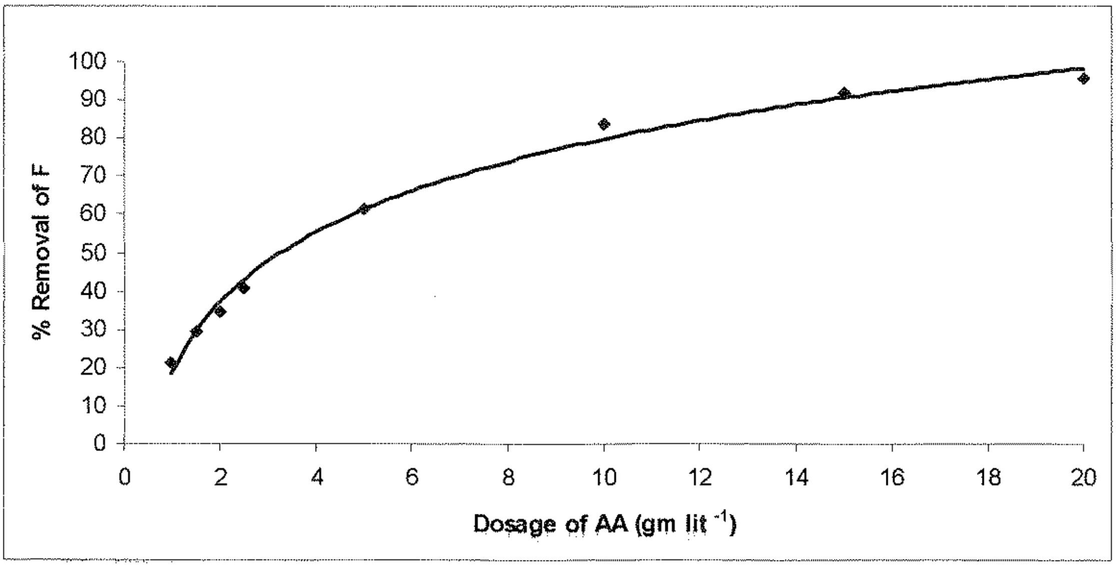

Fig. 9. Variation of percentage removal of fluoride with increasing dosage of AA.

Table 2. Sum of Square Errors of Modelled Data from Experimental Data

Model	Sum of Square Errors
Ist Order	0.04691
2nd Order	0.00048
Intraparticle Diffusion	0.03886
Elovich Equation	0.00037

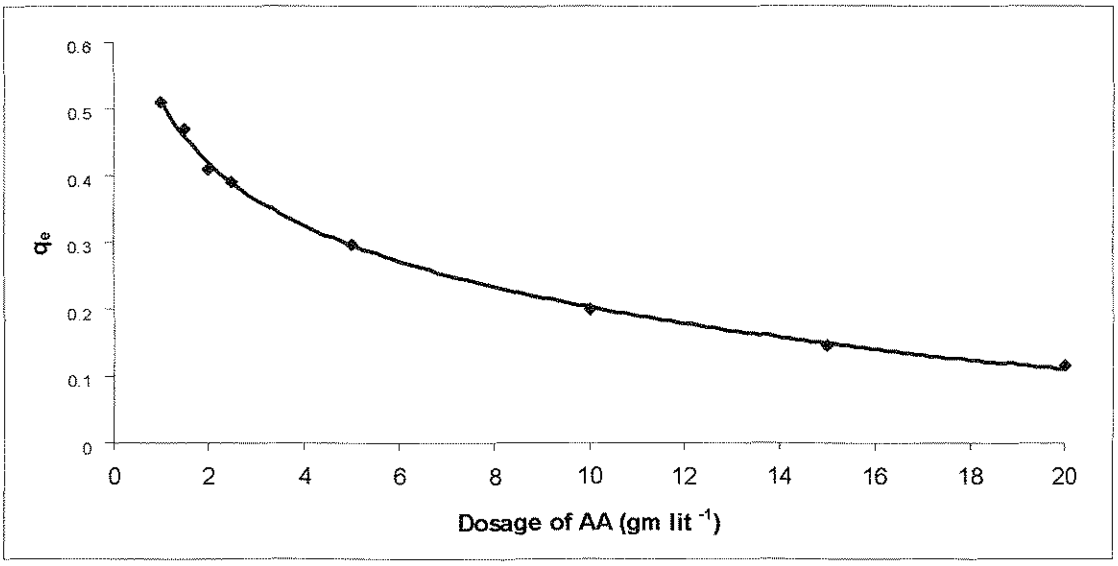

Fig. 10. Variation of equilibrium absorption capacities of AA with increasing dosage of AA.

whole adsorption process. Notice that the intraprticle diffusion model closely describes the adsorption process at the initial 5 to 30 min. (fig 8).

In order to test the effect of increasing dosage of activated alumina on fluoride removal ground water was equilibrated with increasing quantities (1-20 gm/lit) of AA. It was found that as dosage of activated alumina was increased, percentage removal of fluoride removal increased logarithmically ($R^2 = 0.9932$) (fig. 9).

This is attributed to increase in number of available active sites for fluoride adsorption. However, as dosage of AA is increased, adsorption capacity q_e decreases logarithmically ($R^2 = 0.9982$) (fig. 10). The minimum dosage of activated alumina which causes the maximum percentage removal of fluoride from water, while at the same time brings forth its highest equilibrium absorption capacity can be determined by solving the equations of the fitted lines simultaneously. A value of 0.5 gm lit^{-1} of AA has been obtained in this case. It is postulated that with increase in adsorbent dose fluoride ions are not able to saturate the active sites and consequently there is lowering of the adsorption capacity. Alternatively, adsorbent particles may agglomerate at higher adsorbent does, which would lead to decrease in surface area available for adsorption. This would in turn result in increase of diffusional path length for fluoride ions resulting in lowering of adsorption equilibrium capacity.

CONCLUSION

From the kinetic analysis of fluoride removal process it is concluded that the adsorption process of fluoride on AA DF-101 from natural water tested follows an overall pseudo second order kinetics. Good correlation coefficient values are obtained from Elovich equation also. Sum of square error calculations also supports the above findings. Intraparticle diffusion is the significant mechanism of fluoride adsorption from 5 to 30 min though it is not the sole adsorption mechanism as the plot of q_t vs. $t^{0.5}$ does not pass through the origin. In all probability the fluoride removal is through a combination of intraparticle diffusion and surface adsorption. On increasing the dosage of AA its adsorption capacity to remove fluoride decreases. This is attributed to unsaturation of the active sites and agglomeration of AA particles at higher dosages.

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