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FLUORIDE SORPTION USING *MORRINGA INDICA*-BASED ACTIVATED CARBON

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ABSTRACT

Batch adsorption experiments using activated carbon prepared from *Morringa Indica* bark were conducted to remove fluoride from aqueous solution. A minimum contact time of 25 min was required for optimum fluoride removal. The influence of adsorbent, dose, pH, co-ions (cations and anions) on fluoride removal by the activated carbon has been experimentally verified. The adsorption of fluoride was studied at 30 °C, 40 °C and 50 °C. The kinetics of adsorption and adsorption isotherms at different temperatures were studied. The fluoride adsorption obeyed both Langmuir and Freundlich isotherms and followed a pseudo first order kinetic model. The thermodynamic studies revealed that the fluoride adsorption by *Morringa Indica* is an endothermic process indicating an increase in sorption rate at higher temperatures. The negative values of $\Delta G°$ indicate the spontaneity of adsorption. SEM and XRD studies confirmed the surface morphological characteristics of the adsorbent and the deposition of fluoride on the surface of the material.

Key words: Fluoride, adsorption, langmuir isotherm, freundlich isotherm, intraparticle diffusion, thermodynamic parameters

INTRODUCTION

Fluoride is an important micro nutrient for the production and maintenance of healthy bones and teeth. Although a certain amount of fluoride gives good protection against dental decay, excess intake of fluoride ions cause dental fluorosis. When the concentration of fluoride is more than 4 mg/L it causes softening of bones, ossification of tendons and ligaments and neurological damage in severe cases (Karthikeyan, 2005). Fluoride can be removed from water by several methods. Most prevalent defluoridation technologies involve precipitation, adsorption and ion exchange mechanisms. Different adsorbent materials employed for defluoridation include activated carbon obtained from several sources, bone charcoal, tricalcium phosphate, activated alumina, alum and lime. Precipitation of fluoride with calcium, aluminum salts and lime can be done but the treated water have high pH resulting in a supplementary difficulty of eliminating excess chemicals (Fan, 2003). Adsorption is another technique in which fluoride is adsorbed onto a membrane or a fixed bed packed with resin or other mineral particle. Many techniques such as reverse osmosis, electrodialysis, Donnan dialysis, etc also have been reported to be successful defluoridation methods.(Elmidaoui, 1998).In recent years a large number of cost effective adsorbents have been reported to possess fluoride removal capacity. Few are flyash (Singh, 1990), bauxite (Express India,1998), silica gel (Wang, 1995) , zeolites (Mayadevi, 1996), spent catalyst (Liu, 1996), natural soil (Balkema, 1998) and clay minerals which were established to remove fluoride from aqueous medium through adsorption. The fluoride adsorption efficiency of these materials mainly depends on the nature of adsorbents. Fluoride adsorption capacity of activated carbon prepared from agriculture waste is experimentally verified. Activated carbon obtained by burning and carbonization of the *Morringa Indica* bark, possess appreciable defluoridation efficiency. The charred material is carbonized and the activated carbon having different pore structures and surface area were prepared by the method of pyrolysis and activation (Lee, 2003). This material has high

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surface area and strong sorption capacity towards various sorbates. The crystalline structure, fracture, surface edges, nature and distribution of pores also regulate the adsorption efficiency. (Sarin, 2004). We report here the results of defluoridation studies using activated carbon prepared from *Morringa Indica*. This study leads to the assumption that fluoride deposition occurs by the forces of adsorption over the surface of the activated carbon and this was characterized by the surface morphological studies of the adsorbent material. The dynamics and kinetics of the adsorption process also are discussed.

MATERIALS AND METHODS

Morringa Indica bark was cut into thin slices and the pieces were washed several times with water to remove the dirt and other materials attached to its surface. Final washings were done with distilled water and the pieces were dried in shade. About 25 grams of this material was treated with 20mL of concentrated H_2SO_4 and the charred material was kept over night. The charred material was heated in an oven at 150°C for about 6hours. This was cooled and washed with double distilled water to remove any trace of acid. The material was dried in an oven for one hour and later it was activated in a Muffle furnace at 400°C. The activated carbon was cooled to room temperature, washed with double distilled water till the excess acid present in the material was removed completely. The adsorbent material of uniform particle size was prepared by using scientific sieves BSS 52 (ASTM50). All fluoride adsorption experiments were conducted using the material of this particle size, which gave the optimum fluoride adsorption. Fluoride stock solutions were prepared using AR grade sodium fluoride, which was supplied by Sigma Aldrich Company.

Adsorption studies

Batch adsorption experiments were carried out using 3g of adsorbent material with 50mL of fluoride solutions. The adsorbent and adsorbate were mixed at room temperature and adsorption experiments were conducted using a mechanical shaker. The influence of anions like chloride, nitrate, sulphate, and bicarbonate and cations like calcium and magnesium on the defluoridation efficiency of the activated carbon were verified. Fluoride measurements were made using the ion selective electrode, Orion EA940. The defluoridation studies were conducted in the pH range 2 to 12 in order to understand the effect of pH on the fluoride removal capacity of activated carbon. The point of zero charge (zpc) of the adsorbent sample was determined by pH drift method, using 0.1M NaCl solution (Thomas, 2002). Adsorption experiments were conducted at 30°C, 40°C and 50°C using a temperature controlled water bath (Remi make), to determine the thermodynamic parameters.

RESULTS

The results obtained from the sorptive removal of fluoride ions by the adsorbent are conducted by varying the parameters such as contact time, dosage, pH, pHzpc , co-ions and temperature. These processes clearly show the dominance of ongoing adsorption and summarized as follows.

Effect of contact time

The fluoride adsorption behaviour of the activated carbon of *Morringa Indica* is illustrated in Fig. 1.

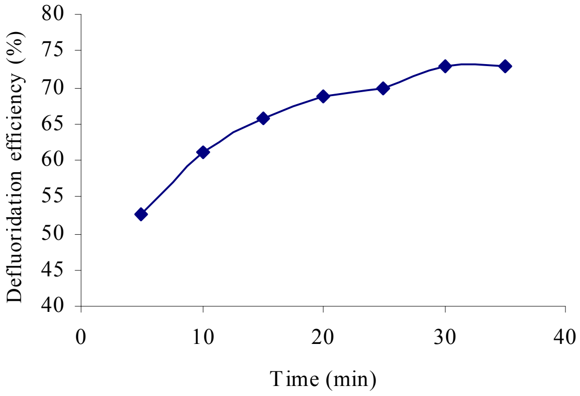

Fig. 1: Effect of contact time on fluoride adsorption

Effect of dose

The experimental results using eight doses of adsorbent material with 3 mg/L of fluoride solution are given in Fig. 2.

Effect of pH

The adsorption of fluoride on the activated carbon was examined at seven different pH levels in the range of 2 to 12 is shown in Fig. 3.

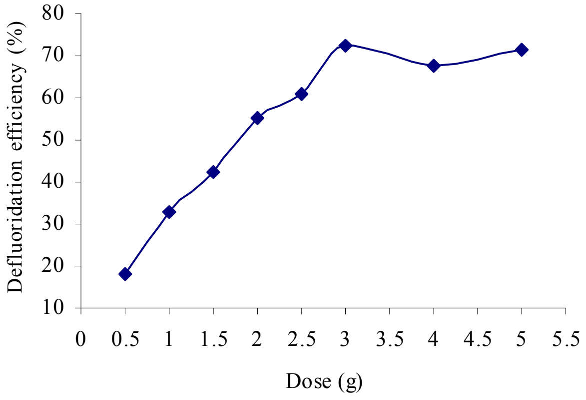

Fig. 2: Effect of dose on fluoride adsorption

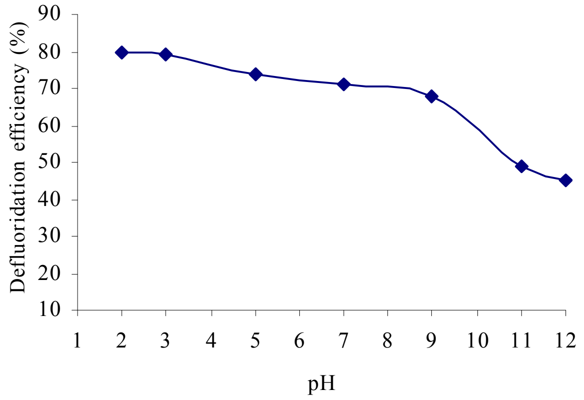

Fig. 3: Effect of pH on defluoridation efficiency

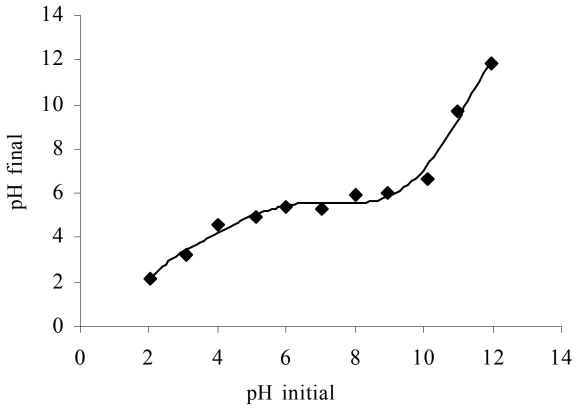

Fig. 4: Deterioration of pH_{ZPC}

The determination of pH_{zpc} is illustrated in Fig. 4. Fig. 5 represents the effect of common anions and cations over the fluoride adsorption rate of the material. The temperature dependence of the adsorption of fluoride by *Morringa Indica* carbon was studied over the range of 303-323 °K.

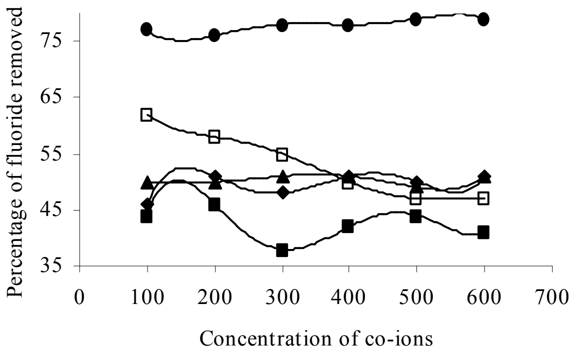

Fig. 5: Effect of co-ions on fluoride removal

Table 1: K_o values of various concentrations of fluoride at different temperatures

Concentration of fluoride, mg/L	Temperature °C		
	30	40	50
2	1.39	1.45	1.50
4	2.59	2.65	2.78
6	3.79	3.93	4.02
8	4.80	5.00	5.20
10	5.90	6.10	6.38

Table 2: Thermodynamic parameters

Concentration of fluoride (mg/L)	$K\ eq_{ads}$	ΔG° (kJmol)	ΔH° (kJmol)	ΔS° (kJmol)
2	2.2787	-2.075	11.432	0.0446
4	1.8369	-1.532	8.959	0.0346
6	1.7149	-1.359	7.017	0.0276
8	1.5000	-1.021	8.876	0.0326
10	1.4390	-0.917	8.431	0.0308

The thermal nature of the process is determined throgh k_0 value (Table 1). Values of the thermodinamic equiliberium constants are shown in Table 2.

Adsorption isotherms

The relationship between the amount of substance adsorbed at constant temperature and its concentration in the equilibrium solution is called the adsorption isotherm (Dogan, 2005). Freundlich and Langmuir models of isotherms have been tested in the present study Fig.s 6-8 and Tables 3-5.

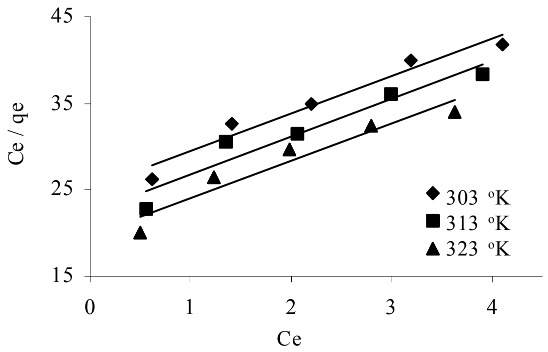

Fig. 6: Langmuir plot

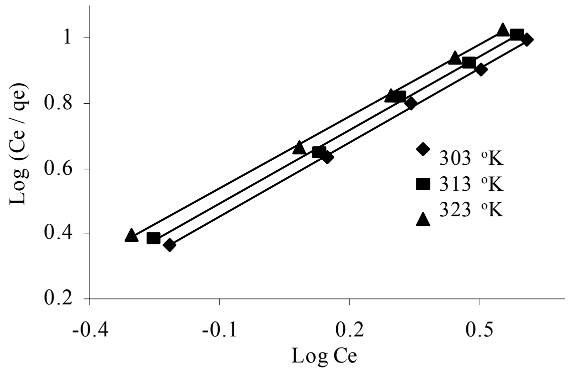

Fig. 7: Freundlich plot

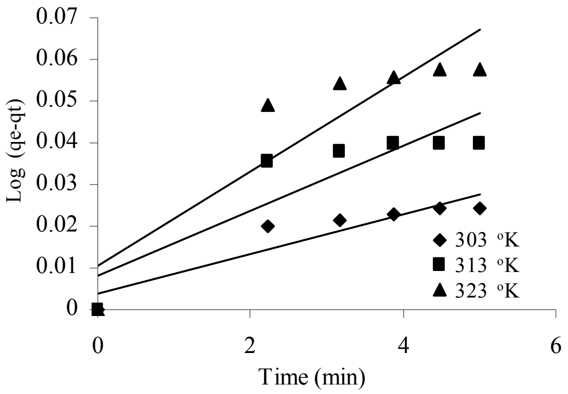

Fig. 8: Legergran plot

Table 3: Freundlich constants at different temperatures

Temperature (°K)	1/n	K
303	0.7584	3.3712
313	0.7389	3.7092
323	0.7306	4.0929

Table 4: Values of C_e and $C_e/\ q_e$ at different temperatures

Concentration of fluoride (mg/L)	C_e (mg/L)			C_e/q_e (mg/L)		
	Temperature (K)			Temperature (K)		
	303	313	323	303	313	323
2	0.61	0.55	0.5	0.038	0.044	0.05
4	1.41	1.35	1.22	0.031	0.033	0.038
6	2.21	2.07	1.98	0.029	0.032	0.034
8	3.2	3.00	2.8	0.025	0.028	0.031
10	4.1	3.9	3.62	0.024	0.026	0.029

Table 5: Langmuir constants at different temperatures

Temperature (°K)	b (L/mg)	a (mg/g)
303	0.1724	0.2308
313	0.1959	0.2286
323	0.2193	0.2314

The essential characteristics of Langmuir equation can be expressed in terms of a dimensionless separation factor or equilibrium parameter R_L which can be calculated from the formula $R_L = 1/(1+ b\ C_0)$ (Karthikeyan, 2004) for which:

Type of adsorption	Value of R
Linear	$(R_L = 1)$
Unfavourable	$(R_L > I)$
Favourable	$(0 < R_L < 1)$
Irreversible	$R_L = 0$

The values of R_L obtained for this system are provided in Table 6.

Table 6: R_L values at different temperatures

Concentration of fluoride (mg/L)	30 °C	40 °C	50 °C
2	0.744	0.719	0.695
4	0.592	0.561	0.533
6	0.492	0.460	0.432
8	0.420	0.390	0.363
10	0.367	0.338	0.313

The intraparticle diffusion model theory was proposed by Weber and Morris (Morris, 1964). In order to show the existence of intra particle diffusion in the adsorption process, the amount of fluoride sorbed per unit mass of adsorbent, q at any time t, was plotted as a function of square root of time, $t^{1/2}$.

A representative plot of the *intraparticle diffusion model* in three fluoride concentration viz., 2, 4, and 6 mg/L in 303 °K is given in Fig. 9.

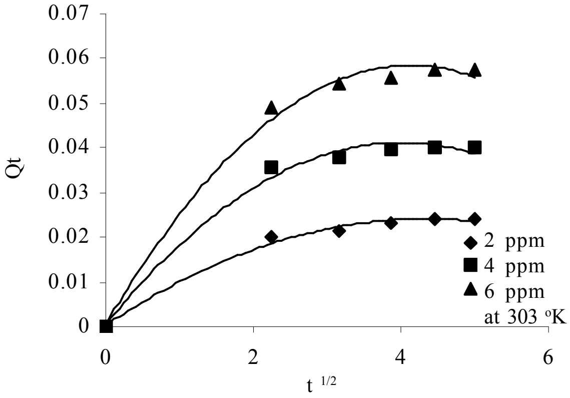

Fig. 9: Determination of intraparticle diffusion rate in three fluoride concentration

Real world situation with field water samples of endemic areas having different fluoride concentrations

The drinking water samples from five fluoride endemic habitations of Dindigul district of Tamil nadu in South India were analyzed using *Morringa Indica* as the defluoridating medium. The experimental data pertaining to fluoride and other water quality parameters are provided in Table 7. The changes in the fluoride levels before and after the adsorption process are given in Fig. 10.

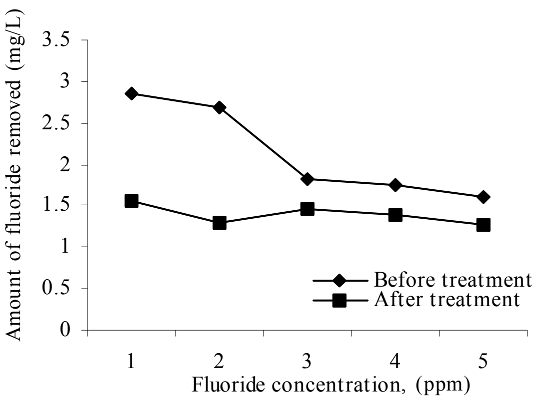

Fig.10: Changes in fluoride concentration in real water samples

Table 7: Water quality parameters of five real field samples

Sample No.	Name of the village	Fluoride (mg/L)		pH		Conductivity (mµ)		Alkalinity (mg/L)		Hardness (mg/L)		TDS (mg/L)	
		Initial	Final	Initial	Final	Initial	Final	Initial	Final	Initial	Final	Initial	Final
1	Ramanchettipatti	2.8	1.5	8.06	7.49	1.00	2.19	340	106	835	810	740	715
2	Thethampatti	2.6	1.3	7.72	7.40	0.81	2.74	420	100	850	825	820	785
3	Soriparaipatti	1.7	1.1	7.31	7.34	1.92	2.05	352	160	735	715	940	915
4	Pethanayakanpatti	1.8	1.2	7.82	7.47	1.43	2.15	564	152	580	565	760	730
5	Sankarapuram	1.6	1.3	7.82	7.39	3.69	4.73	540	155	780	765	840	820

DISCUSSION

Referring to Fig. 1, A gradual, definite increase in adsorption rate is observed in the initial stages up to 25th minute. The fluoride adsorption remained unchanged after 30th minute. No further adsorption was evident and this indicated the formation an equilibrium at 30th minute. The defluoridation capacity of the material therefore is illustrated to be maximum at 30th minute. This means that the minimum period of contact required for the maximum fluoride removal is 30 minutes. The time variation curve showing the contact time against amount of fluoride adsorbed is smooth and continuous indicating the formation of a monolayer coverage of the outer interface of the adsorbent (Pehilvan, 2005). As it is shown in Fig. 2, a definite increase in the adsorption capacity of the material with dosage indicated the availability of a large number of active sites on its surface (Namasivayam, 2004). The adsorption rate of fluoride increased steadily upto 3g/50 mL, beyond which any increase in fluoride adsorption was absent. In view of this, 3g/50 mL of the adsorbent is fixed as the optimum amount of the adsorption material for further studies.

Effect of pH

Fig. 3 indicates the variation of adsorption at different pH levels. An examination of the figure indicates that maximum fluoride removal had occurred in strongly acidic medium and fluoride adsorption decreases with increase in pH. However, at neutral pH fluoride removal is considerably high, of the order of 71%. In the alkaline range, the fluoride adsorption remains slow. Higher adsorption rate of fluoride in the acidic range can be explained by the surface charge of the adsorbent. In acid medium the surface of adsorbent is highly protonated and hence more fluoride can be attracted towards the surface. That is, high fluoride sorption rate in the acid medium is attributed to strong columbic forces between the positively charged surface and negatively charged fluoride ions. The repulsion between the negatively charged surface and fluoride ions leads to comparatively low adsorption rate at alkaline range. The pH $_{zpc}$ for the activated carbon is determined and the value is 6.2 as shown in Fig. 4 The optimum fluoride removal capacity of the adsorption material is thus explained in terms of zpc also.

Effect of co-ions

The influence of anions like chloride, sulphate, nitrate and bicarbonate on the fluoride adsorption of the material has been experimentally verified. Among the anions bicarbonate ions interfere to a considerable extent resulting in the reduction of the fluoride adsorption rate. For example, the percentage of adsorption rate was reduced from 62% to 45% in presence of about 500mg/L of bicarbonate ions. Other anions do not change the fluoride adsorption capacity. However, the presence of excess of calcium and magnesium ions also did not show any significant influence on the fluoride adsorption rate of the material. The increase in the amount of fluoride adsorbed with temperature confirms the endothermic nature of the process. The enhancement of fluoride adsorption capacity with temperature is attributed to the possible increase in the number of active sites available for adsorption on the surface. The kinetic energy of fluoride ion increased with increasing temperature of solution. The collision frequency between the adsorbent and adsorbate increased and hence greater the adsorption on the surface of the adsorbent particles (Oguz, 2005). The endothermic nature of adsorption is indicated by increase in the k_o values of thermodynamic equilibrium constant, with a rise in temperature (Table 1). Thermodynamic parameters are calculated from the variation of the thermodynamic equilibrium constants, k_o using the following equations (Table 2):

$$\Delta G^\circ = -RT \ln K \qquad (1)$$

$$\Delta H^\circ = -(B \times R) \qquad (2)$$

where:

B is slope of the plot lnK vs 1/T and R is the gas constant:

$$\Delta S^\circ = \Delta H^\circ - \Delta G^\circ / T \qquad (3)$$

The negative values of ΔG° indicate the feasibility of the process and also the spontaneity of adsorption reaction. The positive value of ΔS° show the increased randomness at the solid/ solution interface during the adsorption of fluoride on carbon .The value of ΔH° is positive and it confirms the endothermic character of the reaction (Bouberka, 2005). The ΔH° values in these cases are between 7.017 and 11.432 indicating that the adsorption is mainly governed by physisorption. Our observations agree well with those of A. Loannou *et al.,* (Doula, 2000), who employed the values of enthalpy of sorption process to distinguish between chemical and physical sorption.

Freundlich isotherm

Batch adsorption isothermal data, fitted into the linear form of the Freundlich isotherm are shown in Fig. 6. The linear form of Freundlich is:

$$\text{Log } q_e = \log K + 1/n \log C_e \qquad (4)$$

Where:

q_e = amount of fluoride adsorbed per unit weight of activated carbon

C_e = equilibrium concentration, K = adsorption capacity and 1/n = adsorption intensity

The adsorption capacity, K and the adsorption intensity, 1/n are directly obtained from the slopes and the intercepts of the linear plot, (log q_e vs log C_e) respectively and the data are provided in Table 3.

The K is a measure of adsorption capacity, and it increased with temperature. The magnitude of the exponent, n gives an indication of the favourability and capacity of the adsorbent/adsorbate system. Treybal has reported that 'n' values between 1 and 10 represent favorable adsorption conditions. (Treybal, 1980). In all cases reported here the exponent is $1 < n < 2$ showing beneficial adsorption. The plot of log q_e versus log C_e for various initial concentrations is linear and this indicates the applicability of Fruendlich adsorption isotherm ($0.995 < r < 0.999$) and ($0.00908 < s\,d < 0.0074$). The fit of the data to the Freundlich model indicate that the forces of adsorption by this carbon is governed by physisorption.

Langmuir isotherm

This system obeys the Langmuir adsorption isotherm. The Langmuir constant a and b were obtained from the linear regression analysis of the Langmuir equation.

$$C_e/ q_e = 1/ab + C_e/ a \qquad (5)$$

Where:

a and b are Langmuir constants related to adsorption capacity and energy of adsorption respectively. The C_e and C_e/q_e values and the Langmuir constants, a and b for different temperatures are calculated and presented in Tables 4 and 5 respectively. The linear plots of C_e/q_e versus C_e at three different temperatures (Fig. 7) indicate the applicability of Langmuir adsorption isotherm on the adsorption process occurring through monolayer coverage (Dogan, 2005).

The values of R_L obtained for this system are provided in Table 6. The R_L values lie between 0 and 1 and this indicates favorable adsorption at three temperatures (Table 6).

Adsorption kinetics

The mechanism of adsorption depends on the physical and or/chemical characteristics of the adsorbent. In order to investigate the mechanism of fluoride adsorption Lagergren proposed a pseudo first order kinetic model. The integral form of the model is:

$$\mathrm{Log}\ (q_e - q) = \log q_e - K_{ad}/2.303\ t \qquad (6)$$

where:

q is the amount of fluoride sorbed (mg/g) at time t and q_e is the amount of fluoride sorbed (mg/g) at equilibrium. The plot of log (q_e – q) vs t gives straight line showing the applicability of pseudo first order kinetics (Meikap, 2005). (Fig. 8) The Intraparticle diffusion model theory was proposed by Weber and Morris (Morris, 1964). In order to show the existence of intra particle diffusion in the adsorption process, the amount of fluoride sorbed per unit mass of adsorbent, q at any time t, was plotted as a function of square root of time, $t^{1/2}$.

The rate constant for *intraparticle diffusion model* was obtained using the equation

$$q = k_p t^{1/2} \qquad (7)$$

where:

k_p is the *intraparticle diffusion model* rate constant. The plot for intraparticle diffusion shows that initial curved portion reflects film or boundary layer diffusion (Fig. 9) effect and subsequent linear portion attribute to the intraparticle diffusion effect. The linear portions of the curves do not pass through the origin indicating that mechanism of fluoride removal on this activated carbon is complex and both the surface adsorption as well as intraparticle diffusion contribute to the rate determining step (Pant, 2005).

Instrumental analysis

Powdered X ray diffraction studies indicated changes occurring in the crystal structures of the adsorbent due to the adsorption of fluoride on its surface. XRD pattern of the adsorbent material before the fluoride treatment exhibited significant changes in the intensity of peak corresponding to the 2θ values at 25. In the case of the treated sample the intensity registered a marked decrease from 860 to 800 which is due to the coverage of the surface by the adsorbed fluoride. The SEM images of the adsorbent and the fluoride loaded adsorbent indicated the presence of coverage of fluoride ions over the adsorbent material.

Real water samples

The percentage of fluoride removed by the adsorbent material in these cases ranged from 31-50. A similar trend in the case of alkalinity of the water samples also was observed. Defluoridation of the water samples from Thethampatti and Ramanchettipatti villages which contained 2.6 and 2.8 mg/L respectively of fluoride was of the order of 47-50 % while in case of the remaining three villages with low fluoride level (1.6-1.8 mg/L) the percentage of defluoridation ranged between 31-35. However, with test solutions the percentage of defluoridation efficiency in the laboratory conditions was of the order ~70. The reduction in alkalinity ranges of the five water samples is significant while no remarkable change in the case of pH, hardness, and TDS was evident. A 100 % increase in the conductivity was observed in the case of water samples with high fluoride levels and this is attributed to the dispersion and suspension of pollutants (Sulochana, 1999).

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