Adsorption kinetics and thermodynamics of fluoride onto *Phyllanthus emblica* based thermally activated carbon

Veeraputhiran V.* and Alagumuthu G.

Chemistry Research Centre, Sri Paramakalyani College, Alwarkurichi – 627412, Tamilnadu, India.

*Corres. Author: alagupathi@gmail.com
Mobile: +919944825986

Abstract: The sorption of fluoride ion onto *Phyllanthus emblica* was studied by performing batch kinetic sorption experiments. The batch sorption model, based on a pseudo-first-order, pseudo-second-order, Elovich and intraparticle diffusion mechanism, were applied to predict the rate constant of sorption, the equilibrium capacity and the initial sorption rate with the effects of the initial solution fluoride concentration and temperature. Thermodynamic parameters, such as ΔG^o, ΔH^o, and ΔS^o were calculated using adsorption equilibrium constant obtained from the Langmuir isotherm. Results suggested that the fluoride adsorption on *Phyllanthus emblica* is a spontaneous and endothermic process. Spectral studies like FT-IR, SEM and EDAX were performed to analyze the binding nature of adsorbent with fluoride.

Keywords: Fluoride; *Phyllanthus emblica*; thermodynamic study; kinetic study.

1. Introduction

Although a suitable low concentration of fluoride in drinking water is beneficial to health, a high concentration can produce dental and skeletal fluorosis, which has been early recognized in the 1930s [1,2]. According to the World Health Organization (2008) [3], the acceptable fluoride concentration is generally in the range of 0.5–1.5 mg/L. However, the excess of fluoride in groundwater is found in many regions of the world [4–7]. Except for natural dissolution from geologic formations, significant sources of fluoride in water body are the effluents from the aluminum smelters, electronic device and semiconductor industries [8,9]. It is, therefore, essential that there are technologies for controlling the concentrations of fluoride in aqueous

emissions. One effective approach is to use alternative adsorbents. These are low-cost, often naturally occurring, products which have good adsorbent properties. Many of the adsorbents has been reported for best of fluoride removal, such as clay, red mud, fly ash, plant materials [10] and nut shell carbons [11,12].

Phyllanthus emblica is the one of the best available cheapest adsorbent, specifically in India. In this study, the fluoride removal from aqueous solution by adsorption onto the activated carbon, which was derived from *Phyllanthus emblica*, was investigated. The mechanism, the performance of the fluoride uptake under various initial fluoride concentrations and temperature were examined in detail.

2. Materials and methods

2.1. Adsorbent preparation

The *Phyllanthus emblica* sample (powdered seed), common name, Indian Gooseberry, was purchased from market. Then the material was dried at 378-383K for 24 hours. It was washed with doubly distilled water to remove the free acid and dried at the same temperature for 3 hours. Later the dried adsorbent was thermally activated in Muffle furnace at 1073K (here we avoid acid treatment for charring). The resulting product was cooled to room temperature and sieved to the desired particle sizes, namely, <53, 53 - 106, 106 -150, 150 - 225 and 225 - 305 mesh. Finally, the product was stored in vacuum desiccators until required.

2.2. Experimental Procedures

Batch adsorption experiments were carried out at the desired temperature (303, 313, 323 and 333K) on a thermostatic shaker at 200rpm using capped 250mL conical flasks. In the adsorption isotherm and kinetic tests, adsorbent (0.75 g) was thoroughly mixed with aqueous solutions of fluoride (100 mL), with initial fluoride concentrations (C_0) ranging from 2 to 10mg/L. The reagents used in this present study are of analytical grade. A fluoride ion stock solution (100 mg/L) was prepared and other fluoride test solutions were prepared by subsequent dilution of the stock solution. Fluoride ion concentration was measured with a specific ion selective electrode by use of total ionic strength adjustment buffer II (TISAB II) solution to maintain pH 5–5.5 and to eliminate the interference effect of complexing ions [10]. The pH of the samples was also measured by Orion ion selective equipment. The fluoride concentration retained in the adsorbent phase, q_e (mg/g), was calculated according to [13],

$$q_e = \frac{(C_O - C_e)}{W} \qquad \ldots\ldots\ldots\ldots(1)$$

where q_e is the amount of fluoride adsorbed (mg/g); C_o and C_e are the initial and residual concentration at equilibrium (mg/L), respectively, of fluoride in solution; and W is the weight (g) of the adsorbent.

2.3. Characterization of sorbents

The Fourier transform infrared spectra were recoded using Nicolet 6700, Thermo Electronic Corporation, USA made spectrophotometer. The scanning electron microscopy (SEM) and Energy Dispersive X-ray Analysis (EDAX) were performed using a Philips XL-20 electron microscope. Computations were made using Microcal Origin (Version 6.0) software. The accuracy of fit are discussed using regression correlation coefficient (r)

and chi-square analysis (SSE). The chi-square statistic test is basically the sum of the square of the difference between the experimental data and data obtained by calculating from the models, with each squared difference divided by the corresponding data obtained by calculating from the models. The equivalent mathematical statement [14] is:

$$\chi^2 = \sum \frac{(q_e - q_e,m)^2}{q_e,m} \qquad \ldots\ldots\ldots(2)$$

where q_e,m is equilibrium capacity obtained by calculating from the model (mg/g) and q_e is experimental data of the equilibrium capacity (mg/g).

3. Results and Discussion

3.1. Adsorption Kinetics

The kinetic models pseudo first order, pseudo second order, intra particle diffusion and Elovich models are used to analyze the present adsorption data to determine the related kinetic parameters.

Pseudo-first-order kinetic model, the Lagergren rate equation, has been the most widely used rate equation for assigning the adsorption of an adsorbate from a liquid phase since 1898 [15]. The linear form of pseudo first order equation is represented as

$$\log(q_e - q_t) \quad \log q_e - \frac{k_L}{2.303}t \quad \ldots\ldots(3)$$

where q_e and q_t are the amount of fluoride adsorbed at equilibrium (mg/g) and the amount of fluoride adsorbed time t (mg/g), respectively; k_L (min^{-1}) is the rate constant of pseudo-first order adsorption reaction. The plot of log (q_e–q_t) versus t should give a straight line (Fig.1) from which rate constant k_L and q_e can be calculated from the slope and intercept of the plot, respectively. If the plot was found to be linear with good correlation coefficient, it indicates that Lagergren's equation is appropriate to fluoride sorption on *Phyllanthus embilica*. So, the adsorption process is a pseudo-first-order process [15,16]. The Lagergren's first-order rate constant (k_L) and q_e determined from the model are presented in Table 1, along with the corresponding regression correlation coefficient. It was observed that the pseudo-first-order model did not fit well. It was found that the calculated q_e values did not agree with the experimental q_e values (Table 1). This suggests that the adsorption of fluoride did not follow first-order kinetics.
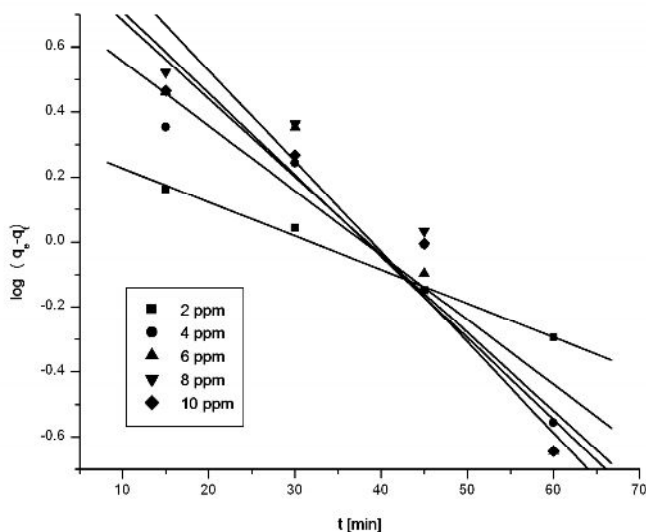
Fig.1 Pseudo-first-order kinetic fit for fluoride adsorption onto *Phyllanthus emblica* at room temperature for different initial fluoride concentration.

Table 1. Kinetic parameters for sorption of fluoride on *Phyllanthus emblica* for various fluoride concentrations at room temperature.

Kinetic Model	Parameters	Initial fluoride concentration (mg/dm^3)				
		2.0	**4.0**	**6.0**	**8.0**	**10.0**
Pseudo-first-order	k_L (min^{-1})	0.024	0.046	0.058	0.064	0.055
	q_e (mg/g)	2.142	5.680	9.123	12.160	8.350
	r	0.996	0.949	0.966	0.945	0.962
	SSE	0.004	0.051	0.034	0.055	0.038
Pseudo-second-order	k_2 (g/(mg min))	0.011	0.011	0.010	0.009	0.013
	h (mg/(g min))	0.094	0.240	0.377	0.448	0.590
	r	0.991	0.994	0.995	0.996	0.998
	SSE	0.003	0.009	0.012	0.008	0.003
Intra-particle diffusion	k_p (mg/(g min$^{0.5}$))	0.186	0.299	0.388	0.444	0.425
	C	0.280	0.770	1.179	1.382	1.660
	r	0.947	0.920	0.905	0.907	0.894
	SSE	0.013	0.012	0.027	0.031	0.026
Elovich model	α (mg/(g min))	0.236	0.047	0.006	0.002	0.061
	β (g/mg)	1.184	0.681	0.512	0.452	0.529
	r	0.963	0.974	0.972	0.987	0.995
	SSE	0.010	0.011	0.017	0.009	0.003

Pseudo-second order model was developed by Ho and McKay [17] to describe the adsorption of some metal ion onto the adsorbent. The linear form of the pseudo-second-order adsorption kinetic rate equation is expressed as

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad \text{........ (4)}$$

where q_e and q_t have the same meaning as mentioned previously, and k_2 is the rate constant for the pseudo-second-order adsorption reaction (g/mg min). The value of q_e and the pseudo-second-order rate constant (k_2) can be calculated from the slope and intercept of the straight line obtained from the plot of t/qt versus t (Fig.2). It can be seen from Table 1 that the pseudo-second-order model better represented the adsorption kinetics, suggesting that the adsorption process was controlled by chemisorption. A similar result was reported for the adsorption of fluoride from aqueous solution onto zirconium impregnated cashew nut shell carbon [11].

The initial adsorption rate can be obtained as q_t/t when t approaches zero:

$$h_0 = k_2 q_e^2 \qquad \text{............... (5)}$$

where h_0 is the initial adsorption rate (mg/g min) and the results are listed in Table 1. It was found that the initial rate of adsorption increases with increasing initial fluoride concentration, which would be expected due to the increase in driving force at higher concentration.

Intraparticle Diffusion Model; As the above kinetic models were not able to identify the diffusion mechanism, thus intraparticle diffusion model based on the theory proposed by Weber and Morris [18] was tested. It is an empirically found functional relationship, common to the most adsorption processes, where uptake varies almost proportionally with $t^{1/2}$ rather than with the contact time t. According to this theory:

$$q_t = k_{id} t^{1/2} + C \qquad \text{............... (6)}$$

where k_{id} is the intraparticle (pore) diffusion rate constant (mg/g min$^{0.5}$) and C is the intercept that gives an idea about the thickness of the boundary layer, is

obtained from the slope of the straight line of qt versus $t^{1/2}$ (Fig. 3). The larger the value of C, the greater the boundary-layer effect. The values of k_{id}, C and regression correlation coefficient, R obtained for the plots are given in Table 1. If intraparticle diffusion occurs, then qt versus $t^{1/2}$ will be linear and if the plot passes through the origin, then the rate limiting process is only due to the intraparticle diffusion. Otherwise, some other mechanism along with intraparticle diffusion is also involved [19]. For intraparticle diffusion plots, the first, sharper region is the instantaneous adsorption or external surface adsorption. The second region is the gradual adsorption stage where intraparticle diffusion is the rate limiting. In some cases, the third region exists, which is the final equilibrium stage where intraparticle diffusion starts to slow down due to the extremely low adsorbate concentrations left in the solutions [19]. Referring to Fig. 3, for all initial concentrations, the first stage was completed within the first 75min and the second stage of intraparticle diffusion control was then attained. The different stages of rates of adsorption observed indicated that the adsorption rate was initially faster and then slowed down when the time increased. As seen from **Fig. 3,** the plots were not linear over the whole time range, implying that more than one process affected the adsorption. Thus, the adsorption data indicated that the removal of fluoride from the aqueous phase onto the studied adsorbent was a rather complex process, involving both boundary-layer diffusion and intraparticle diffusion.

Elovich Model [20], which is based on chemisorption phenomena, is expressed as in a linear equation [21] as,

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

where q_t is the sorption capacity at time t (mg/g), α is the initial sorption rate (mg/g min) and β is the desorption constant (g/mg) during the experiment. From the intercept and slope of the straight line obtained from the plot of q_t versus log t (Fig.4), the values for α and β were calculated. From the Table 1, the regression correlation coefficient varied from 0.963 to .995 and indicating that the adsorption process is fairly adapting to chemisorption.
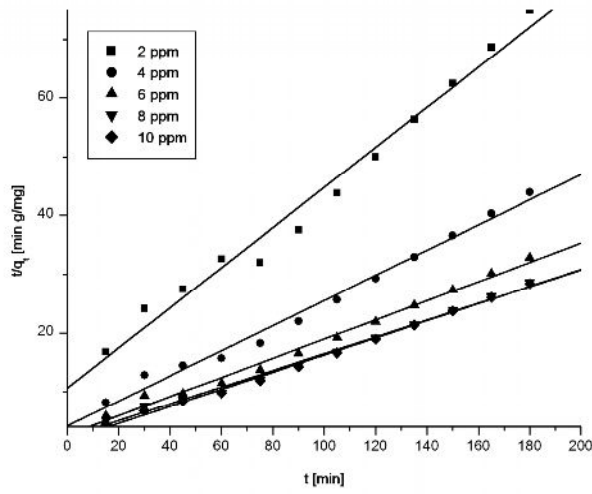
Fig.2 Pseudo-second-order kinetic fit for fluoride adsorption onto *Phyllanthus emblica* at room temperature for different initial fluoride concentration.
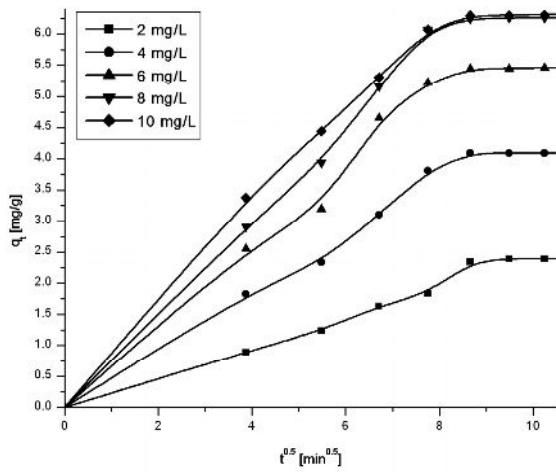
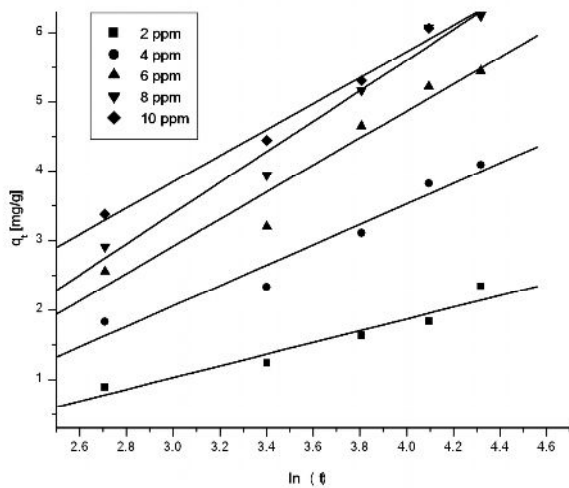**Fig.3 Plot for constant intra-particle diffusion at different temperature.**

Fig.4 Linear plot for Elovich kinetic model for the temperatures 303, 313, 323 and 333K.

3.2 Thermodynamic parameters

Thermodynamic considerations of an adsorption process are necessary to conclude whether the process is spontaneous or not. The Gibbs free energy change, ΔG^o, is an indication of spontaneity of a chemical reaction and therefore is an important criterion for spontaneity. Both energy and entropy factors must be considered in order to determine the Gibbs free energy of the process. Reactions occur spontaneously at a given temperature if ΔG^o is a negative quantity. The free energy of an adsorption, considering the adsorption equilibrium constant K_a is given by the following equation,

$$\Delta G^\circ = -RT \ln K_0 \qquad \ldots\ldots\ldots (8)$$

where ΔG° is the standard free energy change (kJ/mol), T is the absolute temperature (K) and R is universal constant (8.314 $Jmol^{-1}K^{-1}$). The sorption distribution coefficient K_0 for the sorption reaction was determined from the slope of the plot $\ln(q_e/C_e)$ against C_e at different temperatures and extrapolating to zero C_e[10].

The sorption distribution coefficient may be expressed in terms of ΔH° and ΔS° as a function of temperature:

$$\ln K_0 = \frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \qquad \ldots\ldots.(9)$$

where ΔH° is the standard enthalpy change (kJ/mol) and ΔS° is standard entropy change ($kJmol^{-1}K^{-1}$). While simplifying the Eq. (9) with ΔG^o, it becomes,

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \qquad \ldots\ldots(10)$$

A plot of ΔG° versus temperature, T, will be linear and the values of ΔH° and ΔS° are determined fromt he slope and intercept of the plot **(Fig. 5).** The parameter ΔG° for the adsorption process using the K_a from the Langmuir isotherm is shown in **Table 2**. The values of ΔG° calculated using the K_a were negative for the adsorption of fluoride onto *Phyllanthus emblica* at all temperatures. The negative values confirm the feasibility of the process and the spontaneous nature of the adsorption.

The values of ΔG°,were found to decrease -1.546 to -2.556 kJ/mol using the equilibrium constant, K_a. The decrease in the negative value of ΔG° with an increase in temperature indicates that the adsorption process of fluoride on *Phyllanthus emblica* activated carbon becomes more favorable at higher temperatures [10]. The values of ΔH° and ΔS° calculated from the plot of ΔG° versus T were given as 8.802 kJ/mol and 0.0342 J/mol K, respectively. The value of ΔH° was positive, indicating that the adsorption reaction was endothermic. The positive value of ΔS° reflects the affinity of the adsorbent for the fluoride. Spontaneous and endothermic adsorption have also been reported for the system of fluoride on varies shell carbons [11,12].
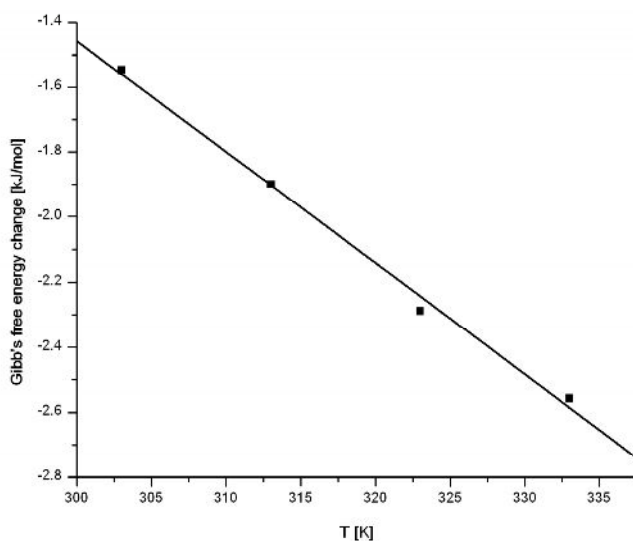

Fig.5 Plot of Gibbs free energy change ΔG°, versus temperature T.

Table 2. Thermodynamic parameters of fluoride sorption on *Phyllanthus emblica*.

S.No	Thermodynamic Parameters	Temperature (K)	Thermodynamic Values
1	ΔG^o (kJ/mol)	303	-1.546
		313	-1.900
		323	-2.289
		333	-2.556
2	ΔH^o (kJ/mol)		8.802
3	ΔS^o (J/(mol K))		0.0342
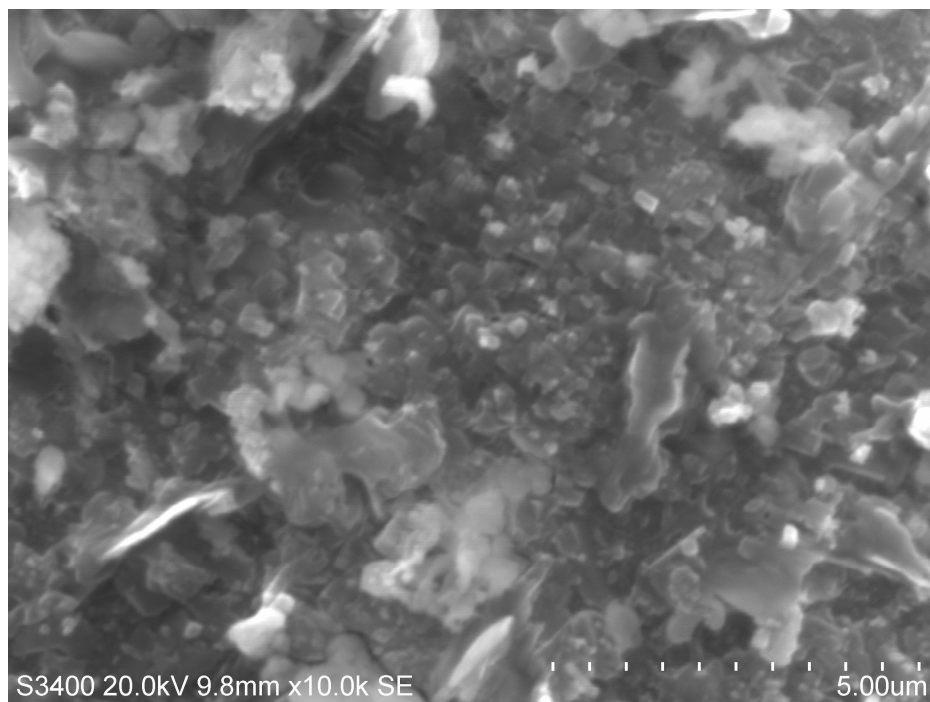
Fig.6 SEM image of thermally activated *Phyllanthus emblica*
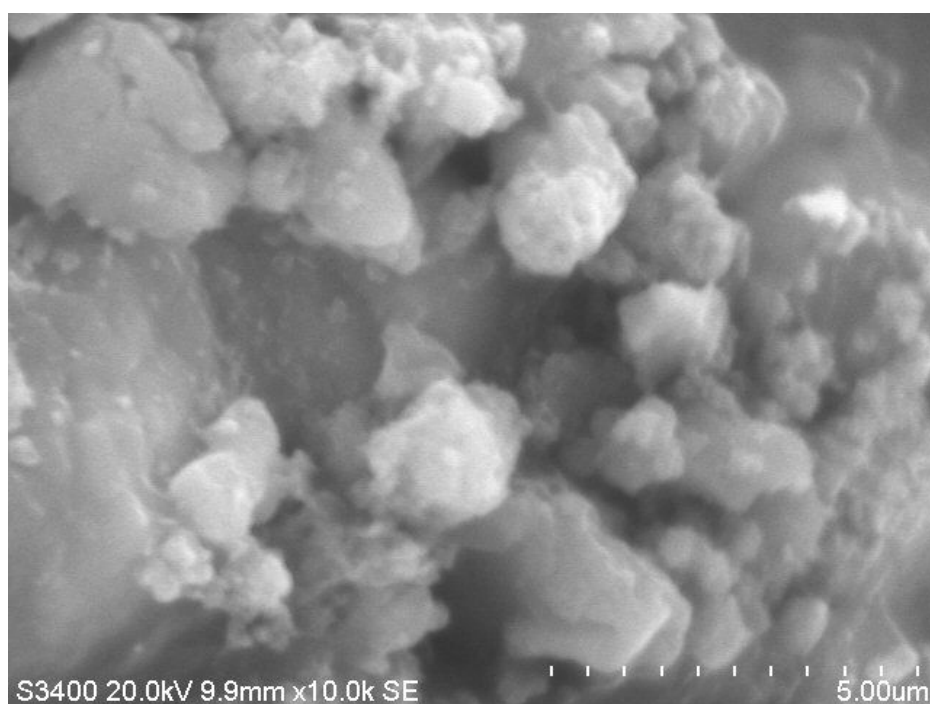
Fig.7 Scanning Electron Microscope view of fluoride treated thermally activated
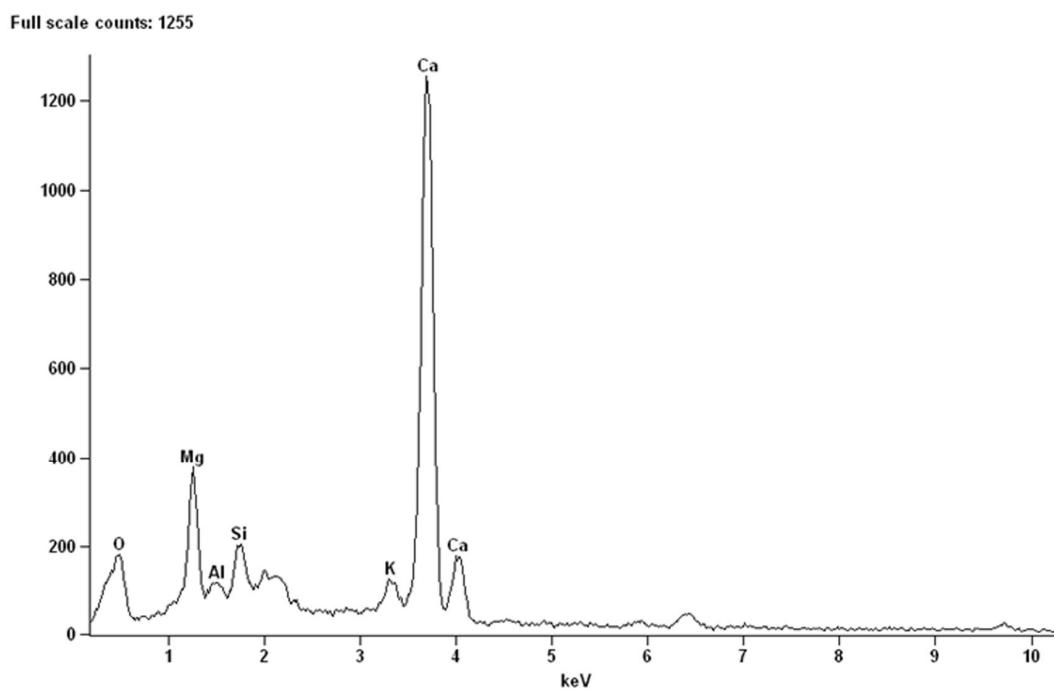***Phyllanthus emblica* adsorbent**

Fig.8 EDAX pattern of thermally activated *Phyllanthus emblica*
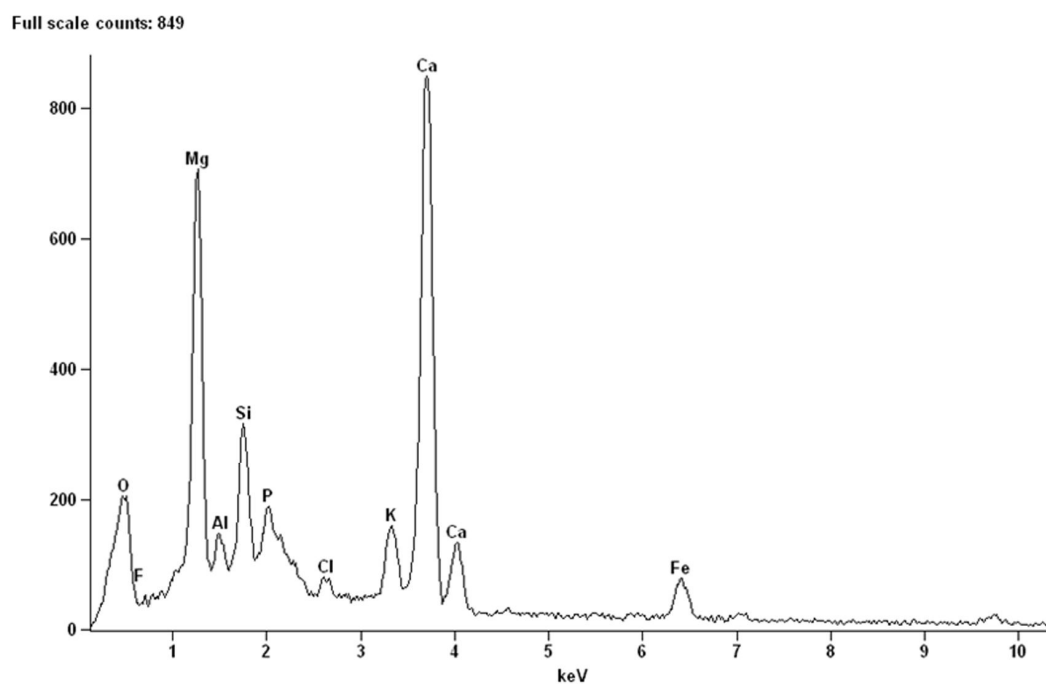

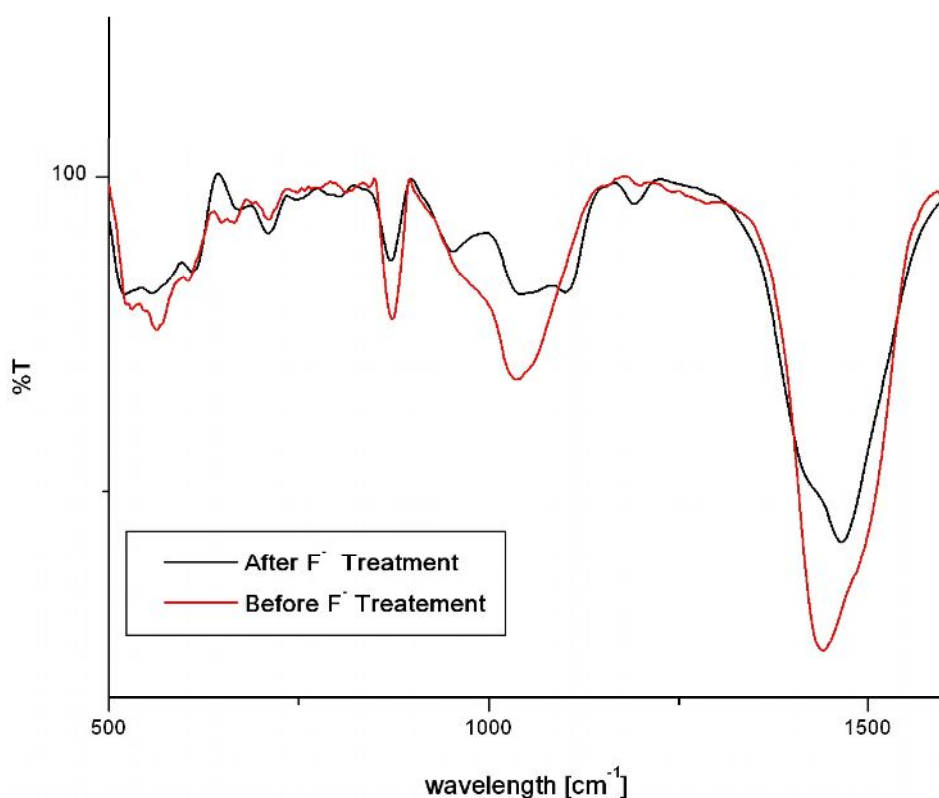**Fig.9 EDAX pattern of fluoride treated thermally activated *Phyllanthus emblica***

Fig.10 FTIR spectra of before and after fluoride treatment on adsorbent

3.3. Spectral Characterizations

Figs. 6 and 7 shows the SEM micrographs of *Phyllanthus embilica* samples before and after fluoride adsorption. Fig. 6 shows that the *Phyllanthus embilica* possesses a rough surface morphology with pores of different sizes. These pores are useful for fluoride adsorption.The surface of fluoride loaded adsorbent (Fig. 7), however, shows that the surface of *Phyllanthus embilica* is covered with fluoride ions. The occurrence of fluorine in the EDAX spectrum gives the support of binding ability of *Phyllanthus embilica* with fluoride (Figs. 8 and 9). Adsorption of fluoride has also resulted in several changes like the disappearance of some bands, shifts and decrease in the percentage of transmittance in the IR spectra of the solid surface in the range 4000–300cm^{-1}. FT-IR analysis of the sorbent surface before and after the sorption reaction has provided information regarding the surface groups that might have participated and also about the surface sites at which sorption might have taken place (Fig. 10). . The FTIR spectrum obtained (Fig. 10) for the adsorbent displayed the following major bands: 3436.58 cm^{-1}: O-H stretch; 1041.38 cm^{-1}: C-O stretch; 563.12 cm^{-1}: C-OH twist. It is reflecting the complex nature of adsorbent and

shows significant band shifting and intensity changes due to fluoride sorption.

Conclusion

The present work shows that *Phyllanthus emblica*, abundantly available in India, is an efficient adsorbent for the fluoride removal from the aqueous solutions and it may be an alternative to more costly adsorbents such as activated carbon. The adsorbent has been shown to have a high capacity for the removal of fluoride ions from solution. It was also revealed that the fluoride ions/adsorbent interaction is endothermic with higher activation energy, indicating that adsorption is chemical in nature. In addition, this sorption process is involving both boundary-layer diffusion and intraparticle diffusion. The adsorption equilibrium capacity, the adsorption rate constant and the initial adsorption rate are function of the initial fluoride concentration and the reaction temperature.

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