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# Removal of Fluoride from Aqueous Solutions by *Eichhornia crassipes* Biomass and Its Carbonized Form

Sarita Sinha,<sup>\*,†</sup> Kavita Pandey,<sup>†</sup> Dinesh Mohan,<sup>‡</sup> and Kunwar P. Singh<sup>‡</sup>

Environmental Sciences Division, National Botanical Research Institute, Rana Pratap Marg, Lucknow 226 001 (U.P.), India, and Environmental Chemistry Division, Industrial Toxicology Research Centre, Post Box No. 80, Mahatma Gandhi Marg, Lucknow 226 001 (U.P.), India

The purpose of this paper is to suggest an efficient defluoridation process that does not require a large investment. The conventional processes of fluoride removal from water are ion exchange, reverse osmosis, and electrodialysis. However, the utility of these processes has been limited because of their expensive operation and subsequent problem of disposing of the waste being generated. Sorption is an effective technology for the treatment of industrial wastewater. *Eichhornia crassipes* and the activated carbon derived from this plant were examined to assess their capacity for the removal of fluoride from wastewater by batch techniques. Systematic batch studies on fluoride adsorption equilibrium and kinetics by *E. crassipes* and low-cost activated carbons prepared from *E. crassipes* were carried out. Studies were conducted to determine the optimum operating system parameters required for the establishment of columns such as contact time, dose, and size of the adsorbent. The adsorption of fluoride on noncarbonized and carbonized *E. crassipes* increases with increasing temperature (25, 35, 45 °C), thereby indicating that the process is endothermic in nature in all of the cases examined. The adsorption data were very well fitted by the Freundlich adsorption isotherm model. The Lagergren first-order rate equation was applied for the determination of the rate constants. Carbonized *E. crassipes* showed better removal efficiency than the noncarbonized plant. Further, the activation temperatures in the preparation of activated carbon played an important role. Carbon activated at 600 °C exhibited better performance than that activated at 300 °C. Column studies were also performed with an initial concentration of 15 ppm. The effluent volume at breakthrough was found to be 100 bed volumes, and the column capacity was calculated as 4.4 mg/g.

## 1. Introduction

Fluorine is one of the most electronegative of all chemical elements and is so reactive that it is rarely encountered in nature in the elemental form. Combined chemically in the form of fluorides, fluorine is abundant in the earth's crust. Fluoride exists fairly abundantly in the earth's crust and can enter groundwater by natural processes; the soil at the foot of mountains is particularly likely to be high in fluoride from the weathering and leaching of bedrock with high fluoride content. Water is a major source of fluoride intake. The WHO<sup>1</sup> guidelines suggest that, in areas with a warm climate, the optimal fluoride concentration in drinking water should remain below 1 mg/L, whereas in cooler climates, it could go up to 1.2 mg/L. The guideline value (permissible upper limit) for fluoride in drinking water was set at 1.5 mg/L. The WHO guideline value for fluoride in water is not universal: India, for example, lowered its permissible upper limit from 1.5 to 1.0 ppm in 1998. Fluoride levels in water vary from (essentially) 0 to 7 mg/L. The U.S. public health service recommends that fluoride level in community water supplies range from 0.7 to 1.2 mg/L. The environmental impact of fluorides has been very well documented since at least 1937. Fluoride in drinking water is beneficial at low

concentrations, but presents health concerns at higher concentrations. The effects of excessive intake of the fluoride ion range from stiffness and rheumatism to permanent crippling or skeletal fluorosis and kidney damage.<sup>2</sup> Throughout many parts of the world, high concentrations of fluoride occurring naturally in groundwater and coal have caused widespread fluorosis, a serious bone disease. The problem of high fluoride concentration in groundwater resources has become an important health-related geo-environmental issue in some areas. Examples include the state of Rajasthan, India, where nearly 3 million people are reported to consume excess-fluoride-containing water<sup>3,4</sup> and the upper regions of Ghana, where 23% of wells have fluoride concentrations above the WHO-recommended maximum guideline limit<sup>5</sup> of 1.5 mg/L.

Although millions of people in developing countries are suffering from fluorosis, mainly due to the high fluoride concentrations in drinking water, no method of defluoridation of water has been reported to be carried out successfully and routinely in any of these countries so far. This is quite remarkable, especially considering that several defluoridation methods have been studied in detail and even reported as appropriate methods for quite a number of years.<sup>6</sup> This oddity is probably due to the fact that the available defluoridation methods do have disadvantages. Classical procedures of defluoridation involve precipitation, adsorption, electrodialysis, ion exchange, electrocoagulation, membrane techniques,<sup>7–10</sup> etc. An overview of defluoridation methods was very well presented in the review articles by

\* To whom correspondence should be addressed. Tel.: 0091-522-205831-35. Fax: 0091-522-205836/205839. E-mail: sinha\_sarita@rediffmail.com.

<sup>†</sup> National Botanical Research Institute.

<sup>‡</sup> Industrial Toxicology Research Centre.

Killedar and Bhargava.<sup>11,12</sup> Among the methods mentioned above, the most popular and cost-effective method is precipitation of fluoride with lime, but the problem associated with this approach is the production of sludge, which gives rise to the problem of disposal. Selective adsorption utilizing biological materials, mineral oxides, activated carbon, or polymer resins has generated much excitement among researchers, environmental engineers, and scientists. Despite the prolific use of activated carbon for water/wastewater treatment, it is an expensive treatment process,<sup>13</sup> which has prompted a growing search for a good substitute for activated carbon. A viable substitute for activated carbons should be easily available, economically feasible, and above all able to be regenerated chemically with simultaneous quantitative recovery of the adsorbate material. Many investigators have studied the feasibility of less expensive materials such as hydrous tin oxide,<sup>14</sup> impregnated alumina,<sup>15</sup> impregnated silica gel,<sup>16</sup> resin,<sup>17</sup> granular calcite,<sup>18</sup> precipitate flotation,<sup>19</sup> fly ash,<sup>20,21</sup> clays and low-cost materials,<sup>22</sup> spent catalyst,<sup>23</sup> ion-exchange resins,<sup>24</sup> activated alumina,<sup>25</sup> mixed adsorbent,<sup>26</sup> bone char,<sup>27</sup> soil,<sup>28</sup> aragonite,<sup>29</sup> and fish bone charcoal.<sup>30</sup> However, the problems associated with these adsorbents are the regeneration and recovery of the useful materials, which make them unattractive for wider commercial applications. This calls for a research effort to develop an industrially viable, cost-effective, and environmentally compatible technology for the removal of fluoride from wastewater.

For quite some time, we have been involved in developing some low-cost activated carbons/adsorbents for the removal and recovery of organics/metal ions from wastewater.<sup>31–34</sup> We have recently utilized different coals<sup>2</sup> for the removal of fluorides from wastewater successfully. Continuing our activities in this direction, we have developed specific adsorbents utilizing *Eichhornia crassipes* that we then applied for the removal of fluoride from aqueous solution. *E. crassipes*, commonly known as water hyacinth, is an aquatic weed, and its disposal is a major problem all over the world because of its vigorous growth in water bodies. Rapid vegetative growth is the main secret of the quick accumulation of *E. crassipes* into blankets of dense tough mats. It can spread up to 7-fold in 50-days time. Attempts have been made to control this weed through physical, chemical, and biological methods, which were not found very effective, so its disposal is still a great problem. Thus, it seems relevant to elaborate a use for this aquatic weed that can remove pollutants through a cost-effective and ecofriendly technique.

## 2. Materials and Methods

All reagents were AR-grade chemicals. For the experimental studies, sodium fluoride (AR, BDH) solution in doubly distilled water was used. From a stock solution of 1000 mg/L, working solutions of different concentrations were prepared and stored in polythene containers at 4 °C for further experimental studies. The pH of the test solutions was adjusted using reagent-grade dilute sulfuric acid and sodium hydroxide.

**2.1. Equipment.** The fluoride concentrations were measured using Orion ion analyzer EA940. The pH measurements were made using a pH meter (model CT No. CL46, Toshniwal India). The scanning electron microscopy was performed using a Philips XL-20 electron microscope. The surface area was determined using

a model QS-7 Quantasorb surface area analyzer. X-ray diffractograms were obtained on a Philips diffractometer unit (model PW 1710) using Cu K $\alpha$  radiation by Ni filter at the scanning speed of 1° per minute. An ion liquid chromatograph (Metrohm Switzerland) was used for the estimation of other anions in the wastewater. The data were modeled using Sigma Plot 2001.

**2.2. Adsorbent.** In the present study, *E. crassipes* (Mart.) Solms-Laubach, common name, water hyacinth, and the activated carbons derived from *E. crassipes* were utilized for the removal of fluoride from wastewater. The *E. crassipes* plant was dried at 105 °C and then powdered to the desired particle size and kept in a desiccator for utilization in sorption studies. The activated carbon was also prepared from the plant by treating three parts of *E. crassipes* with one part (by weight) of concentrated sulfuric acid, and the same was kept in an oven maintained at 150–165 °C for a period of 24 h. The carbonized material was washed well with doubly distilled water to remove the free acid and dried at 105–110 °C for 24 h. The dried material was thermally activated at two different temperatures, viz., 300 and 600 °C, for 3 h in a muffle furnace. The temperature and time were optimized by observing the surface properties such as surface area of the activated product obtained by treating the raw material for different intervals of time at varying temperatures. The resulting product was cooled and sieved to the desired particle sizes, namely, <40, –40 to +40, and >40 mesh. Finally, the product was stored in a vacuum desiccator until required. The analysis, characterization, and batch-to-batch reproducibility of the material were strictly controlled.

**2.3. Sorption Procedure. (a) Equilibrium Studies.** Batch sorption studies were performed at different temperatures (25, 35, and 45 °C) to obtain the equilibrium isotherms and the data required for the design and operation of fixed-bed reactors for the treatment of fluoride-containing wastewater. For isotherm studies, a series of 250-mL conical flasks was employed. Each conical flask was filled with 25 mL of fluoride solution of varying concentrations (2–25 mg/L) and adjusted to pH 5.5. A known amount of dried plant and activated carbon derived from the same plant was added into each conical flask separately and agitated intermittently for the desired time periods up to a maximum of about 8 h. The contact time and other conditions were selected on the basis of preliminary experiments that demonstrated that equilibrium was established in 6–8 h, as can be seen from the results in Figure 5 below. Equilibration for longer times, that is, between 8 and 24 h, gave practically the same uptake. Therefore, the contact period was selected as 24 h in all equilibrium tests. After this period, the solution was filtered using Whatman no. 42 filter paper and analyzed for the concentration of the fluoride remaining in the solution by Orion ion analyzer. All experiments were conducted in triplicate, and the mean of triplicate was reported.

The fluoride concentration retained in the adsorbent phase,  $q_e$  (mg/g), was calculated according to

$$q_e = \frac{(C_o - C_e)V}{W} \quad (1)$$

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



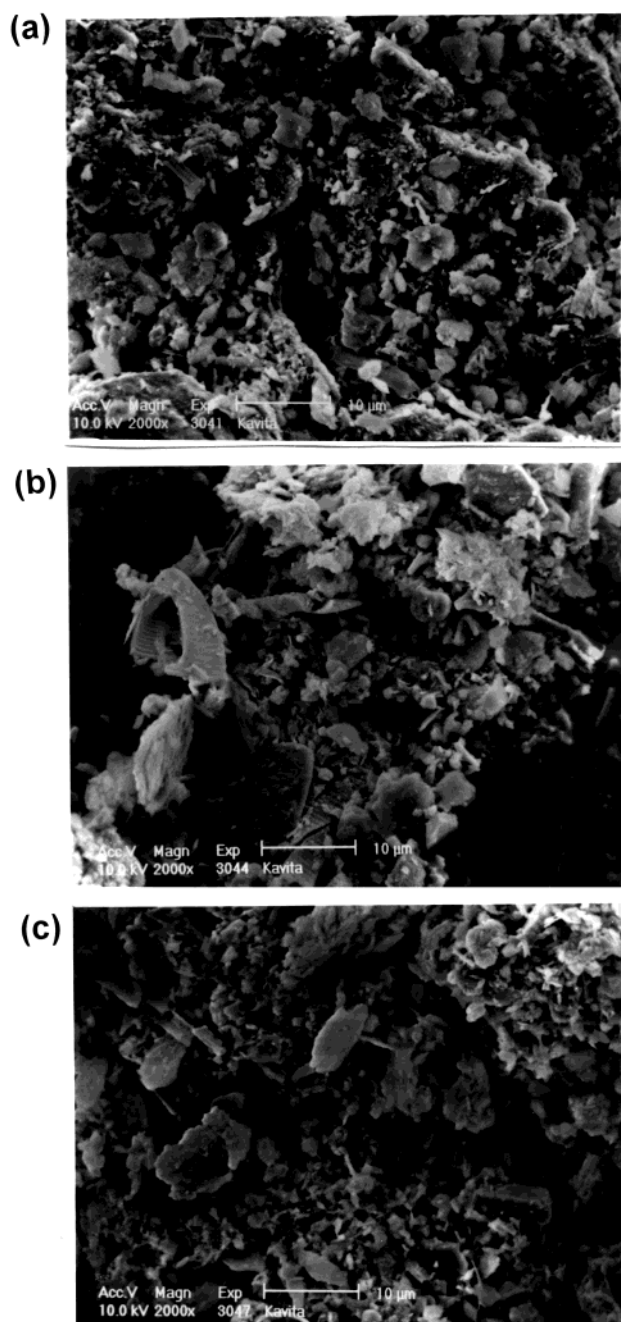
**(b) Kinetic Studies.** Batch tests were performed to determine the kinetics of adsorption of fluoride on the two adsorbents. For this purpose, 50-mL conical Pyrex glass flasks were prepared with the desired amounts of reagent solution and were placed in a thermostat-controlled shaking assembly. When the desired temperature had been reached, a known amount of adsorbent was added into each tube, and the solutions were agitated by mechanical shaking. At predetermined intervals of time, the solutions of the specified tubes were separated from the adsorbent using Whatman no. 42 filter paper and analyzed to determine the uptake of fluoride. The effects of contact time, adsorbent dose, and effect shaking were studied. All experiments were conducted in triplicate, and the mean of triplicate was taken.

**(c) Column Studies.** Adsorption isotherms have traditionally been used for preliminary investigations and fixing the operating parameters. In practice, however, the final technical systems normally use column-type operations. Moreover, the isotherms cannot provide accurate scale-up data in a fixed-bed system, so the practical applicability of products in column operations has also been investigated to obtain a factual design model. The column tests were performed in a 1.20-cm-diameter column. The column was filled with a 10-g sample of the activated carbon (particle size 50–200 mesh). This weighed quantity of adsorbent was made into slurry with hot water and fed slowly into the column, displacing a heel of water. The bed height was 18 cm, and the bed volume was 20 mL. The inlet concentration was 10 mg/L, and the solution pH was 5.5. The flow rate was 1.7 mL/min, and the residence time was 12 min.

### 3. Results and Discussion

**3.1. Characterization.** X-ray spectra (not included) of the activated carbon did not show any peak, thereby indicating the amorphous nature of the activated carbons derived from *E. crassipes*. To characterize the activated carbons, a 1-g sample of each carbon was stirred with 100 mL of deionized water at a pH of 6.8 for 2 h and left for 24 h in an airtight stoppered conical flask. A slight increase in pH was observed for carbon activated at 600 °C, whereas a lowering of pH was observed for the carbon activated at 300 °C. Thus, according to Mattson and Mark,<sup>35</sup> these samples can be classified as H- and L-type carbons, respectively. SEM photographs (Figure 1) at different magnifications of the carbons activated at different temperatures and of unactivated carbon clearly reveal the surface texture, flocs, and different levels of porosity in the materials under study. It is evident that the carbon particles are in the form of spheres with a wide range of sizes.

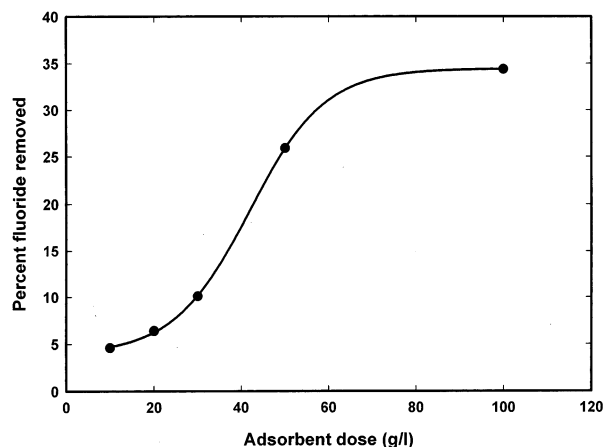
**3.2. Sorption Studies.** In the present study, a comparative evaluation of the removal of fluoride from wastewater on dried *E. crassipes* and the carbons prepared from the plant was conducted. According to Mattson and Mark,<sup>35</sup> activated carbons can be classified into two groups: carbon activated at low temperatures, 200–400 °C, termed as L carbons, generally will develop acidic surface sites and will lower the pH value of neutral or basic solutions. Such carbons primarily adsorb bases from solution, are hydrophilic, and exhibit a negative zeta potential. The carbon activated at higher



**Figure 1.** Scanning electron micrographs of (a) *E. crassipes*, (b) carbon derived from *E. crassipes* (activated at 300 °C), and (c) carbon derived from *E. crassipes* (activated at 600 °C) at 2000 $\times$ .

temperatures, 600–1000 °C, termed as H carbon, will develop basic surface sites and will increase the pH value of neutral or acidic solutions. They will adsorb acids and exhibit a positive zeta potential. However, cooling H carbons in contact with air will change the zeta potential to negative values, apparently through the formation of acidic surface sites. In the present investigation, both L-type (carbon activated at 300 °C) and H-type (carbon activated at 600 °C) carbons were derived from *E. crassipes* and were utilized for the removal of fluoride from synthetic wastewater. Sorption of the fluoride was carried out at different adsorbent doses, equilibration times, concentrations, and shaking periods.

**3.2.1. Effect of Adsorbent Dose and Equilibration Time.** The percent fluoride removal by untreated



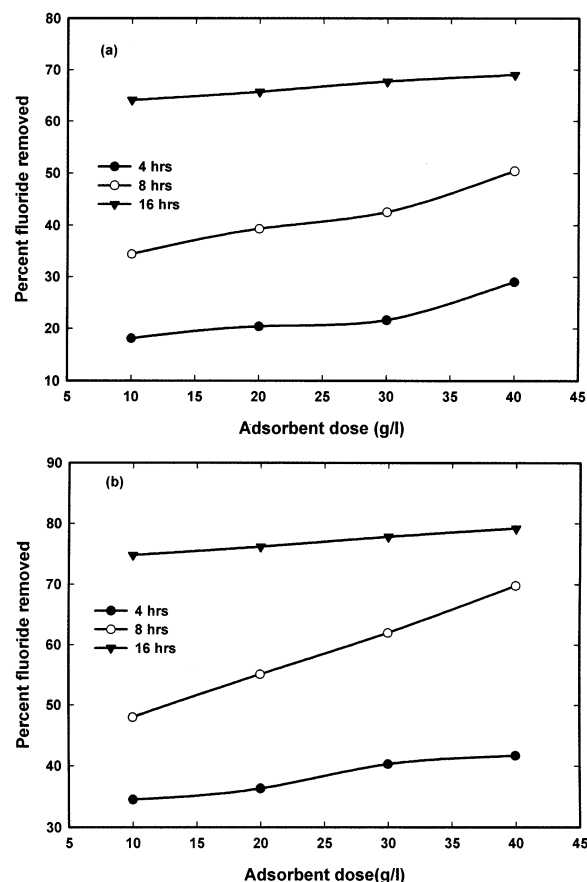
**Figure 2.** Effect of adsorbent dose on the removal of fluoride from wastewater on dried *E. crassipes* (fluoride concentration = 10 mg/L, temperature = 25 °C, and particle size < 40 mesh).

plant biomass at different adsorbent dose and at 25 °C was measured, and the results are presented in Figure 2. It is clear from the figure that there is a substantial increase in the adsorption as the adsorbent dosage increases from 10 to 50 g/L, whereas with the introduction of additional amounts, the increase in adsorption is not as significant. Keeping this in view, the amount of untreated plant biomass was kept at 50 g/L in all subsequent studies.

The effect of adsorbent dose on the removal of fluoride from wastewater using activated carbon derived from *E. crassipes* was studied at different equilibrium times, viz., 4, 8, and 16 h, without any shaking. The data are presented graphically in Figure 3. It is clear from Figure 3 that the adsorption of fluoride increases with increasing contact time and adsorbent dose. The contact time significantly affects removal efficiency, increasing it from 18 to 64% (dose, 10 g/L) for L-type carbon and from 34 to 74% (dose, 10 g/L) for H-type carbon as the contact time is increased from 4 to 16 h. Further, the percent fluoride removal increases with increasing adsorbent dose from 10 to 40 g/L, but the increase is not very significant. It is very interesting to note that the percent removal is very much higher in the case of the carbon activated at 600 °C in comparison to the carbon activated at 300 °C. Also, the removals for both the carbons derived from *E. crassipes* plant were higher than the removal for the same plant used without any treatment.

### 3.2.2. Effect of Temperature and Concentration.

The adsorption studies were carried out at 25, 35, and 45 °C to determine the adsorption isotherms and the necessary parameters to set up pilot plants on a large scale. An adsorption isotherm equation is an expression of the relation between the amount of solute adsorbed and the concentration of the solute in the fluid phase at a given temperature. The adsorption data for fluoride at a pH of 5.8 on both of the activated carbons derived from *E. crassipes* are given in Table 1, along with the standard deviations, at three different temperatures. The uptake of fluoride increased with increasing temperature, thereby indicating the process to be endothermic. The uptake of fluoride was found to be higher (72–98%) on H-type carbon (activated at 600 °C) than on L-type carbon (51–93%). Thus, it can be concluded that the H-type carbon is very much suited for defluoridation. In the surface adsorption studies, the relationship between the solution concentration and the species



**Figure 3.** Effect of adsorbent dose on the removal of fluoride from wastewater on *E. crassipes* carbon activated at (a) 300 °C and (b) 600 °C (fluoride concentration = 10 mg/L, temperature = 25 °C, and particle size < 40 mesh).

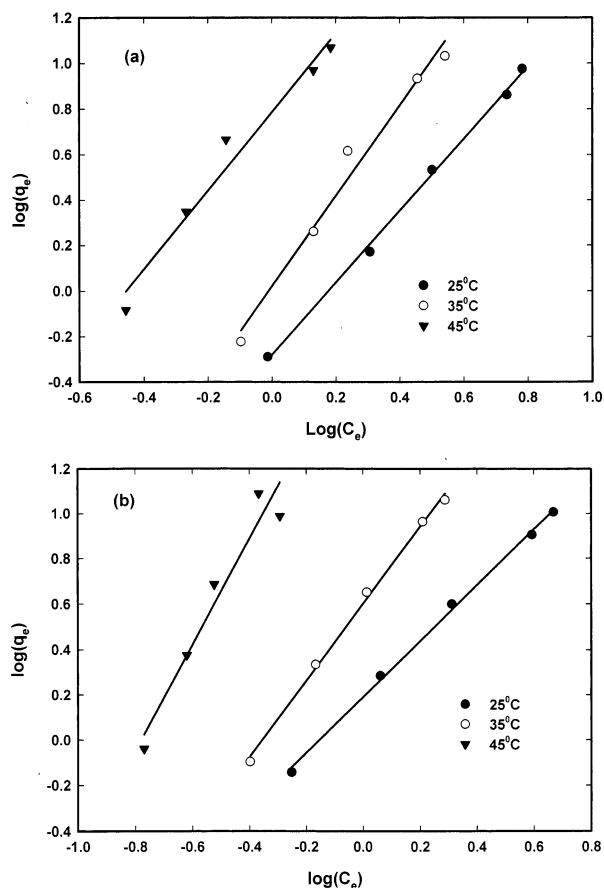
uptake can be described in terms of either a Freundlich- or a Langmuir-type isotherm; therefore, the data were evaluated using Langmuir and Freundlich isotherms.<sup>36</sup>

The adsorption data for the prepared activated carbons at different temperatures were fitted by the Freundlich and Langmuir models. It was found that the data do not follow the Langmuir adsorption isotherm, as the regression coefficients were found to be very low and even negative in some cases, so that the Langmuir parameters could not be evaluated. On the other hand, the adsorption data were very well correlated by the Freundlich model, as can be seen in Figure 4. The corresponding Freundlich isotherm parameters at different temperatures along with correlation coefficients are given in Table 2. The correlation coefficients show that, in general, the Freundlich model fitted the results very well over a wide range of concentrations. It is very well established that the Freundlich model fits the data significantly better when a change in the mechanism of adsorption with concentration is considered. The monolayer adsorption capacity ( $Q^0$ ) cannot be calculated given that the Langmuir model does not fit the data. However, the value of  $K_F$ , which also indicates the sorption capacity, was found to increase with increasing temperature, further corroborated by the experimental data, and one can utilize the Freundlich parameters for assembling the fixed-bed columns.

**3.3. Kinetics Studies.** The kinetics of adsorption of fluoride on both the activated carbons is graphically shown in Figure 5. It is clear from this figure that the adsorption increases with increasing temperature,

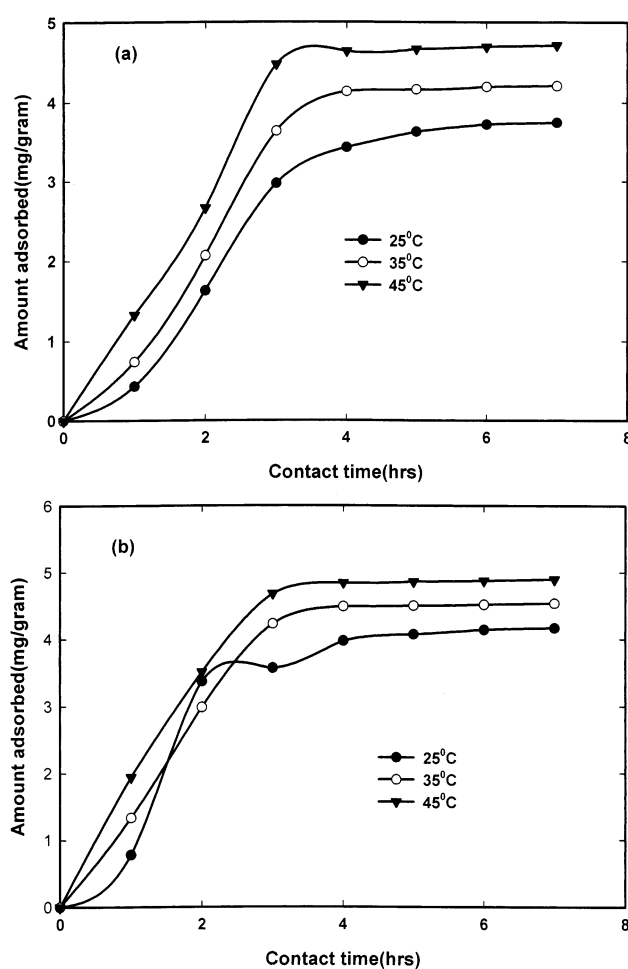
**Table 1. Effect of Temperature on the Adsorption of Fluoride from Wastewater on Activated Carbons Derived from *E. crassipes* at Different Temperatures and at Particle Size < 40 Mesh<sup>a</sup>**

initial	fluoride concentration (mg/L)					
	final					
	carbon activated at 300 °C			carbon activated at 600 °C		
	25 °C	35 °C	45 °C	25 °C	35 °C	45 °C
2	0.97 ± 0.02 (51.5)	0.80 ± 0.02 (60)	0.35 ± 0.01 (82.5)	0.56 ± 0.03 (72.0)	0.40 ± 0.02 (80)	0.17 ± 0.02 (91.5)
5	2.03 ± 0.01 (59.4)	1.35 ± 0.02 (73)	0.54 ± 0.02 (89.2)	1.15 ± 0.03 (77)	0.68 ± 0.02 (86.4)	0.24 ± 0.02 (95.2)
10	3.17 ± 0.02 (68.3)	1.73 ± 0.02 (82.7)	0.72 ± 0.02 (92.8)	2.05 ± 0.03 (79.5)	1.03 ± 0.02 (89.7)	0.30 ± 0.02 (97)
20	5.43 ± 0.02 (72.85)	2.85 ± 0.03 (85.75)	1.35 ± 0.02 (93.25)	3.92 ± 0.02 (80.4)	1.62 ± 0.01 (91.9)	0.51 ± 0.03 (97.45)
25	6.06 ± 0.02 (75.76)	3.48 ± 0.04 (86.04)	1.53 ± 0.02 (93.88)	4.66 ± 0.02 (81.36)	1.94 ± 0.03 (92.24)	0.43 ± 0.03 (98.28)

<sup>a</sup> Values in parentheses represent percent fluoride removal.**Figure 4.** Freundlich adsorption isotherms of fluoride removal from wastewater on (a) L-type and (b) H-type activated carbon derived from *E. crassipes* at different temperatures and particle size < 40 mesh.**Table 2. Freundlich Adsorption Isotherm Constants on the Adsorption of Fluoride from Wastewater on Activated Carbons Derived from *E. Crassipes* at Different Temperatures and at Particle Size < 40 Mesh**

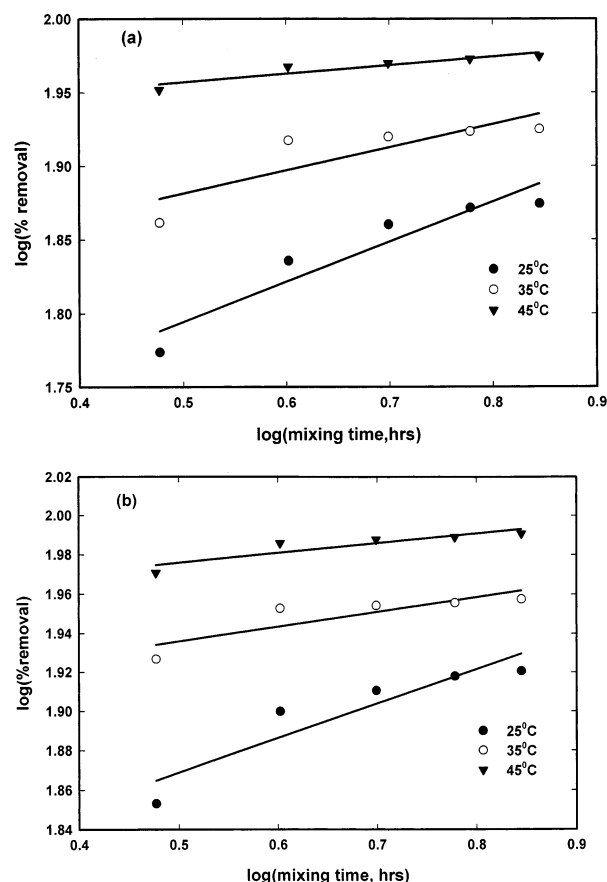
temp (°C)	carbon activated at 300 °C			carbon activated at 600 °C		
	$K_F$ (mg/g)	$1/n$	$R^2$	$K_F$ (mg/g)	$1/n$	$R^2$
25	0.523	0.6315	0.9976	1.54	0.8104	0.9978
35	1.04	0.5006	0.9790	3.995	0.588	0.9972
45	11.10	0.5790	0.9703	66.32	0.4280	0.9425

thereby indicating that the process is endothermic in nature. The kinetic studies further corroborated the equilibrium studies. The removal of fluoride, as depicted

**Figure 5.** Kinetics of fluoride uptake on carbon prepared from *E. crassipes* and activated at (a) 300 °C and (b) 600 °C at different temperatures, pH 5.8, particle size < 40 mesh, and fluoride concentration = 10 mg/L.

in Figure 5, takes place in two phases. The first phase involves immediate solvent removal obtained within 2–3 h and is followed by the subsequent removal of solvent, which continues for a longer period of time. Preliminary investigations on the rate of uptake of fluoride on the two activated carbons indicated that the processes are quite rapid and typically 50–60% of the ultimate adsorption occurs within the first 2–3 h of contact (Figure 5). This adsorption subsequently gives way to a very slow approach to equilibrium, and in 4–6 h, saturation is reached.





**Figure 6.** Logarithmic rate of fluoride uptake on carbon prepared from *E. crassipes* and activated at (a) 300 and (b) 600 °C.

**Table 3.**  $m$  and  $K_t$  Values for the Adsorption of Fluoride from Wastewater on Activated Carbons Derived from *E. crassipes* at Different Temperatures and at Particle Size < 40 Mesh

temp (°C)	carbon activated at 300 °C			carbon activated at 600 °C		
	$m$	$K_t$	$R^2$	$m$	$K_t$	$R^2$
25	0.27	5.24	0.8961	0.17	5.92	0.8588
35	0.16	6.06	0.7163	0.075	6.67	0.7395
45	0.05	6.86	0.8642	0.049	7.02	0.8119

The equation that can be used to evaluate the adsorption kinetics is<sup>37</sup>

$$\Delta S = K_t t^m \quad (2)$$

where  $\Delta S$  is the percent solvent removal,  $t$  is the contact time in minutes, and  $m$  and  $K_t$  are constants. The slope  $m$  reflects the adsorption mechanism, and  $K_t$  represents the rate factor. Fairly linear plots between the logarithm of the time and the logarithm of the percentage solvent removal were obtained, as shown in Figure 6. The values of  $m$  and  $K_t$  are reported in Table 3. For proper interpretation of the experimental data, it is necessary to determine which of the steps in the adsorption process governs the overall removal rate under the specified experimental conditions.

The three consecutive steps in the adsorption of an organic/inorganic species by a porous adsorbent are (i) transport of the adsorbate to the external surface of the adsorbent (film diffusion); (ii) transport of the adsorbate within the pores of the adsorbent, except for a small amount of adsorption that occurs on the external surface (particle diffusion); and (iii) adsorption of the adsorbate on the exterior surface of the adsorbent.

It is generally accepted that process iii is very rapid and does not represent the rate-determining step in the uptake of organic/inorganic compounds.<sup>36</sup> For the remaining two steps in the overall transport, three distinct cases arise: (I) external transport > internal transport, (II) external transport < internal transport, and (III) external transport  $\approx$  internal transport. In cases I and II, the rate is governed by film and particle diffusion, respectively. In case III, the transport of ions to the boundary might not be possible at a significant rate, thereby leading to the formation of a film with a concentration gradient surrounding the sorbent particles.

According to Weber and Moris,<sup>38</sup> a value of  $m = 0.5$  reflects intraparticle diffusion as the rate-determining step, whereas smaller values indicate the involvement of both of the processes to almost equal extents. This approach was used by Srivastava et al.<sup>37</sup> and recently by Lalvani et al.<sup>39</sup> for different adsorbent–adsorbate systems successfully. In the present study, the values of  $m$  are found to be less than 0.5, the sorption rate seems to be equally dependent on both processes, and neither appears to be sufficiently slow as to be the rate-determining step as given in Table 3. The lower values of  $m$  for fluoride uptake on the carbon activated at 600 °C indicate a better adsorption mechanism or stronger bonds between the fluoride and the activated carbon. This justifies subsequent removal of fluoride by diffusion through activated carbon, when the concentration gradient is large at the solid–solute interface. Higher values indicate an increase in the solute removal rate.

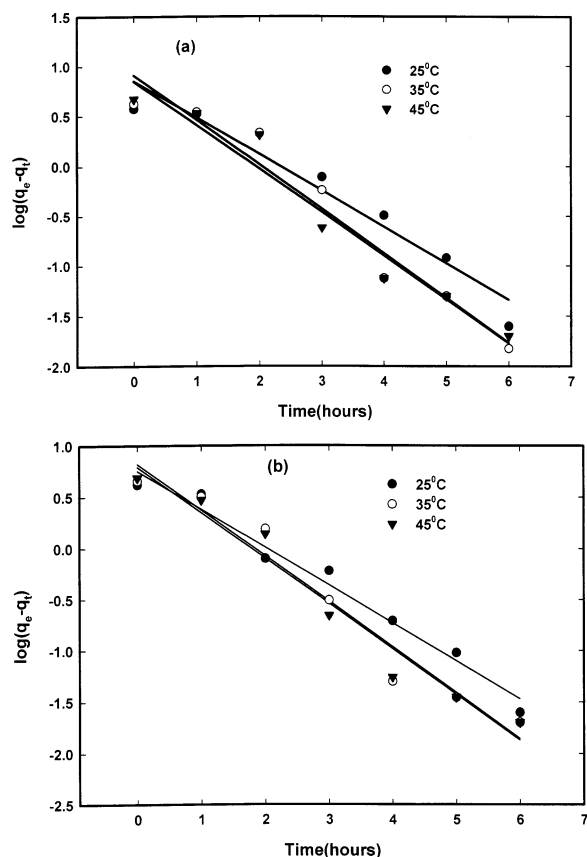
The effect of temperature on the uptake of fluoride is shown in Figure 5. The rate of the removal of fluoride increased with increasing temperature, as discussed before. The data are shown as Lagergren plots in Figure 7 to facilitate the analysis. The Lagergren first-order rate equation<sup>2,32</sup> is written as

$$\log(q_e - q_t) = \log q_e - \frac{K_{ad}}{2.303} t \quad (3)$$

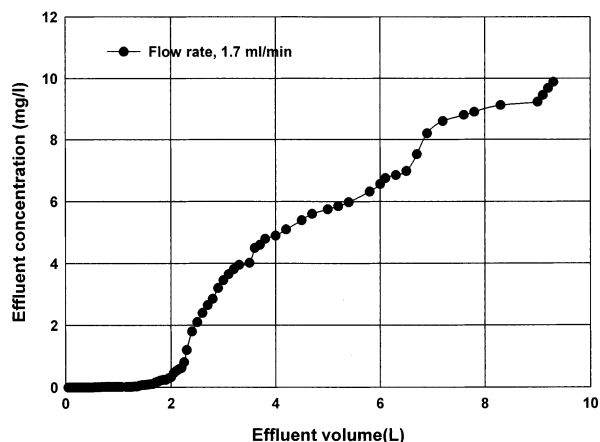
where  $q_e$  is the adsorption at equilibrium (mg/g),  $q_t$  represents the sorption at time  $t$  (mg/g), and  $K_{ad}$  is the rate constant ( $\text{min}^{-1}$ ).

A plot of  $\log(q_e - q_t)$  vs  $t$  gives a straight line, as can be seen in Figure 7, confirming the applicability of first-order rate expression of Lagergren. The adsorption parameter,  $K_{ad}$ , was calculated from the slope of the plot at different temperatures, and the values are presented in Table 4. The parameter  $K_{ad}$  does not change much with change in temperature, as expected, thus reconfirming the applicability of the first-order rate equation.

**3.4. Column Studies.** The column studies were carried out only on H type activated carbon (activated at 600 °C) because of its superior performance in batch studies. The column tests were performed in a 1.2-cm-diameter column. The column was filled with a 10-g sample of the activated carbon (particle size 50–200 mesh). The bed height was 18 cm, and the bed volume was 20 mL. The inlet concentration was 10 mg/L, and the solution pH was 5.5. The hydraulic flow rate was  $1.7 \text{ mL min}^{-1}$ . The breakthrough curve is presented in Figure 8. Initially, all of the fluoride was adsorbed nonselectively, and a fluoride-free effluent was produced. The effluent volume at breakthrough was 100 bed volumes. The column capacity was 4.4 mg/g. In separate tests, it was observed that the column loading



**Figure 7.** Lagergren plots for the adsorption of fluoride on carbon prepared from *E. crassipes* and activated at (a) 300 and (b) 600 °C.



**Figure 8.** Breakthrough curve for the adsorption of fluoride on activated carbon derived from *E. crassipes* at pH 5.5 and a hydraulic flow rate of 1.7 mL/min.

**Table 4. Rate Constants for the Adsorption of Fluoride from Wastewater on Activated Carbons Derived from *E. Crassipes* at Different Temperatures and at Particle Size < 40 Mesh**

temp (°C)	carbon activated at 300 °C		carbon activated at 600 °C	
	$K_d \times 10^2$ (min <sup>-1</sup> )	$R^2$	$K_d \times 10^2$ (min <sup>-1</sup> )	$R^2$
25	1.40	0.9437	1.42	0.9760
35	1.71	0.9508	1.70	0.9564
45	1.67	0.9566	1.70	0.9645

capacity could be increased to 13 mg/g of carbon by using three columns in series (figures omitted for brevity). These results demonstrated that higher capacities could

be attained in industrial-size columns. Further studies are needed to design a treatment system based on this concept. Carbon columns are, in general, subjected to thermal regeneration, where 5–10% of adsorbent is usually lost by attrition during each cycle and the recovery of adsorbate is also not possible. Elution of adsorbate with simultaneous chemical regeneration by a suitable solvent is a definite alternative to thermal regeneration. Therefore, aluminum sulfate solution (0.25%) was used as a solvent. The wet carbon after exhaustion could be readily regenerated using 6 bed volumes (1 BV = 20 mL) of aluminum sulfate solution (0.25%). Initially, 5 bed volumes of aluminum sulfate solution were percolated at a flow rate of 5 mL/min. In the first aliquot of 1 bed volume, 50–55% of the adsorbed amount elutes, and the rest is desorbed in five increments of 1 bed volume each. The final bed volume was left in contact with the carbon overnight. The regenerated carbons, after being washed thoroughly until free of aluminum, were put to repeated use. It was found that there was no change in capacity even after four cycles of operation. A significant decrease in the sorption capacities of various columns has been found after the fourth cycle. The data might be helpful in designing a fixed-bed adsorber for the treatment of fluoride-containing wastewater.

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