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PREPARATION AND DEVELOPMENT OF ADSORBENT CARBON FROM *ACACIA FARNESIANA* FOR DEFLUORIDATION

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ABSTRACT : Batch adsorption dynamics and equilibrium studies for the removal of Fluoride ions from aqueous solution using indigenously prepared Acacia farnesiana carbon (AFC), has been carried out under various experimental conditions at room temperature (30±1^{0}C). Results found that percentage removal of Fluoride (F^-) ions is increased with the decrease in initial concentration and is increased with increase in contact time initially and after 40-45 minutes, the % removal is found to be almost constant. Adsorption is highly pH sensitive and optimum pH range for appreciable or maximum adsorption of F- ion is found to be 6.5-7, with maximum absorption around 6.9. Adsorption data are modeled with isotherms and the different kinetic equations. Kinetics of adsorption is observed to be second order with intraparticle diffusion as one of the rate determining steps. The interactions of the adsorbent with Fluoride samples are characterized by making surface studies using X-ray Photo Electron Spectroscopy (XPS), Fourier Transform Infrared spectroscopy (FTIR), Scanning Electron Microscope (SEM) and Energy Dispersive Spectrum (EDS) techniques. XPS and SEM-EDS data show evidence for Fluoride sorption on the AFC surface via inner-sphere complexation accompanying increased hydrogen bonding and surface oxidation. Removal of F- ions by indigenously prepared activated carbon, AFC, is found to be effective and hence AFC could be employed as an alternative adsorbent to the Commercial Activated Carbon (CAC) for water treatment for the removal of Fluoride ions.

Keywords : Adsorption of Fluoride ions, Acacia farnesiana Carbon, surface characterization, adsorption isotherms, adsorption kinetics, intra-particle diffusion model

INTRODUCTION

Fluoride is an essential nutrient for the human body at low concentrations [1]. However, high concentrations of Fluoride lead to many health issues, such as thyroid disorder, neurological damage, mottling of teeth, and Fluorosis of skeleton [2,3]. The current US EPA drinking water maximum contaminant permissible limit level for Fluoride is 4 mg/L [4]. However, this concentration is considered too high based on recent investigations [5]. The World Health Organization has set a guidance value of 1.5 mg/L for Fluoride in drinking water [6]. Adsorption [7,8], precipitation [9,10], ion exchange [11], donnadialysis [12], electrodialysis [13], reverse osmosis [3], and nanofiltration [14], have been used to remove Fluoride from water. Among these methods, adsorption is the most convenient, effective, and economical, especially for point-of-use applications [15,16]. Several adsorbent materials have been tried in the past to find out an efficient and economical defluoridating agent. Activated alumina, activated carbon, activated alumina coated silica gel, calcite, activated saw dust, activated coconut shell carbon and activated fly ash, groundnut shell, coffee husk, rice husk, magnesia, serpentine, tricalcium phosphate, bone charcoal, activated soil sorbent, carbion, defluoron-1, defluoron-2, etc., are different adsorbent materials reported in the literature [18–29].

Activated carbon is one of the most important types of adsorbents widely used as a tool in environmental protection in various industrial and domestic applications [17]. It is interesting to note that activated carbons produced from different sources differ markedly in their surface characteristics [30]. Exploring the surface phenomenon of active carbons obtained from different flora origin for the removal of pollutants, is an interesting aspect of pollution control studies. Because the active carbons find applications in various water treatment processes in controlling the pollutants, the selection of a suitably activated carbon is an integral part of the design of carbon treatment plants of polluted waters.

A primary characterization of the active carbon product before its application in adsorption process shows the primary sign of versatility in a convinced manner. The adsorptive properties of any activated carbon is highly dependent upon active surface sites incorporating functional groups, specific surface area, particle size, pore volume, pretreatment if any, etc. These factors have remarkable effects on the adsorption capacity and hence, play important role in examining the suitability of the adsorbent for a system. Due to this, modification of the surface chemistry of porous carbons is a viable attractive route towards novel applications of these materials. A modified activated carbon containing different functional groups can be used for technological applications. It is thus, expected that the application of more sophisticated techniques such as FTIR, XPS, NMR spectroscopy, and TGA-DTA, SEM-EDX etc will contribute significantly to a more precise knowledge about these surface chemical groups.

Thus, it is important to develop or find cheaper adsorbents having greater affinity towards Fluoride for the removal of Fluoride from polluted waters. This paper endeavors on to investigate low cost material for Fluoride sorption that can effectively remove Fluoride from aqueous solutions at relatively low levels**.** The novel adsorbent obtained by burning, carbonization and thermal activation of the Acacia farnesiana fruit carbon (AFC) has been chosen for study and found that it possesses appreciable defluoridation efficiency. This adsorbent is abundantly available in all dry and wet lands in huge amount. We report here the results of defluoridation studies using AFC. This study leads to the assumption that Fluoride deposition occurs by the forces of adsorption over the surface of the activated carbon and this aspect has been characterized in the present study by the surface morphological studies of the adsorbent material and further, the dynamics and kinetics of the adsorption process are also discussed lucidly.

MATERIAL AND METHOD

Reagents and chemicals

All chemicals and reagents used were AR grade purchased from Merck. India Pvt. Ltd. and Sd. Fine Chemicals and double distilled water was used to prepare solutions through out this study.

Adsorbent carbon preparation

Acacia farnesiana (Sweet acacia (English), Kasturitumma, Nagatumma (Telugu), Belati babool, Belaiti kikar (Hindi), belongs to Mimosaceae family in plant kingdom. Dry fruits of Acacia were collected in bulk and washed in cold water to remove dust on fruit. Dried in sunlight about one week and cut into small pieces, carbonized in muffle furnace (in absence of air) about 7 hours at 700ºC. After carbonization, carbon was poured in fluoride free water (double distilled water), filtered and washed in several times with cold fluoride free water and dried in an air oven at 110ºC for over night. Then, the carbon was sieved into desired particle sizes. The carbonized material (AFC) in powder form (about 50 g) was taken in a one liter volumetric flask and mixed with approximately 700-800 ml of 0.1M solution HNO_3 and boiled for 2 to 3 hours on flame for Liquid phase oxidation. After acid treatment they were filtered and washed several times with hot water to remove un-reacted acid from carbon surface, until the effluent pH was retained i.e. 6.90.

Defluoridation

100 ml of standard fluoride solution (5 mg/L) was pipette out into a 500 ml beaker. To it, 0.5g/L of the prepared carbon was added and stirred at 200 rpm mechanically for 30 minutes. Then, solution was filtered through Whatman No- 42 filter paper. The F^- ion concentration in the sample after defluoridation was determined using ion-selective electrode specific to fluorides. The same procedure has been adopted for the experiments carried out by varying other parameters.

Fluoride ion analysis

Fluoride ion concentrations were measured using a specific fluoride combination electrode (ISE 25) connected to an Orion 3-Star ion meter after the total ionic strength adjustment. A total ionic strength adjustment buffer was used to adjust pH during the measurement. The percentage removal of F- ion and amount adsorbed (in mg/g) were calculated using the following relationships:

$$\textbf{Percentage removal } (\%\textbf{R}) = \frac{Ci - Ce}{Ce} \times \mathbf{100}$$

$$\textbf{Amount adsorbed } (\mathbf{q_e}) = \frac{Ci - Ce}{m}$$

where Ci and Ce are the initial and final concentrations (in mg/L) of F- ion respectively and ‘m’ is the mass of carbon (in mg/L). Blanks containing no F- ions were used for each series of experiments as controls. The average values of duplicate runs were obtained and analyzed. Error in data: ±1– 2% for percentage removal, ± 0.005–0.01 mg/g for amount adsorbed

Adsorbent characterization

The Brunauer–Emmett–Teller (BET) surface area was determined using computer-controlled nitrogen gas adsorption analyzer at 77 K. Surface functional group distribution of the carbon was evaluated by adsorption experiments [30]. This technique is based on the selective neutralization of surface acid groups by varying strengths of bases and basic groups by a strong acid and is described by Kadirvelu et al.[30]. The pH_{ZPC} for the sorbent was determined using the pH equilibrium method described by Kadirvelu et al.[30] Elemental analysis of C, H, N, and O (by difference) in the activated carbon was carried out on a Perkins Elmer elemental analyzer. Particle size was determined using American Standard Test Method (ASTM) sieves [31]. The prepared activated carbon samples were analyzed on KRATOS AXIS 165 under 10^{-9} torr vacuum with dual Al-Mg-anodes using Mg Kα radiation. The samples were dried at 283 K for 24 hrs before the analysis. Survey and high resolution narrow scans were recorded for C1s, O1s, and F1s photoelectron peaks. The scanning electron microphotographs (SEM) of the carbon sample was recorded using SEM JEOL model, JSM-5600 equipped with EDX Analyzer, an accelerating voltage of 5 kV, at high vacuum mode. The maximum magnification possible in the equipment is 300000 times with a resolution of 3 nm, typically setting at various magnifications for all the samples of study. The adsorbents were examined using Fourier Transform Infrared spectroscopy (FTIR). The sample discs were prepared by mixing of 1 mg of powdered carbon with 500 mg of KBr (Merck; for spectroscopy) in an agate mortar, then pressing the resulting mixture successively under a pressure of 5 tones/ cm^2 for about 5 min., and at 10 tones/ cm^2 for 5 min., under vacuum. The spectra were measured from 4000 to 400 cm-1 on a JASCO-FTIR-5300 model.

RESULTS AND DISCUSSION

Adsorbent characterization

The results pertaining to the sorbent properties of AFC were examined. The BET surface area for AFC was higher (720 m^2/g) than those of some other carbons of agricultural origin reported in literature such as peanut hull (208 m^2/g) [32], coir pith (595m^2/g) [31] eichhornia (266 m^2/g) [33] cassavapeel (200 m^2/g) [34] and coconut tree saw dust carbon (325 m^2/g) [35]. This property is more important for adsorption processes [36]. From the present investigation study, it can be noted that the oxidized AFC possess lower (8.02) pH_{ZPC} values.

This implies that acidic properties are more dominant in this carbon sample and are attributed to the higher number of weakly acidic functional groups. From the studies of elemental analysis, it was observed that a small amount of nitrogen (0.65%) was introduced in to the adsorbent due to nitric acid oxidation. This is confirmed by the presence of specific peek for the N-O stretching in FTIR spectrum (Figure 3). Further, a marked difference obtained from elemental analysis studies, observed in carbon 74.7%, hydrogen 2.23% and sulphur 0.02% contents, reveals the ability of modified sample.

XPS provides valuable information by examining the C1s core region. The high resolution narrow scan for C1s shown in Figure 1 could be resolved into three individual component peaks representing graphite carbon BE = 284.608 eV, carbon present in alcohol or ether groups 286.513 eV, carbonyl groups BE = 287.294 eV and shake up satellite peaks due to $\pi-\pi^*$transitions in aromatic rings BE = 291.493 eV. The surface oxygen peak O 1s was observed (Figure 1) in the region 529.8 to 533.4 eV and it reveals the presence of peak corresponding to C-OH or C-O-C groups with binding energy at 532.05 eV. After the defluoridation of standard fluoride solution with AFC, the representative high-resolution narrow scan for F 1s is shown in Figure 1. The main peak at nearly 688.6 eV indicates the adsorption of fluoride on activated carbon. In the present investigation with XPS the peak for fluoride is not observed before defluoridation with AFC. It is concluded from the obtained results that the percentage of C, is relatively low than O and F. This may be assumed from that of C1s BE's it is clear that graphitic carbon. But the concentration of O is high due to excess of carbonyl (C=O), lactone (O-C=O), and alcohol (OH) etc. From the F1s spectra, C-F type bonding is expected. Examination of the SEM micrograph (Figure 2) of the activated carbon particles showed rough areas of the surface from activated carbon at ×1800 magnification and microspores are clearly identifiable. The EDX spectra of AFC, before and after defluoridation are shown in Figure 2. These spectra show the presence of C, O and F with a major contribution from C. The sample is richer in carbon and Oxygen than any other elements. Some F-ions are found to be trapped at the surface of the activated carbon. FTIR spectral analysis AFC before and after defluoridation was examined and corresponding spectra were given Figure 3. FTIR spectrum band assignments before treatment are: 2924.35 cm-1 and 2852 cm^{-1} and these have been shifted to 2937.06, 2922.42 cm^{-1} after treatment with fluoride solution. These belong to C-H stretching vibrations in methyl and methylene group. Due to making of some new bonds like C-F etc., peaks around 1610-1670 cm^{-1} correspond to C=C stretching vibration in aromatics, around 1433, 1446, 1425 and 1520 cm^{-1} belongs to C-H deformation vibration in alkane, 1260, 1105, 1081 and 1024 cm^{-1} belongs to C-O stretching vibration in alcohol. Beniak et al.[18] reported that tertiary C–N stretching vibration may also result in the contribution of the peak in the region of 1240 cm^{-1}. Band of O-H stretching vibrations were observed around 3600 - 3200 cm^{-1} due to the existence of surface hydroxyl groups and chemisorbed water.

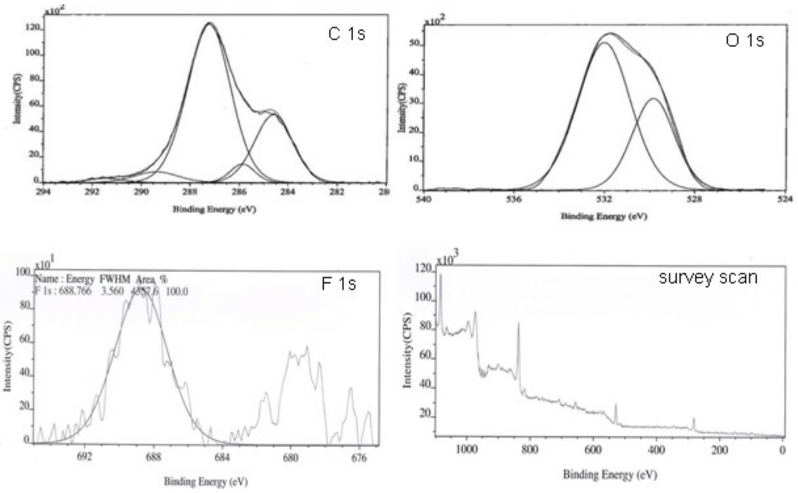

Figure 1: XPS spectral analysis of AFC before and after defluoridation

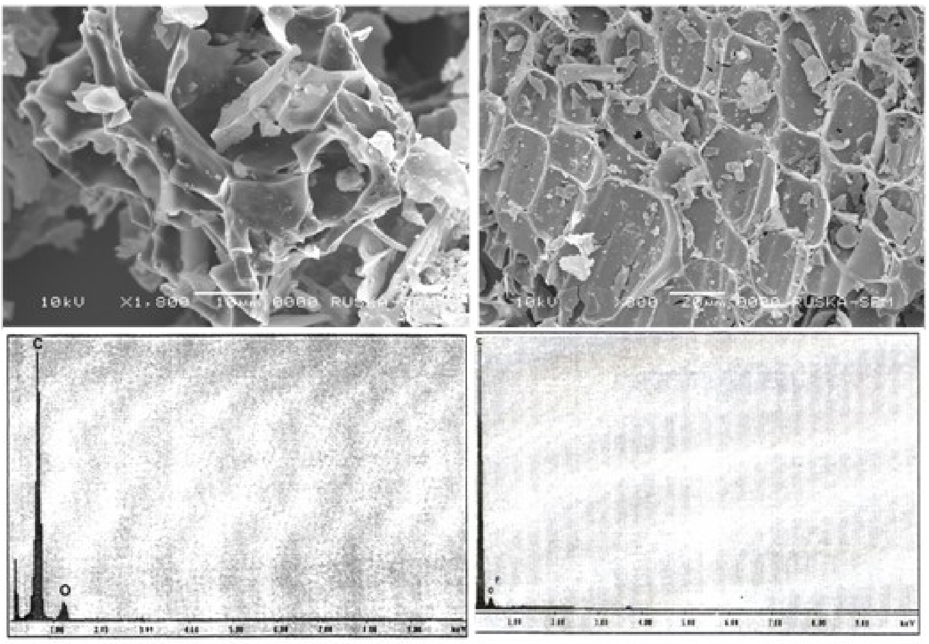

Figure 2: SEM-EDX analysis of AFC before and after analysis

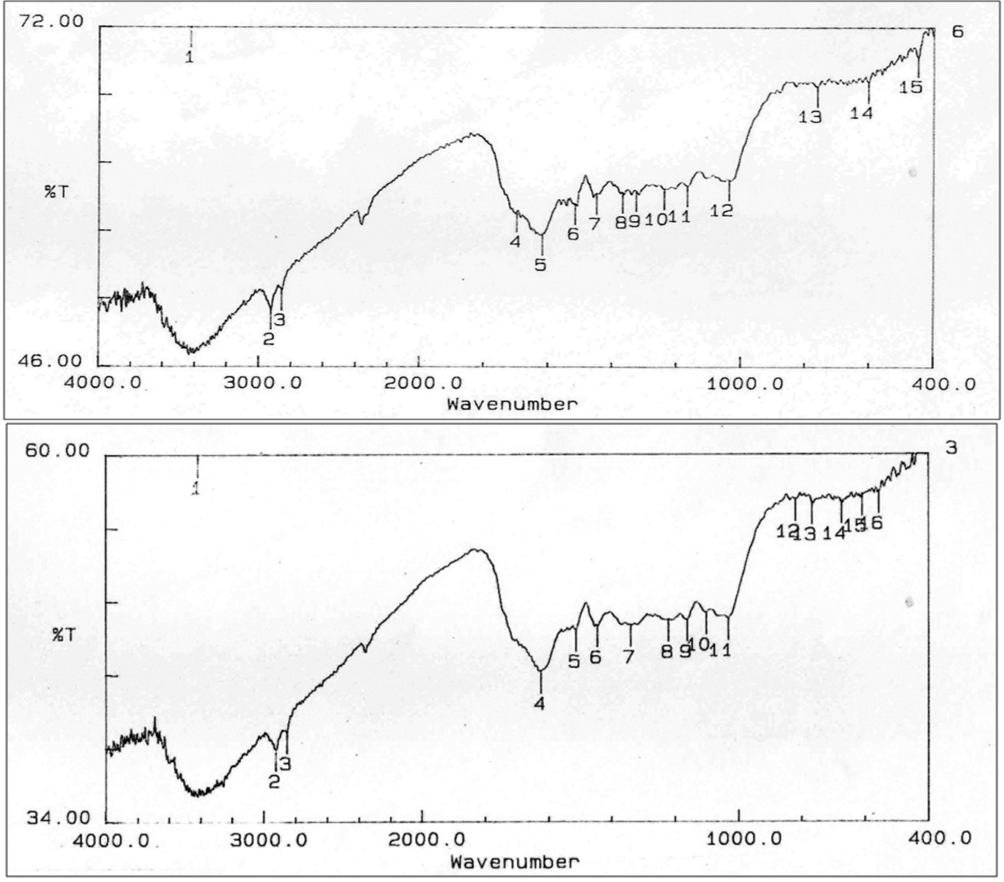

Figure 3: FTIR analysis of AFC before (above) and after (below) analysis

Effect of pH and surface loadings

The effect of pH on fluoride adsorption was examined at 5 mg/L F-ion concentration and at a constant sorbent concentration of 4.0 g/L. The natural pH of the fluoride solution was approximately 6.9. Figure 4 shows adsorption maxima is occurring near 6.5-7.0 and is more than 65% in the pH range of 5.0 – 8.0.

The pH range of maximum adsorption is found to be broader under lower surface loading conditions, and is narrower under higher surface loading conditions. Because protonated surface sites are normally responsible for anion adsorption, fluoride ion adsorption onto AFC is favored under acidic pH conditions. However, according to fluoride speciation, hydrofluoride is predominant for pH condition less than 3.0 [37]. Therefore, the decrease of fluoride adsorption, when the pH was less than 5, was caused by the formation of HF species, which is considered less adsorbable than F-. Under alkaline pH conditions, deprotonation of AFC surface sites occurs and it reduces the total amount of protonated surface sites, i.e., fluoride binding sites. Therefore, the adsorption of fluoride is decreased significantly in the alkaline pH range. As a result, pH is the most important factor controlling fluoride adsorption on AFC and optimum pH rang is found to be 6.5 to 7.0 wherein more than 80% of removal of fluoride is found.

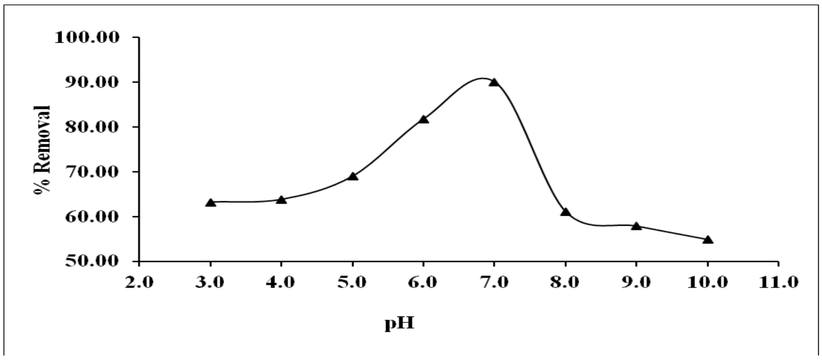

Figure 4: Effect of pH of the fluoride ion solution on the percentage removal

Effect of initial adsorbate concentration

The effect of initial concentration of fluoride on the extent of removal of fluoride in terms of amount of the fluoride adsorbed on the AFC adsorbent has been studied with a fixed dose of adsorbent (4.0 g/L) and constant agitation time (40 minutes) at (30 ± 1^{o}C), by varying the initial concentration of fluoride between 1.50 – 15.0 mg/L. The percentage removal of fluoride exponentially decreases with the increase in the initial concentration of the fluoride (Figure 5). This is due to the lack of sufficient number of available active sites on the adsorbent surface in contrast to the relatively large number of active sites required for the adsorption of high initial concentrations of fluoride ions. The results indicate that when the concentration of fluoride increases from 1.5 to 14.5 mg/L, percent removal of fluoride decreases from 100.0 to 36.00. Further, it is noted that the amount of fluoride adsorbed on the AFC adsorbent, increases exponentially with the increase in the initial concentration of the fluoride. It is found that the fluoride adsorption on the fixed amount of adsorbent (4.0 g/L) is changed from 0.333 to 2.622 mg/g as the concentration of fluoride increases from 1.5 to 14.5 mg/L._

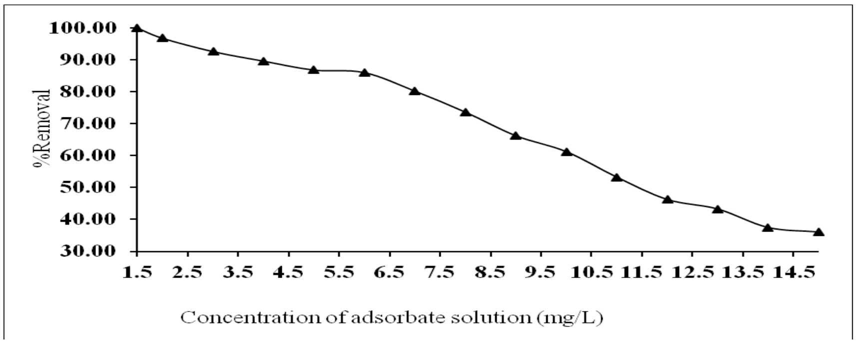

Figure 5: Effect of fluoride ion concentration on the percentage removal

Adsorption isotherms

The adsorption isotherm is the most extensively employed method for representing the equilibrium states of an adsorption system. The purpose of an adsorption isotherm is to relate the adsorbate concentration in the bulk solution to the amount adsorbed at the solid/solution interface. The analysis of isotherm data is important in developing an equation which accurately represents the results and which can be used for design purposes.

The Langmuir and Freundlich adsorption isotherm equations [38] are in common use for describing adsorption isotherms at a constant temperature for water and wastewater treatment application.

Linear form of Freundlich isotherm equation is: $\log(q_e) = \log Kf + (1/n) \log Ce$

where, Kf and 1/n are the Freundlich constants, q_e is the amount of F- ions adsorbed per unit weight of the adsorbent (in mg/g), and if $1/n < 1$, bond energies increases with surface density, if $1/n > 1$, bond energy decreases with surface density and if $1/n = 1$, all surface sites are equivalent, related to sorption capacity and sorption intensity respectively. The magnitudes of Kf and n are calculated from the intercept and slope of the plots. In the present work, plots of log (Ce) Vs log (qe) at different F- ion concentrations are found to be linear as shown in the Figure 6 and confirm the applicability of Freundlich isotherm model for the removal of F- ion by the AFC.
The linearized Langmuir equation is commonly written as: $qe = a\, b\, Ce / (1 + b\, Ce)$,

where *qe* is the amount adsorbed (mg/g) and *Ce* is the equilibrium concentration of adsorbate (mg/L), *a* and *b* are the Langmuir constants related to capacity and energy of adsorption, respectively. In the present work, when *Ce/qe* is plotted against *Ce*, a straight line with slope 1/*ba* is obtained which shows that the adsorption follows the Langmuir isotherm as shown in Figure 7. The Langmuir constants '*b'* and '*a'* are calculated from the slope and intercept with Y-axis.
The values of the Freundlich constants and Langmuir adsorption constants together with the correlation coefficients are presented in Table 1. The observed linear relationships are statistically significant as evidenced from the correlation coefficients (r-values) close to unity, which indicates the applicability of these two adsorption isotherms and the monolayer coverage of F- ion species on the carbon surface.
The important features of the Langmuir isotherm model can be defined by the dimensionless constant separation factor RL which is expressed by the following equation [39].

$$RL = 1/(1+b\, Ci)$$

where, C_i is the initial concentration of fluoride ion (mg/L) and 'b' is the Langmuir constant (in g/L). According to Hall et al [40] the separation factor R_L indicates the isotherm's shape and the nature of the adsorption process as unfavorable ($R_L > 1$), linear ($R_L = 1$), favourable ($0 < R_L < 1$) and irreversible ($R_L = 0$). In the present study, the computed values of R L (Table 1) are found to be fraction in the range of 0-1, indicating that the adsorption process is favorable for the adsorbent in the removal of F- ions.

Table 1: Adsorption isotherm data

S.No.	Isotherm	Parameter	Value
1	Freundlich	K_F	0.0866
		1/n	0.6031
		R^2	0.9806
2	Langmuir	B	0.5145
		A	0.268
		R^2	0.9799
		RL	0.242

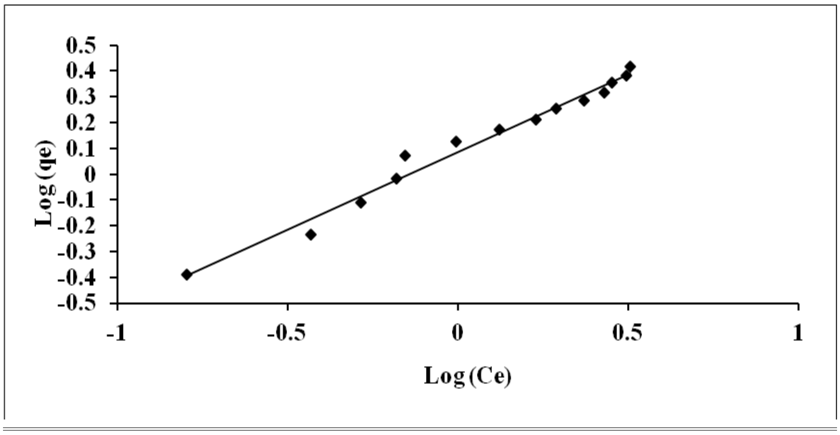

Figure 6: Freundlich isotherm of fluoride adsorption onto AFC

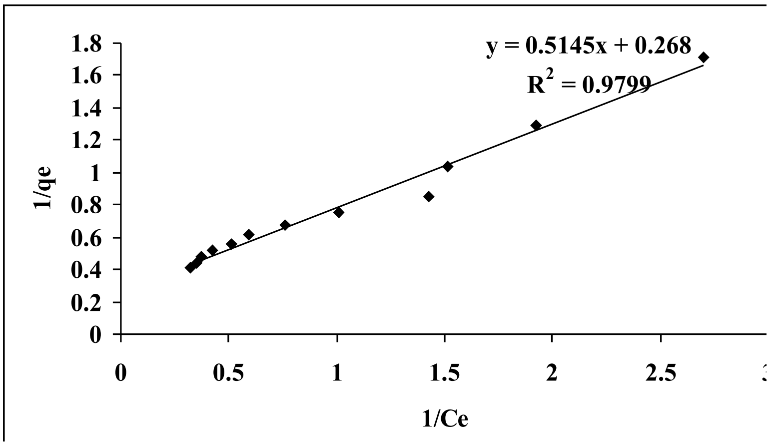

Figure 7: Langmuir isotherm modeling of fluoride adsorption onto AFC

Effect of agitation time

In the adsorption system agitation time plays a vital role irrespective of the other experimental parameters that affect the adsorption kinetics. The adsorption experiments are conducted and the extent of removal of fluoride is known by varying the contact time (5 - 70 minutes) at optimum conditions. The percentage of fluoride removal at different times was worked out and a plot was prepared between the percentage of fluoride removal and contact time (Figure 8). It can be noted that the percentage fluoride removal is increasing with time and attained almost an equilibrium condition in about 40 minutes at which, the rate of adsorption of solute is equal to the rate of desorption. The decrease in the removal of rate of fluoride, particularly towards the end indicates a possible monolayer of fluoride on the outer interface of the activated carbon and pore (intra-particle) diffusion on to the inner surface of the adsorbent particles through the film due to continuous agitation maintain ed during the experiments [41]. The removal of fluoride by this adsorbent sample is rapid at the initial period but becomes slow and almost stagnates with the increase in the contact time. The relative increase in the extent of removal of fluoride is substantially low after 40 minutes of contact time by the adsorbents, which is fixed as the optimum contact time. This indicates that the rate of removal of fluoride is higher in the initial stage due to the availability of adequate surface area of the adsorbent. With increase in contact time, the adsorption process decreases and it is attributed to the decrease in the availability of active sites.

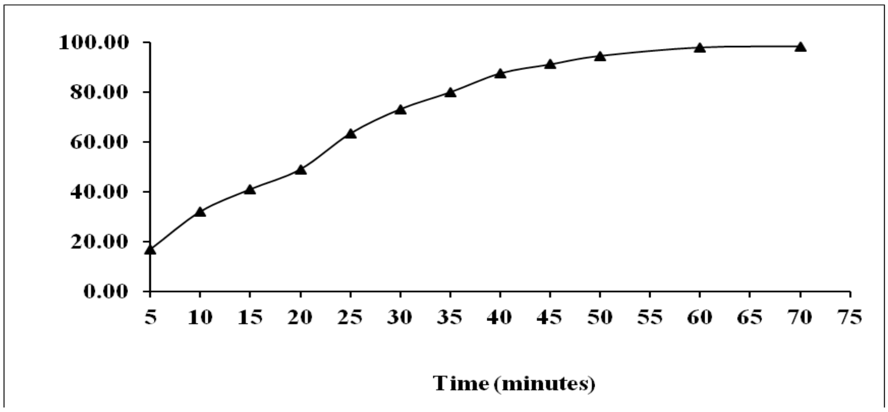

Figure8: Effect of time on the % removal of fluoride ion

Kinetic study of adsorption process

The kinetics of sorption describes the solute uptake rate, which in turn governs the residence time of sorption reaction. It is one of the important characteristics in defining the efficiency of sorption [42]. In the present study, the kinetics of F- ion removal was carried out to understand the behavior of prepared low cost carbon adsorbents and the corresponding data was given in Table 2.

The pseudo first-order equation [43] is: *Log (qe-qt) = log (qe)-* $k_1 t$

It was found in this work that the values of *log (qe - qt)* were linearly correlated with *t*. The plot of *log (qe - qt)* vs. *t* should give a linear relationship from which *k1* and *qe* could be determined from the slope and intercept of the plot (Figure 9), respectively.

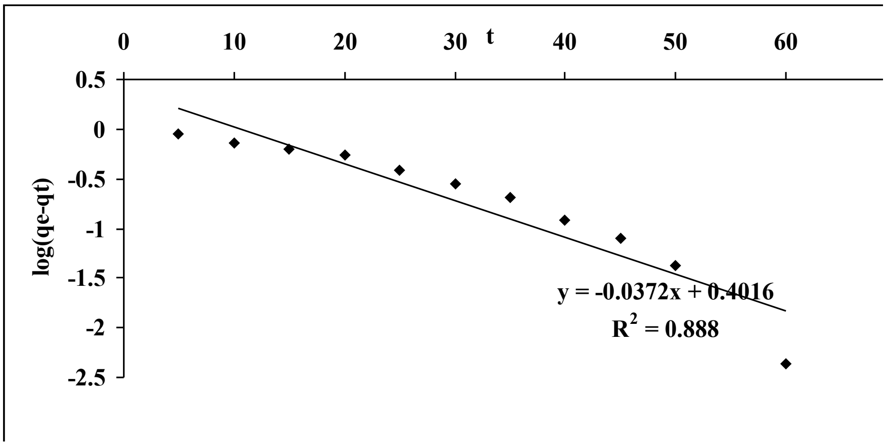

Figure 9: Pseudo-first-order equation

First order kinetics [44]: In order to find out whether the adsorption process followed first order kinetics, the following generalized first order kinetic equation proposed by M. R. Unnithan et al.,[44] was employed. The linearized form of first order equation is represented as follows:

$$\frac{1}{q_t} = \left(\frac{K_1}{q_{max}}\right)\left(\frac{1}{t}\right) + \left(\frac{1}{q_{max}}\right)$$

where qt is the amount of F- ion adsorbed (in mg/g) at various times, t, q_{max} is the maximum adsorption capacity and K_1 is the first order rate constant for the adsorption process (min^{-1}). In the present work, linear correlations of 1/qt Vs 1/t are found (Figure 10) and the results are given in Table 2

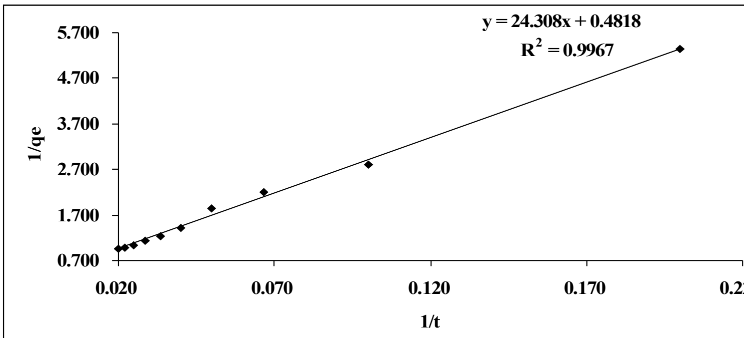

Figure 10: First-order kinetics

Pseudo-second-order kinetic model: The pseudo second-order adsorption kinetic rate equation [45] is expressed as:

$$\frac{t}{qt} = \frac{1}{h} + \frac{1}{qe}\,(t)$$

The plot of (*t/qt*) and 't' should give a linear relationship from which *qe* and *k*$_2$ can be determined from the slope and intercept of the plot (Figure 11), respectively.

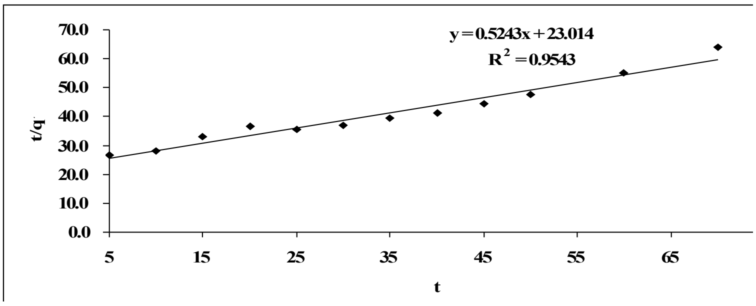

Figure 11: Pseudo-second-order

Second order rate equation [46]: The following integrated rate expression was used to calculate the second order' rate constants

$$\frac{1}{Ce} - \frac{1}{Ci} = K_{ad}\,t$$

where Ci is the initial concentration of the F- ion solution, and Ce is the concentration at time t. From the slopes of the linear plot (t Vs $\frac{1}{Ce}$ -$\frac{1}{Ci}$), as depicted in the Figure 12, the adsorption coefficient (kad) value for AFC was calculated.

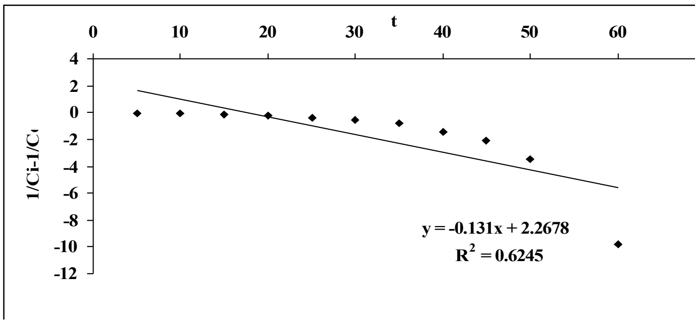

Figure 12: Second order equation

Intraparticle diffusion model [47-48]: The mathematical expression for the intraparticle diffusion model is

$$qe \approx kp\, t^{0.5}$$

where *k*p (mg/g $\text{min}^{-0.5}$) is defined as the intraparticle diffusion rate constant and is related to the intraparticle diffusivity in the following way,

$$k_p = \frac{6qe}{R}\sqrt{\frac{D}{\pi}}$$

where *R* (cm) is the particle radius and *q*e (mg/g) is the solid phase concentration at equilibrium. The plot of the average particle loading, *qe* (mg/g), versus the square root of time, $t^{0.5}$ (Figure 13), would yield a straight line passing through the origin if the adsorption process obeys the intraparticle diffusion model. The slope of the straight line equals to k_p, the intraparticle diffusion rate constant.

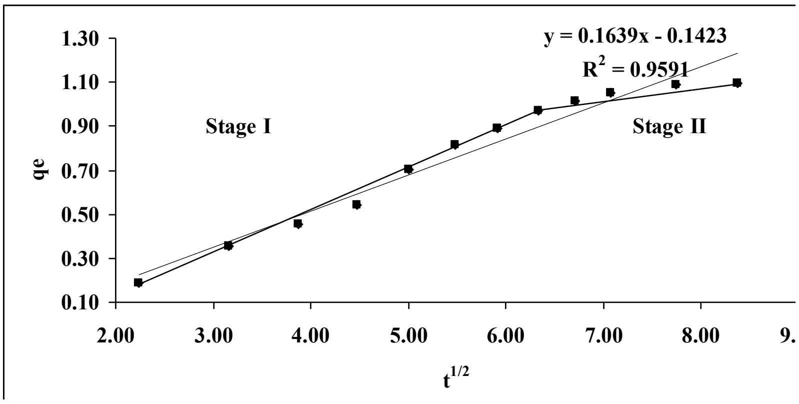

Figure 13: Intra particle diffusion model

Bangham equation [49]: In order to confirm further the occurrence of intraparticle diffusion, the Bangham equation was applied to the sorption data in the following form:

$$\text{Log. Log}\left(\frac{Qo}{Q_0 - Qt.W}\right) = \log\left(\frac{k_0\, W}{2.303\, V} + \alpha \log[(t)]\right)$$

where Qo is the initial concentration (mg/g) of F- ion in the solution, V is the volume of sorbate solution (ml), W is the weight (g) of sorbent, qt is the amount of adsorbate sorbed (g/g) at time t, while α and ko are constants. Using the kinetic data for AFC uptake at room temperature, fair linear plot was obtained between log (log Qo/Qo-Qt) and log (t) (Figure 14) which confirmed the validity of Bangham equation. The values of α and ko, are calculated from the slope and intercept of the linear plot.

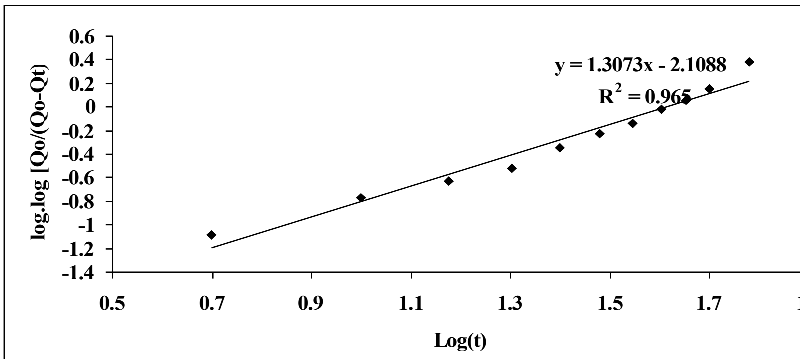

Figure 14: Bhangam isotherm model

Comparison of the applicability of different kinetic models

In order to test the applicability of the five different kinetic models, namely the First-order, pseudo-first-order, pseudo-second-order, second order, and the intraparticle diffusion model, the experimental data was correlated with the linear forms of the five models respectively. The derived rate constants together with the correlation coefficient for the adsorption system, have been listed in Tables 2 and it display the best-fitting results by the First-order rate equation. Several conclusions can be drawn from Tables 2.

Among the five kinetic models, the first-order equation generates the best fit to the experimental data of the present investigated adsorption system. The correlation coefficient obtained is greater than 0.98 and this indicates that the First-order equation is potentially a generalized kinetic model for the adsorption study.

However, it seems that there is no general "second best" model to describe all the adsorption systems. The second best model to generate a good fit to the experiment is the intraparticle diffusion model and well supported by Bhangam model, followed by Pseudo-second-order ($R^2 = 0.9543$), followed by the pseudo-first-order kinetic model ($R^2 = 0.888$) and lastly the second-order kinetic model. It is worth noting that the low correlation coefficients shown in Table 2 do not necessarily mean that the intraparticle diffusion process is not the rate-controlling step. It is a mere indication that the intraparticle diffusion model does not apply to the present investigating adsorption system. This may be due to the following two reasons: first, the intraparticle diffusion model assumes infinite solution volume control, which implies that there is no change in solution concentration during the approach to equilibrium. This is only achieved when the product of the solution volume and solution concentration greatly exceeds the product of the adsorbent mass and the equilibrium sorption capacity of the adsorbent. However, this is not the case for the present investigated adsorption system. Second, the intraparticle diffusion model is derived assuming a constant diffusivity.

Table 2: Kinetics of adsorption fort he removal of F^- ion

S.No	Parameter	Value	S.No	Parameter	Value
1	Pseudo-first-order		4	Second order	
	K1	-0.0372		Kad	-0.131
	R^2	0.888		R^2	0.6245
2	First-order			Qe	
	k1	24.308	5	Intraparticle diffusion model	
	R^2	0.9967		Kp	0.1639
	qe	0.4818		R^2	0.9591
3	Pseudo-second-order		6	Bhangam model	
	K	0.5243		Ko	1.3073
	R^2	0.6245		R^2	0.965
	Qe	23.014		α	-2.1088

Effect of major anions

Natural water may contain many anions that compete with fluoride for adsorption. In this study, effects of HCO^{3-}, SO_4^{2-}, and Cl- were examined at pH 6.9. The initial concentration of fluoride was 5.0 mg/L in all experiments, whereas concentrations of other anions varied from 10 to 300 mg/L. The results show that the fluoride adsorption ratio is decreased from 67% to 40% when the P concentration (in the form of H_2PO_4) is increased from 0 to 300 mg/L. H2PO4 is adsorbed on AFC surface as an inner-sphere complex via ion exchange mechanism and LM He et al [50], suggested H+ ion replaces H_2O or OH^- groups from surface.

Fluoride adsorption also decreased substantially when bicarbonate was present in the system. Bicarbonate is a pH buffering agent and its increasing presence in solution buffers the system pH and thereby diminishes the affinity of the active sites of AFC for fluoride and this result in the reduction of the uptake of Fluoride [51]. Cl- had less impact on fluoride adsorption, as compared to other anions tested. Previous research indicated that Cl- formed outer-sphere surface complexes, while SO_4^{2-} formed both outer-sphere and inner-sphere surface complexes [52]. Therefore, the expected impact of Cl- on Fluoride adsorption is less significant than that of SO_4^{2-}. Overall, the impact of major anions on Fluoride adsorption followed the order: H_2PO_4->HCO_3--> SO_4^{2-}, reflecting the relative affinity of these anions for AFC.

Cost analysis

The relative cost of the material used in the present study is very much lower than that of commercial activated carbons. The Acacia farnesiana fruits are available abundantly through out the year, free of cost, and after considering expenses like transport, chemicals, electrical energy and processing cost, the cost of the material would be approximately US $25/ton. This cost can be further brought down after successful regeneration of the used AFC. The cost of the activated carbon (CAC) used for water treatment in our country is around US $300/ton [53].

CONCLUSIONS

Fluoride adsorption onto AFC obeys a First-order rate law. Results also indicate that the fluoride adsorption reaches a maximum in the pH range of 6.5-7.0, and then decreases with further increasing of pH. For the same pH, the fluoride adsorption follows the Freundlich isotherm, indicating that the AFC surface is highly heterogeneous. XPS, FTIR, and SEM-EDS characterization show evidence for inner-sphere complexation, In addition, a larger population of surface hydroxyl groups accompanied fluoride adsorption along with increased hydrogen bonding present on the AFC surface, indicative of an H···F interactions. Major co-existing anions also affect Fluoride adsorption according to their affinity on the AFC surface. Comparative to the CAC, this adsorbent is low cost material.

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