

## Extraction of Fluoride from Polluted Waters Using Low-cost Active Carbon Derived from Stems of *Acalypha indica* Plant

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**Abstract:** Batch mode adsorption experiments have been conducted successfully for the removal of fluoride from polluted waters with nitric acid active carbon derived from stems of *Acalypha indica* plant (NACIC). The effect of various parameters such as pH, sorbent dosage, agitation time, initial concentration of fluoride, temperature, particle size and presence of foreign ions have been studied in detail and optimized for the maximum extraction of fluoride. Adsorption data have been modelled using Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherms and it has been observed that Langmuir isotherm well describes the experimental data because of  $R_L$  and highest  $R^2$  values. Further, the Dubinin-Radushkevich mean free energy ( $E = 3.16$  kJ/mol) and Temkin heat of sorption ( $B = 0.210$  J/mol) for the NACIC indicates the physisorption. Further, the adsorption kinetics is found to be pseudo-second order rate mechanism followed by pseudo-first order, intra particle diffusion, pore diffusion and Elovich model. FTIR, SEM and EDX studies confirm the fluoride binding ability of adsorbent. Field studies have been carried out with the fluoride-contaminated groundwater samples in order to test the suitability of the NACIC using the same methodology at field conditions and it is found to be remarkably successful.

**Key words:** Activated carbon, adsorption isotherms, adsorption kinetics, application, batch mode studies, fluoride removal, stems of *Acalypha indica* plant, surface characterization.

### Introduction

Deleterious effects of fluoride contamination in groundwaters on the health of human beings such as arthritis, infertility, brittle bones, cancer, brain damage, thyroid disorder, including skeletal and dental fluorosis (Savinelli and Black, 1958; Chaturvedi, 1990; Chinoy, 1991; Lounici et al., 1997; Srimurali et al., 1998; Wang and Reardon, 2001; Cengeloglu et al., 2002; Jamode et al., 2004; Ayoob and Gupta, 2006; Barbier et al., 2010; Gazzano et al., 2010; Ganvir and Das, 2011) are well known and intensive research in controlling this potential pollutant in contaminated waters is being globally pursued by environmental researchers. The

maximum permissible limit of fluoride in water is 1.5 mg/L by WHO (BIS, 1991; WHO, 2004).

Traditional methods based on nano-filtration (Liu et al., 2007), electro dialysis (Adhikary and Tipnis, 1989; Amer et al., 2001), Donnan dialysis (Hichour, 2000; Garmes, 2002; Tor, 2007), reverse osmosis (Simons, 1993; Sehn, 2008), chemical precipitation (Nawlakhe, 1975; Reardon and Wang, 2000; Yadav et al., 2006), membrane-based methods (Lhassani et al., 2001; Mameri et al., 2001; Mjengera and Mkongo, 2003), electro-coagulation (Hu et al., 2003), ion-exchange (Singh et al., 1999; Castel et al., 2000; Meenakshi and Viswanathan, 2010) are found to be tedious, non-economical, generation of secondary pollutant,

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less encouraging for adoption for treating waters on large scale and they suffer from one or the other disadvantage and a universally acceptable, simple and economical methods of de-fluoridation are still eluding the researchers.

In this context the use of the bio-sorbents derived from plant materials either in their native state or chemically modified in controlling this dangerous polluting ion in waste waters, is proving to be potential alternative to the traditional methods and this aspect is stimulating the continuous and expanding research in this field. Activated carbons derived from *Moringa Indica* (Karthikeyan and Siva Elango, 2007), *Cynodon dactylon* (Alagumuthu et al., 2011), *Emblica phyllanthus* (Ramachandra Murthy, 2003), sulphated coconut shell carbon (Seethapathirao, 1964), zirconium impregnated Lapsi seed stone carbon (Joshi et al., 2012), zirconium impregnated coconut fibre carbon (Sai Sathish et al., 2008), neem (*Azadirachta indica*) and kikar (*Acacia arabica*) leaves carbon (Sunil Kumar et al., 2008) have been explored for their abilities for de-fluoridation of polluted water.

In the present work, nitric acid activated carbon pertaining to stems of *Acalypha indica* plant (NACIC) has been probed for its de-fluoridation abilities. The physical and chemical characterization of NACIC has been carried out by adopting standard methods. The surface morphological studies of NACIC have been carried out by Fourier Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray (EDX) analyzers. The performance of NACIC has been evaluated under Batch Conditions of Extraction (Raichur and Basu, 2001; Lounici et al., 2004) by varying the various physico-chemical parameters such as pH, contact time,

adsorbent dose, initial concentration of the fluoride ion, particle size, temperature and effect of interfering ions and the extraction conditions have been optimized for the maximum removal of fluorides from waters. Further, the nature of the adsorption processes have been analyzed by Freundlich, Langmuir, Temkin and Dubinin-Radushkevich (D-R) isotherms and kinetics of adsorption have been studied using pseudo first-order, pseudo second-order, Weber and Morris intraparticle diffusion, Bangham's pore diffusion and Elovich equations. The methodologies developed have been applied to real groundwater samples polluted with fluoride.

## Experimental

### Materials

#### *Reagents and Chemicals*

All the chemicals used were of analytical reagent grade purchased from Merck India Pvt. Ltd. and Sd. Fine Chemicals and all solutions were prepared by using double distilled water throughout this study. Fluoride stock solution of 100 mg/L was prepared by dissolving requisite amount of NaF in double distilled water and the required working standards were prepared by successive quantitative dilution of the stock solution. SPADNS solution, zirconyl-acid reagent, acid zirconyl-SPADNS reagent and reference solution were prepared as described in Standard methods for the Examination of Water and Waste Water (APHA, 1998).

#### *Plant Selected for the Study*

The present work deals with the use of active carbon derived from stems of *Acalypha indica* plant. The *Acalypha indica* plant (Figure 1), also known

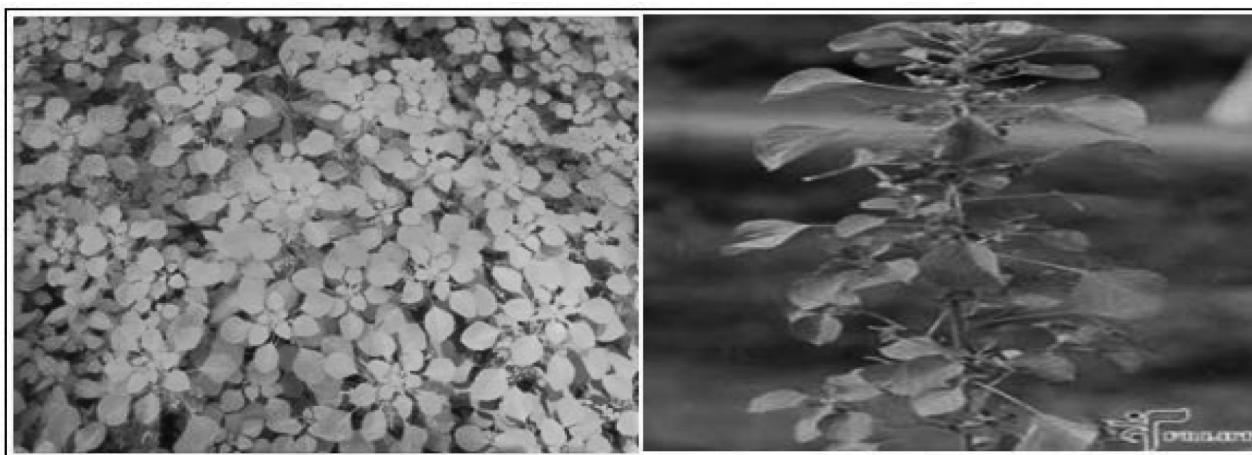


Figure 1: *Acalypha indica* plant.

as Muripinda or Kuppinta chettu (in local Telugu language), belongs to the Euphorbiaceae family in plant kingdom. It is an annual herb and grows up to about 75 cm in height. It is a weed in gardens, in waste places and along the roadsides. Traditional medicines can be prepared from all parts of this plant.

#### Adsorbent Preparation

The bio-sorbent was prepared from stems of *Acalypha indica* plant by initial cleaning of dust particles with double distilled water, dried completely under sunlight. The dried material was cut into pieces and carbonized in muffle furnace in the absence of air at 500°C for about four hours. After carbonization, the carbon was grounded, washed with fluoride-free water, dried in air oven at 110°C and it was sieved into desired particle sizes. Then the carbonized material was mixed with approximately 0.1M HNO<sub>3</sub> and boiled for 2 to 3 hours on flame for liquid phase oxidation.

After acid treatment, the carbon was washed with double distilled water repeatedly to remove the unreacted acid and dried at 150°C for 12 hours. This nitric acid activated carbon prepared from stems of *Acalypha indica* plant was named as NAcIC.

### Methods

#### Batch Mode Adsorption Studies

Batch experiments were designed to investigate the efficiency of fluoride removal with varying conditions extraction. 100 ml of standard fluoride solution (5 mg/L) was pipette out into a 250 ml conical flask and to it weighed quantities of the NAcIC was added, pH was adjusted and the solution was stirred for desired period at 200 rpm on a mechanical shaker at room temperature 30±1°C. Then the solution was filtered through Whatman No. 42 filter paper. The fluoride concentration in the sample after de-fluoridation was determined by SPADNS method using U.V-Visible Spectrophotometer (Model No. Elico U.V-2600) as described in Standard Methods for the Examination of Water and Waste Water (APHA, 1998) at  $\lambda_{\max}$  570 nm. The same procedure has been adopted for the experiments carried out by varying physicochemical parameters such that adsorbent dosage, pH of the fluoride solution, initial concentration of the standard fluoride solution, agitation time, particle size, temperature and in presence of interfering ions.

#### Fluoride Ion Analysis

The percentage removal of fluoride ion and amount adsorbed (in mg/g) were calculated using the following equations.

$$\% \text{ Removal } (\%R) = \frac{c_i - c_e}{c_i} \times 100$$

$$\text{Amount adsorbed } (q_e) = \frac{c_i - c_e}{m} V$$

where  $c_i$  = Initial concentration of the fluoride solution in mg/L,  $c_e$  = Equilibrium concentration of the fluoride solution in mg/L,  $m$  = Mass of the adsorbent in grams, and  $V$  = Volume of fluoride test solution in litres.

#### Characterization of NAcIC

The results obtained from the standard methods for the various physicochemical properties of NAcIC are presented in Table 1. The pH for the activated carbon adsorbent was determined using the Elico pH meter, model LI-120 and the pH<sub>ZPC</sub> was determined using the pH equilibrium method (Newcombe et al., 1993; Kadirvelu et al., 2000; Marsh and Rodriguez-Reinoso, 2006). Particle size was determined using American Standard Test Method (ASTM) sieves (El-Hendawy et al., 2001). Iodine number (Hill and Marsh, 1968; ASTM D4607-94, 2006), decolourizing power (Girgis and El-Hendawy, 2002; Rozada et al., 2005) and other parameters such as apparent density, moisture, loss on ignition, ash, water soluble matter and acid soluble matter were analyzed by using standard test methods (ISI, 1989; Namasivayam and Kadirvelu, 1997). The BET surface area (Brunauer et al., 1938; Hashim, 1994; Kadirvelu et al., 2000) was determined by Quantachrome NovaWin-Data Acquisition and Reduction for NOVA instruments version 10.01 using nitrogen gas adsorption analyzer at 77 K.

The surface acidic and basic functional groups were determined according to Boehm titration (Bandosz et al., 1992; Boehm, 1994). FT-IR spectra of NAcIC, before and after fluoride adsorption, were recorded from 4000 to 500 cm<sup>-1</sup> on a BRUKER VERTEX 80/80v FT-IR spectrometer, optical resolution of <0.06 cm<sup>-1</sup>, with automatic and vacuum compatible beam splitter changer (BMS-c) option with anhydrous KBr as a pellet material. The surface morphology of the NAcIC was determined by LEO 1420 VP Compact variable pressure Digital SEM, manufactured by Leo Electron Microscopy Ltd. (Beam voltage 500 to 2000 V, Magnifications 250 to 65,000 X, Resolution 3 nm at 1000 V) and the elemental analysis was recorded using BRUKER EDX two-dimensional V ANTEC-500 detector.

**Table 1: Physicochemical properties of NAcIC**

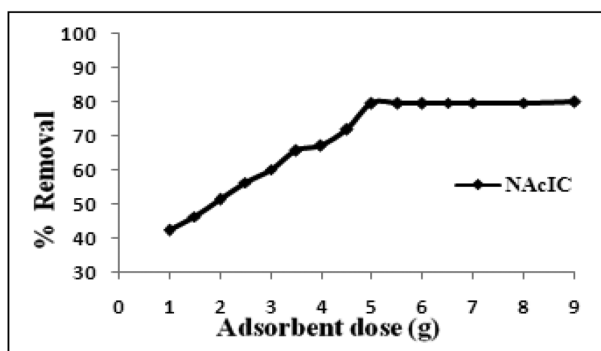
S.No.	Parameter	Value
1	Apparent density (g/ml)	0.323
2	Moisture content (%)	7.62
3	Loss on Ignition (LOI) (%)	89.93
4	Ash content (%)	6.63
5	Water soluble matter (%)	0.65
6	Acid soluble matter (%)	0.88
7	Decolourizing power (mg/g)	302
8	pH	7.38
9	pH <sub>ZPC</sub>	9.64
10	Iodine number (mg/g)	564
11	Particle size ( $\mu$ )	45
12	BET analysis - before	209.4
	Surface area, m <sup>2</sup> /g after	192.8
13	Surface functional groups (meq/g)-Boehm Titration	
I	Carboxyl	0.992
II	Lactonic	1.002
III	Phenolic	1.014
IV	Carbonyl	1.018
V	Total basic groups	5.347

## Results and Discussions

### Effect of Various Physicochemical Parameters on Fluoride Removal

#### Effect of NAcIC Dosage on Fluoride Removal

The effect of adsorbent dosage on the fluoride removal efficiency was studied with increasing NAcIC amount from 1.0 to 9.0 g/L keeping all other parameters constant at optimum levels namely, fluoride ion concentration: 5.0 mg/L, pH: 7, contact time: 60 min, particle size: 45  $\mu$  and temperature: 30 $\pm$ 1°C. The obtained results are plotted and shown in Figure 2.

**Figure 2: Effect of adsorbent dose on fluoride removal.**

It was observed that the fluoride adsorption was rapid and significant up to NAcIC dosage of 5.0 g/L and then remained constant. Therefore, the amount 5.0 g/L was considered as the optimum NAcIC dosage.

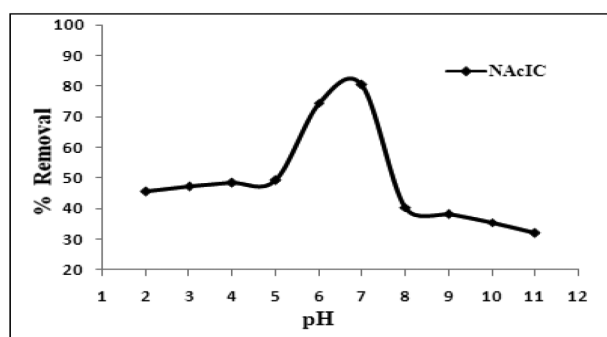
#### Effect of pH on Fluoride Removal

The effect of pH of fluoride solution on the percentage removal of fluoride was studied by varying pH of fluoride solution from 2 to 11 while keeping all other parameters constant at optimum levels i.e. at fluoride ion concentration: 5.0 mg/L, adsorbent dosage: 5.0 g/L, contact time: 60 min, particle size: 45  $\mu$  and at temperature of 30 $\pm$ 1°C. The results obtained are presented in Figure 3.

It may be seen from Figure 3, good extraction of fluoride was observed in the pH range 5 to 8 with maximum at pH: 7. As per Table 1, the pH of the adsorbent surface is 7.38 while pH<sub>ZPC</sub> is 9.64. This indicates that the net surface charge on NAcIC is positive. Hence, the surface has thrust for negatively charged fluoride ion (F<sup>-</sup>). But at low pH less than 3, neutral hydrofluoric acid (HF) species is predominant (Lagergren, 1898) and so, HF being neutral has less affinity towards the surface of the NAcIC. Further, in the alkaline pH range, the decrease in adsorption may be attributed to the competition of the hydroxyl ions with the fluoride ions for adsorption (Karthikeyan et al., 2011). Hence, the optimum pH has been found to be 7 and below and above this range the percentage removal of fluoride ion is less.

#### Effect of Contact Time on Fluoride Removal

Contact time plays a very important role in adsorption kinetics and it is used to evaluate the adsorption rate constants. The effect of contact time on the percentage removal of fluoride was studied by varying contact time from 10 to 100 min while keeping all other parameters constant such as pH (=7), fluoride ion concentration (5.0 mg/L), adsorbent dosage (5.0 g/L) and temperature of 30 $\pm$ 1°C. The results obtained were as shown in Figure 4.

**Figure 3: Effect of adsorbent pH on fluoride removal.**



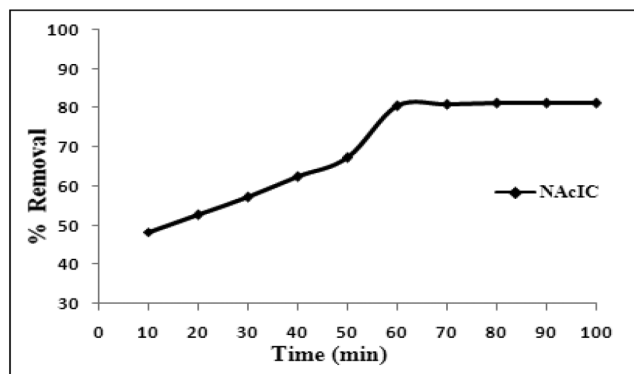


Figure 4: Effect of contact time on fluoride removal.

It was observed that the fluoride adsorption process was rapid initially and then it became slowed down with time and attained equilibrium state at/after 60 min. The first rapid adsorption might be due to the availability of large surface area and consequently the large number of active sites for the adsorption process on the surface of NAcIC (Alagumuthu et al., 2011). But as the time increases progressively, surface has less number of un-occupied active sites and moreover, for fluoride being sorbed, it has to penetrate in search of new inner active sites of the NAcIC as the outer surface site have already been occupied by fluoride in initial timings (Alagumuthu et al., 2011). This factor namely less availability of active sites as the time progresses and the time lag for sorption in the course of penetration, result in the decrease in the adsorption of fluoride (Nawlakhe, 1975; Namasivayam and Kadirvelu, 1994).

#### *Effect of Initial Fluoride Concentration on Fluoride Removal*

The effect of initial fluoride concentration on the percentage removal of fluoride was studied by varying initial fluoride ion concentration from 1 to 12 mg/L keeping all other parameters constant such as pH (=7), adsorbent dosage (5.0 g/L), contact time (60 min) and at temperature of  $30 \pm 1^\circ\text{C}$ . The results obtained are shown in Figure 5.

It was noticed that the percentage removal of fluoride gradually decreased with increasing initial fluoride concentration. This might be due to the fact that for a constant adsorbent dosage, total available adsorption sites were limited and, hence, the binding capacity of the adsorbent had approached saturation resulting in decrease in fluoride adsorption (Onyango et al., 2004; Kagne et al., 2008). With an increase in initial concentration of fluoride ion solution from 1 to 12 mg/L, the percentage removal (%R) decreased from 88.5 to 47.2%.

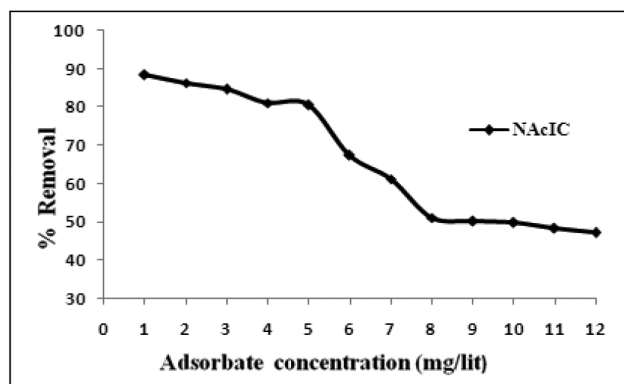


Figure 5: Effect of initial fluoride concentration on fluoride removal.

#### *Effect of Particle Size on Fluoride Removal*

The variation in the percentages of fluoride removal by NAcIC with different particle sizes was studied. The de-fluoridation experiments were conducted using NAcIC with 45 to 150 $\mu$  mesh sized particles while keeping all other parameters constant such as pH (=7), fluoride ion concentration (5.0 mg/L), adsorbent dosage (5.0 g/L), contact time (60 min) and at temperature of  $30 \pm 1^\circ\text{C}$ . The results obtained were as shown in Figure 6.

It can be inferred from the graph that the percentage removal of fluoride ion decreases with increase in particle size of NAcIC and it is attributed to the availability of active sites on the surface of the active carbon. The adsorption is a surface phenomenon. Lesser the particle size more will be the surface area and more will be the number of active sites on the adsorbent surface. Hence, 45 $\mu$  mesh sized particles have high de-fluoridation efficiency due to larger surface area and the efficiency decreases with increase in the particle size.

#### *Effect of Interfering Ions on Fluoride Removal*

The effect of interfering anions such as chloride, nitrate, sulphate, bicarbonate and phosphate on fluoride adsorption by the NAcIC was examined with 50 mg/L

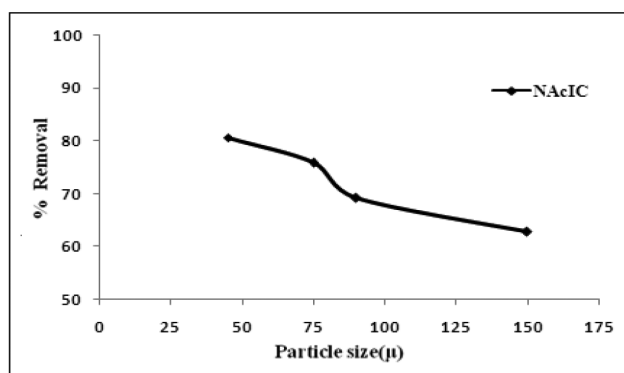


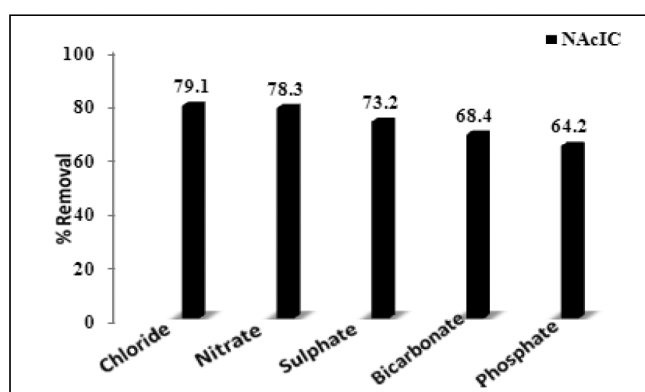
Figure 6: Effect of particle size on fluoride removal.

concentration of interfering ions keeping all other parameters constant such as (pH: 7), fluoride ion concentration (5.0 mg/L), adsorbent dose (5.0 g/L),

contact time (60 min) and at temperature of  $30 \pm 1^\circ\text{C}$ . The results obtained are presented in Table 2 and plotted as shown in Figure 7.

**Table 2: Effect of interfering ions on fluoride ion removal from aqueous solution by NAcIC**

S. No.	Adsorbent	Maximum extractability at optimum conditions	Extractability of fluoride ion of conc. 5 mg/L in presence of 50 mg/L of interfering ions at optimum (pHs)				
			$\text{Cl}^-$	$\text{NO}_3^-$	$\text{SO}_4^{2-}$	$\text{HCO}_3^-$	$\text{PO}_4^{3-}$
1	NAcIC	80.6%, pH: 7, 50 min.	79.1%, pH: 7, 50 min.	78.3%, pH: 7, 50 min.	73.2%, pH: 7, 50 min.	68.4%, pH: 7, 50 min.	64.2%, pH: 7, 50 min.



**Figure 7: Effect of interfering ions on fluoride removal.**

The selective nature of the fluoride by the adsorbent depends on size, charge, polarizability, electro negativity difference, etc. and for NAcIC, the order of interference for fluoride removal observed was in the following order,  $\text{PO}_4^{3-} > \text{HCO}_3^- > \text{SO}_4^{2-} > \text{NO}_3^- > \text{Cl}^-$ .

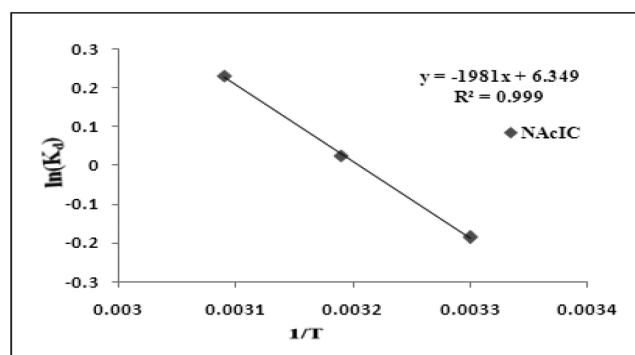
Similar trend was reported while studying Cynodon dactylon as a sorbent for fluoride removal (Alagumuthu et al., 2011). Chloride and nitrate did not perceptibly interfere with fluoride removal as they can form outer-sphere surface complexes while sulphate form both outer-sphere and inner-sphere surface complexes (Onyango et al., 2004) began to show some significant effect on fluoride removal efficiency. However, bicarbonate showed great competitive adsorption with fluoride because the bicarbonate alkalinity of the water reduces the affinity of the active sites of NAcIC for fluoride adsorption (Alagumuthu and Rajan, 2010). Phosphate ion which is having high negative charge compared to other anions needs three close surface groups and adsorbed on adsorbents as inner-sphere surface complex. This inner-spherically adsorbing phosphate ion (Goldberg and Sposito, 1984a, b; Zhang and Spark, 1990) can significantly interfere with the fluoride ion and hence decrease in the percentage

removal of fluoride ion from water. Fluoride sorption was mainly influenced by the presence of phosphate ion followed by bicarbonate, sulphate, nitrate and chloride respectively. Fluoride sorption came down from 80.6 to 79.1, 78.3, 73.2, 68.4 and 64.2% in presence of interfering ions chloride, nitrate, sulphate, bicarbonate and phosphate respectively.

The effect of 10-fold excess of common cations present in natural waters namely  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Cu}^{2+}$ ,  $\text{Fe}^{2+}$  and  $\text{Zn}^{2+}$  on the % removal of fluoride has been studied and the effect is found to be marginal.

#### *Effect of Temperature on Fluoride Removal*

The temperature has a significant influence in the adsorption process and hence, in the present study, the adsorption of fluoride on NAcIC was monitored at three different temperatures, viz., 303, 313 and 323 K by keeping all other parameters constant such as (pH: 7), fluoride ion concentration (5.0 mg/L), adsorbent dose (5.0 g/L) and contact time (60 min). The results obtained are presented in Figure 8 and the corresponding values of various thermo dynamical parameters were found to be:  $\Delta H$  (kJ/mol): 16.47;  $\Delta S$  (J/mol/K): 52.79;  $\Delta G$  (kJ/mol): 0.4746 for 303,  $-0.0533$  for 313,  $-0.5812$  for 323 and  $R^2 = 0.999$ .



**Figure 8: Effect of temperature on the adsorption of fluoride ion.**

The positive values of  $\Delta H$  (Bouberka et al., 2005) and less than 20 kJ/mol (Atkins, 1999) of enthalpy indicate the physisorption and endothermic nature of the adsorption process. The positive value of  $\Delta S$  indicates the increased disorder and randomness at the solid solution interface during the adsorption of fluoride ion on adsorbent (Sairam Sundaram et al., 2009). The  $\Delta G$  values were both negative and positive. The negative values of  $\Delta G$  indicate the spontaneous nature (Chaturvedi et al., 1988) of adsorption process and positive indicates the adsorption is non-spontaneous. These observations are similar to the investigations of Xu Xiaotian et al. (2011) who also reported positive and negative values for  $\Delta G$  with respect to the fluoride adsorption on magnesia-loaded fly ash cenospheres.

#### Adsorption Isotherms

The mechanism of adsorption fluoride on NAcIC was studied using Nadsorbate interaction with adsorbent at equilibrium widely used models, namely Freundlich model which is an indicative of surface heterogeneity of the adsorbent (Freundlich, 1906), Langmuir equation which is valid for monolayer adsorption on to adsorbent surface (Langmuir, 1918), Dubinin-Radushkevich (D-R) isotherm used to describe adsorption on both homogeneous and heterogeneous surfaces (Dubinin and Radushkevich, 1947) and Temkin isotherm describes

the adsorption on heterogeneous surfaces (Temkin and Pyzhev, 1940), were employed. The linear plots of all these four models are presented in Figure 9 and the corresponding constants calculated from the slopes and intercepts of the linear plots and are presented in Table 3 along with correlation coefficients ( $R^2$ -values).

The correlation coefficient ( $R^2$ ) value was higher in the Langmuir isotherm ( $R^2 = 0.972$ ) than in the Freundlich isotherm ( $R^2 = 0.892$ ) and further, the value of dimensionless separation factor ( $R_L = 0.1225$ ) was found to be in the range 0-1 and these facts indicated the favourability of the Langmuir isotherm than the Freundlich isotherm and confirmed the monolayer coverage of fluoride ions on the surface of NAcIC (Altundogan et al., 2000; Dogan et al., 2004).

The Dubinin-Radushkevich mean free energy (Onyango et al., 2004),  $E = 1/\sqrt{2}\beta$  and Temkin heat of sorption ( $B$ ) calculated from the slopes of Temkin linear plots (Hameed, 2009; Nunes et al., 2009) were found to be as 3.16 kJ/mol and 0.210 J/mol respectively for NAcIC. These values confirmed the ‘physisorption’ nature of the adsorption process both as per Mounika et al. (2009) and Atkins (1999). The “Physisorption” is also called nonspecific adsorption and it occurs as a result of long range weak vander Waals forces between fluoride ions and adsorbent.

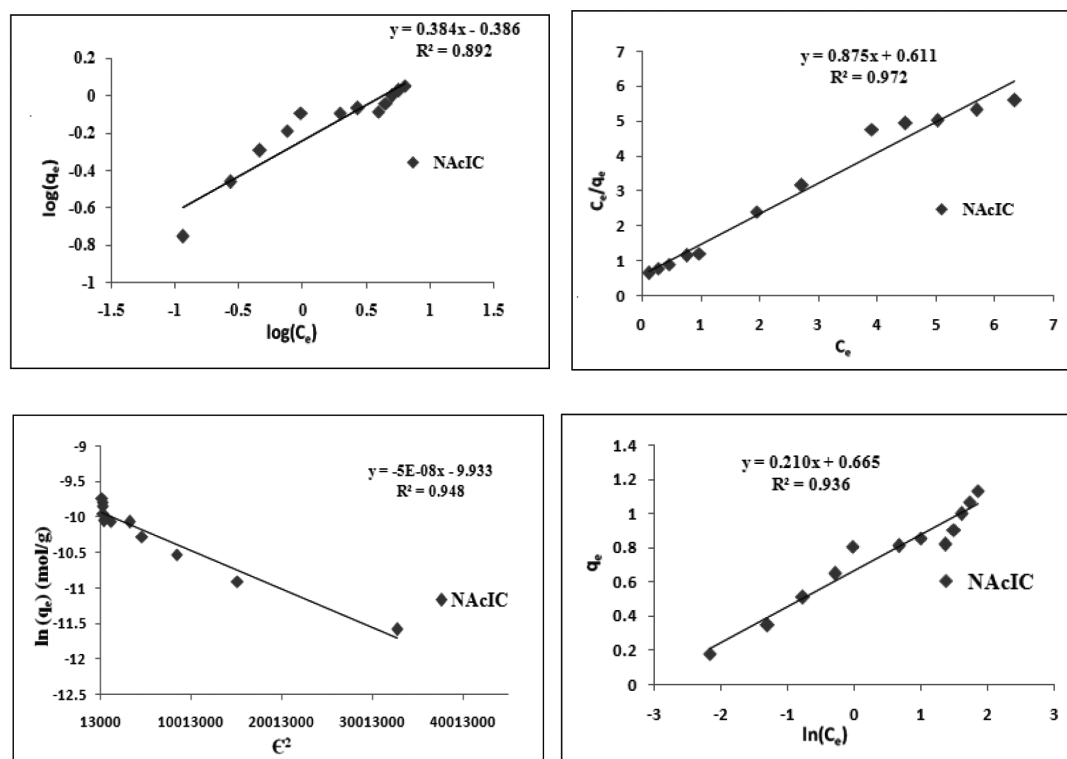


Figure 9: Freundlich, Langmuir, Dubinin-Radushkevich and Temkin isotherms (left to right in each figure).

**Table 3: Adsorption isotherm parameters**

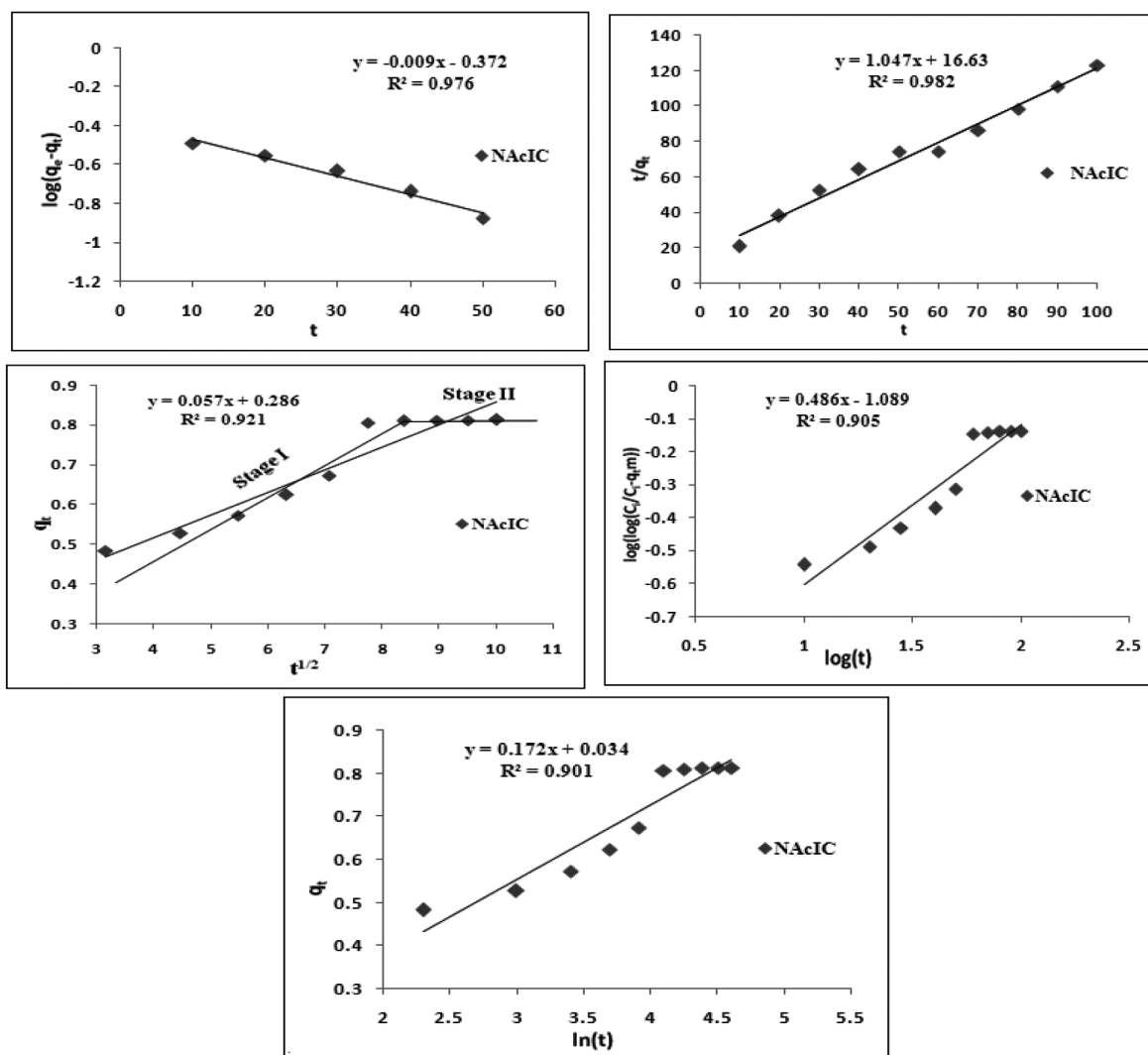
S. No.	Adsorption isotherms		Slope	Intercept	$R^2$
1	Freundlich isotherm		0.384	-0.386	0.892
2	Langmuir isotherm	$R_L = 0.1225$	0.875	0.611	0.972
3	D-R isotherm	$E = 3.16$ kJ/mol	$-5E-08$	-9.933	0.948
4	Temkin isotherm	$B = 0.210$ J/mol	0.210	0.665	0.936

### Adsorption Kinetics

The mechanism of adsorption was studied using pseudo first-order (Lagergren, 1898; Ho and Mackay, 1999, 2000), pseudo second-order (Ho and Mackay, 1999, 2000; Ho et al., 2000; Kumar et al., 2011), Weber and Morris intraparticle diffusion (Weber and Morris, 1963), Bangham's pore diffusion (Aharoni and Ungarish, 1977) and Elovich (Chien and Clayton, 1980; Ozacar and Sengil, 2005; Gerente et al., 2007) as per the well

known equations. The linear plots of all these five kinetic models are presented in Figure 10 and kinetic parameters along with correlation coefficients values are presented in Table 4. The best fit model was selected based on the linear regression correlation coefficient ( $R^2$ ), where the model matches with the experimental data.

The experimental data reveals that the correlation coefficient value for the pseudo second-order model



**Figure 10: Pseudo first-order, pseudo second-order, Weber and Morris intraparticle diffusion, Bangham's pore diffusion and Elovich model (left to right in each figure).**



**Table 4: Kinetic parameters**

S. No.	Adsorption kinetics	Slope	Intercept	$R^2$
1	Pseudo first-order model	-0.009	-0.372	0.976
2	Pseudo second-order model	1.047	16.63	0.982
3	Weber and Morris intraparticle diffusion model	0.057	0.286	0.921
4	Bangham's pore diffusion model	0.486	-1.089	0.905
5	Elovich model	0.172	0.034	0.901

( $R^2 = 0.982$ ) is greater than other kinetic models and this indicates that the pseudo second-order model is the best fit to the experimental data of the present studied adsorption system followed by pseudo first-order model ( $R^2 = 0.976$ ), Weber and Morris intraparticle diffusion model ( $R^2 = 0.921$ ), Bangham's pore diffusion model ( $R^2 = 0.905$ ), Elovich model ( $R^2 = 0.901$ ) respectively.

However, if the intraparticle diffusion is the sole rate determining step, the plots should not only be linear, they should also pass through the origin (Ozcan and Ozcan, 2005). Although, the plots in the present case have good linearity, the plots do not have zero intercept as required by the theoretical considerations. This indicated that the mechanism for fluoride adsorption by NAcIC was a complex one. The results further indicated that the rate of fluoride adsorption on NAcIC, was not solely controlled by pore diffusion but intraparticle diffusion could also have contributed to the rate determining step (Mahramanlioglu et al., 2002). The Elovich equation does not predict any definite mechanism, but it is useful in describing adsorption on highly heterogeneous adsorbents similar to the NAcIC.

### Characterization of NAcIC

#### Physicochemical Properties

By using standard methods (ISI, 1989; Namasivayam and Kadirvelu, 1997), diverse physicochemical properties of NAcIC were explored and important features of these properties are presented in Table 1. An anion adsorption is favoured on the NAcIC due to  $\text{pH} < \text{pH}_{\text{ZPC}}$ . The reduction of BET surface from 209.4 to 192.8  $\text{m}^2/\text{g}$  after de-fluoridation indicates the fluoride ion adsorption on the surface of NAcIC. Boehm titration method determines the total acidic and basic functional groups present on the surface of NAcIC and from Table 1, it is clear that total basic groups are greater than the total acidic groups. This is due to the fact that on the edges of the poly aromatic layers of active carbon, the diketone or quinone groups (Leon y Leon and Radovic, 1994; Contescu et al., 1998) and

polycyclic pyrones (Voll and Boehm, 1971; Boehm, 1994, 2002) can cover a wide range of base strength (about 12 pKa units) (Menendez et al., 1999; Suarez et al., 1999) and the FT-IR studies have confirmed the presence of these groups.

#### FT-IR Analysis

The Fourier Transforms Infrared (FT-IR) spectroscopy method has been adapted to study the nature of surface functional groups of NAcIC. The obtained FT-IR spectra of NAcIC before and after de-fluoridation in the range 4000-500  $\text{cm}^{-1}$  are shown in Figure 11.

FT-IR analysis of NAcIC (vide Figure 11), before and after de-fluoridation, confirmed the occurrence of fluoride adsorption on the active carbon as there were some changes like shifts and decreases in the percentage of transmittance in the FT-IR spectra of the solid surface in the range 4000-500  $\text{cm}^{-1}$ . Of the various functional groups observed, the more pronounced are the carbonyl functional groups (Budinova et al., 2006):

- 1691.25  $\text{cm}^{-1}$  peak is attributed to quinine or quinone or conjugated ketone (Ishizaki and Marti, 1981; Starsinic et al., 1983; Zawadzki, 1989; Biniak et al., 1997; Shin et al., 1997; Moreno-Castilla et al., 1998; Yongbin Ji et al., 2007; Chang et al., 2008);
- 1787.13  $\text{cm}^{-1}$  attributed to the carbonyl, carboxyl groups and lactones (Painter et al., 1985; Zawadzki, 1989; Fanning and Vannice, 1993; Zhuang et al., 1994; Nageswara Rao et al., 2011);
- The band around 2353.35  $\text{cm}^{-1}$  can be attributed to the carbon-oxygen bonds in ketene (Papirer et al., 1987) or result of alkynes (acetylenic) groups, transition metal carbonyl and nitrogen double bond (Coates, 2000).

Further, the peaks pertaining to the following functional groups have been observed.

- -OH and chemisorbed water (Ibrahim et al., 1980; Daifullah et al., 2003; Puziy, 2003; Yang and Lua, 2003);
- -C-H stretching (symmetric and asymmetric) vibration of aliphatic -CH<sub>3</sub> or -CH<sub>2</sub> groups (Biniak

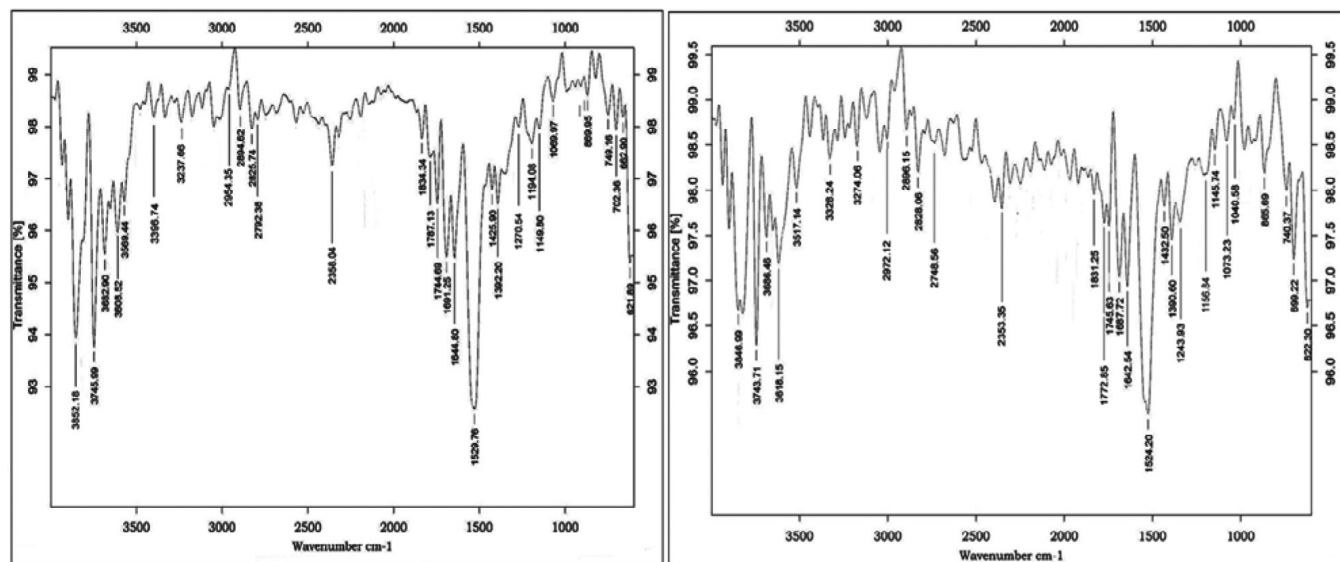


Figure 11: FT-IR spectra of NAcIC before (left) and after de-fluoridation (right).

et al., 1997; Puziy, 2003; Yang and Lua, 2003; Yongbin Ji et al., 2007);

- In plane bending vibration of -C-H of methylene group (Rajeshwari et al., 2001; Budinova et al., 2006; Gercel et al., 2007);
- -C-O- stretching (Gomez-Serrano et al., 1994; Park, 1997; Shin et al., 1997; Lapuente et al., 1998; Figueiredo et al., 1999; Rajeshwari et al., 2001; El-Hendawy, 2003; Attia et al., 2006; Budinova et al., 2006); and
- Out of plane deformation vibrations of -C-H group in aromatic structures (Meldrum and Rochester, 1990a, b; Nageswara Rao et al., 2011).

The absence of specific peak pertains to -C-F, suggested that the adsorption process is 'physisorption' but not chemisorptions.

#### SEM Analysis

Surface features such as pore characteristics, shape and size of the particles making up the surface of carbons have been studied by using SEM micrographs and therefore the SEM become a unique and potent instrument for studying the surface chemistry of activated carbons. The SEM images of NAcIC before and after fluoride adsorption were as shown in Figure 12.

In micrographs, dark areas indicate pores and grey areas indicate the carbon matrix. Before adsorption, the NAcIC consists of particles of different shapes and sizes and the surfaces of the particles are irregular and contain a number of heterogeneous holes and small openings with wavy and highly broken edges. These may have resulted in higher surface area and

consequently, higher adsorption capacity. The grey surface area of every micrograph contains smaller micro particles (nm to  $\mu\text{m}$ ) which may indicate the activated sites or surface functional groups of the carbon. After fluoride adsorption, a change in surface morphology of NAcIC resulting in 'some smoothening' of the surface occurred and it is probably due to fluoride sorption on the pores or active groups on the surface of NAcIC. This change in the surface morphology further revealed that the process of fluoride adsorption on NAcIC is predominantly a surface phenomenon.

#### EDX Analysis

Energy-Dispersive X-ray spectroscopy (EDX), along with SEM, gives the information about the elemental composition on the surface of the activated carbon. In present study, EDX analysis was performed for NAcIC before and after fluoride adsorption. The obtained EDX-spectra are presented in Figure 13 and their composition in Table 5.

It is observed from the EDX-spectra that carbon and oxygen peaks are found both in un-treated and fluoride-treated samples but fluoride peak at 1.1 eV has been observed only in the case of fluoride-treated sample. Further, it may be observed that as the % of fluoride on the surface increases in the treated sample of NAcIC, there is simultaneous decrease of oxygen percentage. This may be due to the replacing of '-OH-' by fluoride on the inter surface of the said active carbon. Moreover, a small peak pertaining to nitrogen was also observed. This may be attributed to the incorporation of nitrogen on the surface of NAcIC at the time of activation process with Nitric acid.

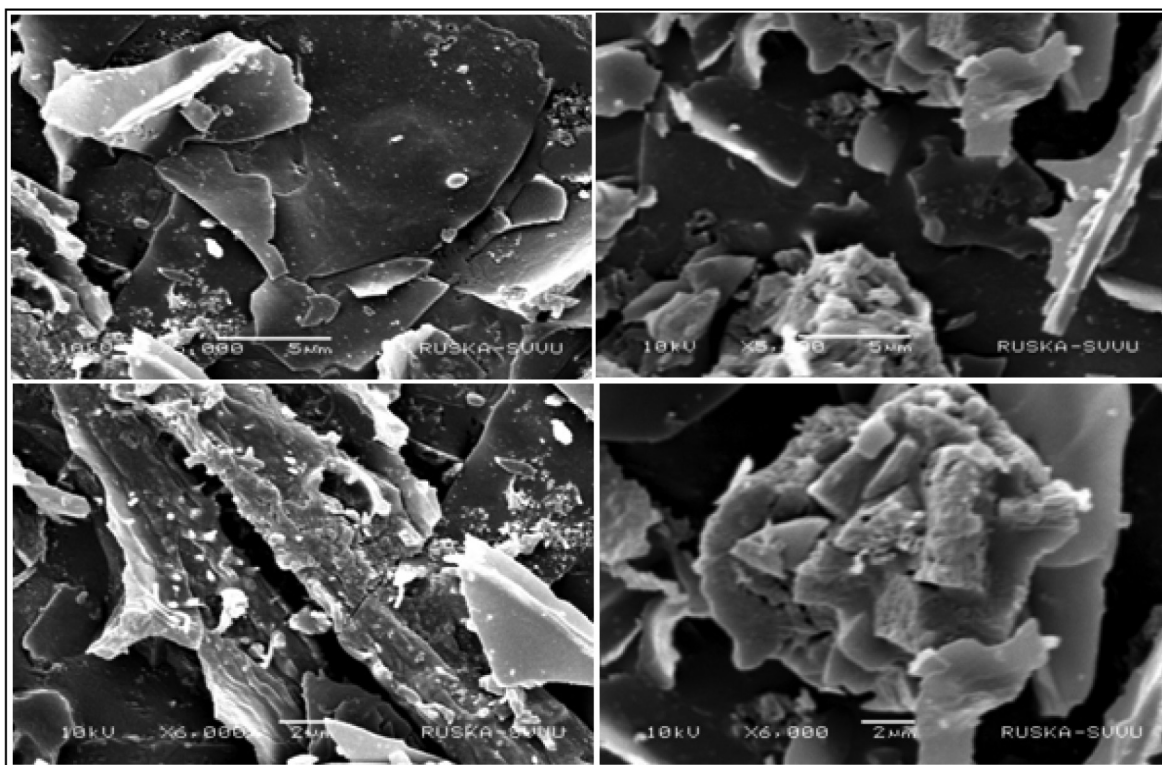


Figure 12: SEM analysis of NAcIC before (left) and after (right) de-fluoridation at  $\times 5000$  and  $\times 6000$  magnifications.

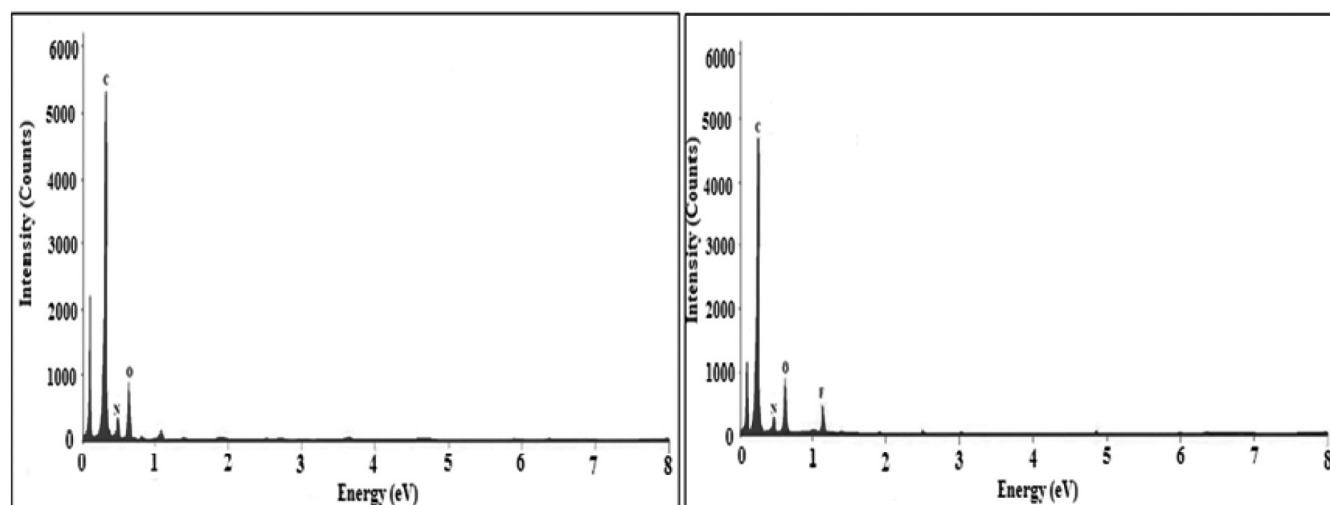


Figure 13: EDX-spectra of NAcIC before (left) and after de-fluoridation.

Table 5: Elemental analysis of NAcIC by EDX spectra before and after defluoridation

Composition	EDX-elemental analysis (before)					EDX-elemental analysis (after)				
	CK	NK	OK	FK	Total	CK	NK	OK	FK	Total
Energy (eV)	0.3	0.5	0.6	1.1		0.3	0.5	0.6	1.1	
Wt% (Mass ratios)	86.1	1.2	12.7	–	100	85.6	1.0	11.6	1.8	100
At% (Atomic percentages)	84.8	1.1	14.1	–	100	86.1	0.9	11.4	1.6	100

Thus from the FTIR, SEM and EDX studies we may conclude that on the surface of the active carbon, there is an accumulation fluoride as has been reflected from the presence of fluoride-peak in EDX spectra in the samples treated with fluoride and this fact is also confirmed by the appearance of smooth surface in the SEM spectra for the same samples; and accumulation of fluoride on the surface is due to the physisorption and not due to the chemisorptions or ion-exchange as there is no specific peak pertaining to -C-F bond in FTIR.

### Applications

The adoptability of the methodology developed with the new bio-sorbent in this work for removing fluoride has been tried with some real water samples collected from groundwaters in fluoride affected areas in Vinukonda Mandal of Guntur District of Andhra Pradesh.

The samples were subjected to extraction for fluoride using NAcIC developed in this work at optimum extraction conditions of pH: 7, equilibration time: 60 min, particle size of NAcIC: 45  $\mu$  and sorbent concentration of 5.0 g/L and temperature: 30 $\pm$ 1°C. The results obtained are presented in Table 6.

From Table 6, column 3, it is evident that the concentration of fluoride in all groundwater samples collected from various villages of Vinukonda Mandal, Guntur Dist. have been varied from 3.37 to 4.27 mg/L which is beyond the permissible World Health Organization limit: 1.5 mg/L (BIS, 1991; WHO, 2004). Hence in the present work, the de-fluoridation studies have been carried out on these particular samples using the adsorbent, NAcIC, in order to find its utility. From Columns 4 and 5 of Table 6, it can be inferred that NAcIC effectively decrease the fluoride content

**Table 6: Fluoride ion concentration (before and after de-fluoridation) of ground water samples**

<i>S. No.</i>	<i>Village name</i>	<i>C<sub>i</sub> (mg/L) (before defluoridation)</i>	<i>C<sub>f</sub>(mg/L) (after defluoridation)</i>	<i>% Removal</i>
<i>With NAcIC</i>				
1	Sivapuram	3.75	0.930	75.2
2	Koppukonda	3.82	0.905	76.3
3	Thimmayapalem	3.56	0.862	75.8
4	Narasayapalem	3.48	0.804	76.9
5	Brahmanapalli	4.27	0.974	77.2
6	Mada manchipadu	3.88	0.912	76.5
7	Andugulapadu	3.69	0.893	75.8
8	Tsouta palem	4.09	0.908	77.8
9	Venkupalem	3.37	0.829	75.4
10	Nagulavaram	3.28	0.764	76.7
11	Peda kancherla	3.68	0.832	77.4
12	Narasarayani palem	3.52	0.887	74.8
13	Dondapadu	3.95	0.976	75.3
14	Vinukonda	3.62	0.883	75.6
15	Gokana konda	4.21	0.993	76.4
16	Enugupalem	3.69	0.948	74.3
17	Surepalli	3.45	0.790	77.1
18	Ummadivaram	3.59	0.840	76.6
19	Perumalla palli	4.12	0.981	76.2
20	Nayanipalem	3.68	0.924	74.9
21	Settupalli	3.72	0.949	74.5
22	Vithamrajupalli	3.43	0.775	77.4
23	Neelagangavaram	3.49	0.834	76.1



in groundwater samples below permissible limits under optimum experimental conditions. Thus the methodology developed in this research work using active carbon NAcIC is remarkably successful.

### Conclusions

The de-fluoridation studies based on the active carbon derived from stems of *Acalypha indica* plant (NAcIC) have been carried out by varying different physicochemical parameters in batch methods of extraction and are optimized. The % of removal of fluoride is found to be maximum at pH = 7, adsorbent dosage: 5.0 g/L, equilibration time: 60 min, particle size: 45 and at a temperature of  $30 \pm 1^\circ\text{C}$ . Further, the interference of commonly found co-ions in waters has been studied.

The adsorption process was found to be spontaneous and endothermic in nature and is satisfactorily fitted with Langmuir adsorption isotherm indicating monolayer adsorption. The Dubinin-Radushkevich mean free energy ( $E = 3.16 \text{ kJ/mol}$ ) and Temkin heat of sorption ( $B = 0.210 \text{ J/mol}$ ) has confirmed the 'physisorption' nature. The kinetics of adsorption process is better explained by Pseudo-second-order model. FT-IR and SEM-EDX techniques have confirmed the adsorption of fluoride on NAcIC surface. Field studies indicated that NAcIC could be used as an effective de-fluoridating agent under the optimum extraction conditions developed in this work and hence, the methodology can be successfully used in waste water treatment technologies in controlling fluorides.

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