



Studies on fluoride removal from polluted waters using active carbon derived from stems of *Abutilon indicum* plant

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ABSTRACT

An inexpensive Nitric acid activated carbon is prepared from stems of *Abutilon Indicum* plant (NAbIC). Its fitness to remove fluoride ions from contaminated water has been studied using batch adsorption methods by varying the major parameters such as pH, contact time, initial fluoride ion concentration, adsorbent dosage, particle size and temperature and these conditions have been optimized for maximum extraction of the fluoride. The effect of co-ions has also been studied. The active carbon has been characterized for various physicochemical parameters to assess the suitability of adsorbent for de-fluoridation waters. Freundlich as well as Langmuir isotherms are plotted and kinetic constants are determined. Correlation coefficient (R^2) and dimensionless separation factor (R_L) values have confirmed that adsorption obeys Langmuir adsorption indicating monolayer formation. Further, Temkin isotherm and Dubinin-Radushkevich isotherm have been analyzed for the system and the values of the Temkin heat of sorption, $B=0.224$ J/mol and the Dubinin-Radushkevich mean free energy, $E = 3.16$ kJ/mol indicate that the adsorption is 'physisorption' in nature. Pseudo-first-order, pseudo-second-order, Weber and Morris intraparticle diffusion, Bangham's pore diffusion and Elovich equations have been applied to identify the rate and kinetics of adsorption process. The adsorption process has good correlation coefficient values with pseudo-second-order model. SEM-EDX techniques of the active carbon have shown a morphological change of the surface after adsorption and FTIR studies indicated the involvement of some surface functional groups in fluoride adsorption. The procedure developed is applied to real fluoride contaminated ground water samples and found to be successful.

Key words: Fluoride, adsorption, inexpensive activated carbon, stems of *Abutilon Indicum* plant, adsorption isotherms and kinetics, characterization studies, application

INTRODUCTION

Fluoride contamination of natural ground waters and its hazardous effects on the living creatures is well known. When the fluoride concentration exceeds the permissible limit of 1.5 mg/lit, it causes dental and skeletal fluorosis, arthritis, infertility, brittle bones, cancer, brain damage and thyroid disorder etc. [1-12]. In India itself, it has been estimated that 62 million people including children suffer from fluoride contamination related diseases [13-14].

The remedial measures in controlling the fluoride concentration in natural waters are being actively probed throughout the Globe by various researchers. Many methodologies have been developed for de-fluoridation based on ion-exchange [15-24], precipitation [25-36], reverse osmosis [37-38], membrane [39-42], electro coagulation [43] electro dialysis [44] and adsorption [45-50]. These methods suffer from one or the other drawback such as high

operational and maintenance cost, the problem of secondary pollution, undesirable effects on water quality and difficult procedures involved in the treatment. De-fluoridation using the surface sorption abilities of various adsorbents such as Alumina [51-54], Iron based materials [55-59], Laterite [60-62], Kaolinite [63-64] and Zeolite F-9 [65], have explored. The bio-sorbents derived from bio-materials are being probed for their abilities in the removal of fluoride from waste waters. Active carbons derived from coconut coir pith [66], rice straw [67], coconut shell [68], Typha Angustata plant [69] and Phyllanthus emblica [70] and also Zirconium impregnated Cashew nut shell carbon [71], have been explored for their adsorption nature towards fluoride. These activated carbons found to be effective in controlling pollutants by virtue of having high surface area, high porosity, more active sites on surface, and high adsorption capacity [72].

In the present study, an attempt has been made to remove fluoride from water using low-cost HNO₃ activated carbons prepared from stem of *Abutilon Indicum* plant (NAbIC). This sorbent has been characterized with respect to various physicochemical parameters. The surface morphology has been analyzed by including such modern techniques like FT-IR and SEM-EDX. The sorption nature of the active carbons towards fluoride ions has been studied by varying pH, contact time, adsorbent dose, initial concentration of the fluoride ion, temperature, and co-ions and these conditions have been optimized for the effective removal of fluoride from polluted waters. The adsorption processes have been analyzed with 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 ground water samples polluted with fluoride.

EXPERIMENTAL SECTION

2.1. Fluoride solution

All the reagents used were of Analytical Reagent grade purchased from Merck. India Pvt. Ltd. and Sd. Fine Chemicals. Double distilled water was used in all the experiments. A stock solution of 100 mg/lit fluoride was prepared by dissolving appropriate amount of Sodium Fluoride (Merck) in double-distilled water and it is diluted as per the need. SPADNS solution, Zirconyl-acid reagent, Acid Zirconyl-SPADNS reagent and reference solution were prepared as per the literature [73].

2.2. Plant description

The active carbons prepared from stem of *Abutilon Indicum* plant were used for fluoride removal from waters.



Fig.1: *Abutilon Indicum* plant

The *Abutilon Indicum* plant (Fig.1), locally known as Duvvenakayala chettu or Thuthurubenda or Mudra benda (in Telugu), belongs to the Malvaceae family in plant kingdom. *Abutilon Indicum* plant is a medium sized, branched perennial shrub and grows up to 2 meters in height. It is a fairly common roadside weed in topological countries. All parts of the plant are being used in making native or traditional medicines.

2.3. Preparation of Nitric acid activated Carbons

The stem of *Abutilon Indicum* plant was collected, cut in to small pieces, washed with double-distilled water and dried under sunlight for two days. In the absence of air at 500^oC, the dried plant material was carbonized for 4 hours in muffle furnace. After carbonization, the carbon was washed with double-distilled water and it was dried in an air

oven at 110°C and sieved into desired particle sizes. The carbonized material was subjected to liquid phase oxidation by treating with 0.1N HNO₃ and boiled for 2 to 3 hours for the removal of unwanted materials. The acid treated carbon was thoroughly washed with double-distilled water to remove the excess acid and thus prepared active carbon was dried at 150°C for 12 hours in an air oven. This Nitric acid activated carbon prepared from stem of *Abutilon Indicum* plant was named as 'NAbiC'.

2.4. Characterization of the Nitric acid activated Carbons

By using standard methods, physicochemical characteristics of NAbiC were studied and the results were presented in Table 1. The pH for the activated carbon adsorbent was determined using the Elico pH meter, model LI-120 and the pH_{ZPC} was determined using the pH equilibrium method [74-76]. Particle size was determined using American Standard Test Method (ASTM) sieves [77]. Iodine number [78-79], Decolorizing power [80-81] 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 [82-83]. The BET surface area [74, 84-85] of the prepared activated carbon was determined by nitrogen gas adsorption analyzer at 77K using Quanta chrome Nova Win-Data Acquisition and Reduction for NOVA instruments version 10.01. The BET-N₂ surface area was obtained by applying the BET equation to the adsorption data. The Boehm titration method [86-88] was used to estimate the acidic and basic groups on the surface of active carbon adsorbent.

Table 1: Physicochemical characteristics of NAbiC

S.No:	Parameter	Value	
1	Apparent density,(g/ml)	0.313	
2	Moisture content, (%)	7.44	
3	Loss on Ignition (LOI), (%)	89.95	
4	Ash content, (%)	5.13	
5	Water soluble matter, (%)	0.72	
6	Acid soluble matter, (%)	0.85	
7	Decolorizing power,(mg/g)	314	
8	pH	7.35	
9	pH _{ZPC}	9.56	
10	Iodine number,(mg/g)	598	
11	Particle size(μ)	45	
12	BET Analysis - Surface area, m ² /g	before	218.3
		after	195.4
13	Surface functional groups (meq/g)-Boehm Titration		
I	Carboxyl	1.013	
II	Lactonic	0.982	
III	Phenolic	1.105	
IV	Carbonyl	1.116	
V	Total basic groups	5.726	

2.4.1. FTIR analysis

The surface functional groups on NAbiC were examined using Fourier Transform Infrared spectroscopy (FTIR). The spectra were measured from 4000 to 500cm⁻¹ on a BRUKER VERTEX 80/80v FT-IR spectrometer, Optical resolution of <0.06 cm⁻¹, with automatic and vacuum compatible beam splitter changer (BMS-c) option. Anhydrous KBr was used as a pellet material.

2.4.2. Scanning electron microscopy (SEM)

The scanning electron microscope (SEM) is one of the most versatile instruments available for the examination and analysis of the microstructure morphology and chemical composition characterizations. The microphotographs of NAbiC were recorded using LEO 1420 VP Compact variable pressure Digital SEM, manufacture by Leo Electron Microscopy Ltd. (Beam voltage 500 to 2000V, Magnifications 250 to 65,000 X, Resolution 3nm at 1000V).

2.4.3. Energy Dispersive Spectroscopy (EDS)

Energy-dispersive X-ray spectroscopy (EDS, EDX, or XEDS) is an analytical technique used for the elemental analysis to identify the elements and their relative proportions (Atomic %) in a sample. Each element has a unique atomic structure allowing unique set of peaks on its X-ray spectrum and it was recorded for NAbiC using BRUKER EDX Two-dimensional V ANTEC-500 detector.

2.5. Removal of fluoride by Nitric acid activated Carbons

2.5.1. Experimental procedure

For the removal of fluoride from the waste waters, batch adsorption studies were adopted. A fluoride solution of 5mg/lit was used in all the experiments as the fluoride affected areas (in India) has the maximum concentration of 5mg/lit [34]. 100ml of 5mg/lit of fluoride solution was pipette out into a 250ml conical flask at room temperature $30\pm 1^{\circ}\text{C}$ and to it, weighed quantity of the prepared **NAbIC** adsorbent was added and shaken in horizontal shaker at 120 rpm. After the equilibration time, the conical flask was allowed to stand for 2 min for settling the adsorbent and it was filtered using Whatman No.42 filter paper. The filtrate was analyzed for residual fluoride concentration by SPADNS method using U.V-Visible Spectrophotometer (Model No: Elico U.V-2600) as described in Standard Methods of Water and Waste Water Analysis [73] at λ_{max} 570 nm.

2.5.2. Fluoride ion analysis

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

$$\% \text{ Removal (\%R)} = \frac{(C_i - C_e)}{C_i} \times 100$$

$$\text{Amount adsorbed (q}_e) = \frac{(C_i - C_e)}{m} \times V$$

Where

C_i = Initial concentration of the fluoride solution in mg/lit

C_e = Equilibrium concentration of the fluoride solution in mg/lit

m = mass of the adsorbent in grams

V = Volume of fluoride test solution in liters

The same procedure has been adopted for the experiments carried out by varying physicochemical parameters such that adsorbent dosage, pH of the fluoride solution, agitation time, initial concentration of fluoride solution, particle size, temperature and in presence of foreign ions.

RESULTS AND DISCUSSION

3.1. Characterisation of Nitric acid activated Carbon

The important features of various physicochemical properties of the active carbon, NAbIC, were presented in Table 1. As $\text{pH} < \text{pH}_{\text{ZPC}}$, an anion adsorption is favored on the adsorbent, NAbIC. The decrease in the BET surface area indicates the fluoride ion adsorption on the surface of the adsorbent. The functional groups of oxygen like Phenol, Carbonyl, Hydroxyl and Lactones were determined according to Boehm titration and from the Table 1, it was clear that the total basic groups were greater than the total acidic groups. The basicity may be due to oxygen functional groups, chromene structures [89-90], diketone or quinone groups [91-92] and pyrone-like groups [87, 93-94]. On the edges of the poly aromatic layers, the polycyclic pyrones can cover a wide range of base strength (about 12 pKa units) [95-96] and the FT-IR studies confirmed the presence of these groups. The observed basicity values were comparable with the activated carbon prepared from rice straw [67].

3.1.1. FT-IR Analysis (Vide Fig.2 and Table 2)

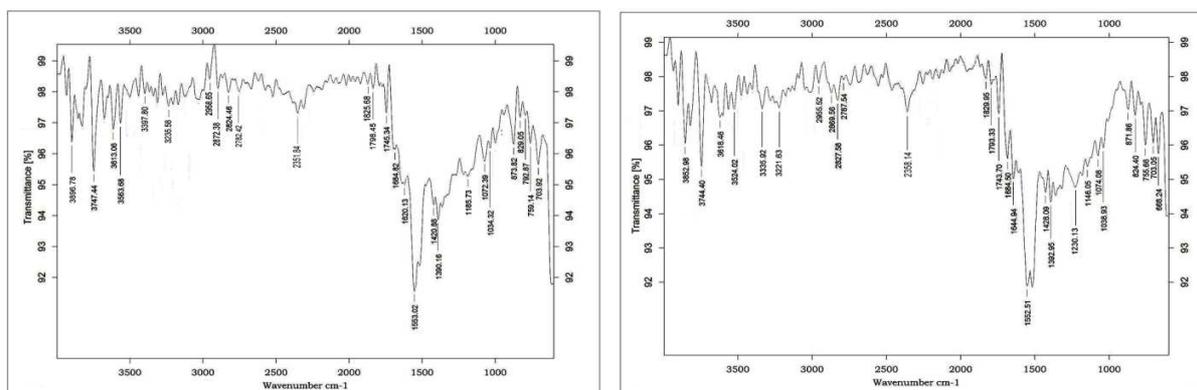


Fig.2: FTIR spectra of NAbIC before (left) and after (right) de-fluoridation

Table 2: Bands assigned to the surface functional groups of NAbIC before and after defluoridation

S.No:	Wave number (cm ⁻¹)		Bond Stretching
	NAbIC (before)	NAbIC (after)	
1	3896.78,	3852.98,	-O-H in Alcohols, Acids Phenols and -N-H in Amines and Amides
	3747.44,	3744.40,	
	3613.06,	3618.46,	
	3563.68,	3524.02,	
	3397.80,	3335.92,	
2	3235.58	3221.63	-C-H in -CH ₃ and -CH ₂
	2958.65,	2955.52,	
	2872.38	2869.56,	
	2824.46,	2827.58,	
3	2782.42	2787.54	-C=O in Carbonyl, Carboxyl groups and Lactones
	1825.68,	1829.95,	
	1798.45	1793.33,	
4	1745.34	1743.70	-C=O in Quinine or Quinone
	1620.13,	1644.94,	
5	1553.02,	1552.51,	-C=C- in Aromatic rings, -C=O in highly conjugated Carbonyl groups and -C-H deformations in Alkanes.
	1420.88,	1428.09,	
	1390.16	1392.95	
6	1185.73	1230.13,	-C-O- in Alcohols, Phenols, Ethers, Esters, Acids, Epoxides, Lactones and Carboxylic anhydrides
	1072.39,	1146.05,	
	1034.32	1074.08,	
7		1038.93	-C-C- deformations and out of plane -C-H deformations in Aromatic rings.
	873.82,	871.86,	
	829.05,	824.40,	
	792.87,	755.66,	
	759.14,	703.05,	
	668.24		

Fourier transforms infrared (FT-IR) spectroscopy give confirmation for the presence of specific functional groups on the surface of carbon materials. For the present adsorbent, the major bands have been displayed and explained based on the previous assignments made in literature.

FTIR analysis of NAbIC (vide Table 2; Fig.2), before and after defluoridation, 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 cm⁻¹. As the carbon surface was subjected to oxidation by conc. HNO₃, the generation of quinone type carbon functional groups occurred and the presence of a band centered around 1684.82cm⁻¹, was attributed to the carbonyl (-C=O) stretching vibration of quinine or quinone or conjugated ketone [97-104]. It is also reported in literature that in oxidized carbon materials, Carbonyl functional groups are known to be prominent than in the original parent carbon material [105]. The stretching vibration bands of -O-H group and chemisorbed water[106-109], stretching (symmetric and asymmetric)

vibrations of aliphatic -C-H group [97-98,108-109], bending vibrations of -C-H of methylene group[105,110-111], and -C-O- stretching [101,105,110,112-117], were noted. Further, the peaks pertaining to the -C=O stretching in carbonyl and carboxyl groups and in lactones [104,118-121] and out of plane deformation vibrations of -C-H group in aromatic structures [118,122-123], have been, also, observed in the IR spectra. The absence of specific peak pertains to -C-F, suggested that the adsorption process was 'physisorption' but not chemisorptions.

3.1.2. SEM Analysis (Vide Fig.3)

The SEM Photo Graphs have been studied for information about the surface features such as pore characteristics (topography), shape and size of the particles making up the surface of carbons (morphology), the elements that the activated carbon is composed of and the relative amounts of these (composition) and how the atoms are arranged in the activated carbon (crystallographic information). In micrographs, dark areas indicate pores and grey areas indicate the carbon matrix. Pores in activated carbons are areas of zero electron density in the carbon matrix. These constitute volume of elements distributed throughout the particle and posses varied sizes and shapes and provides large surface area for adsorption. The grey surface area of every micrograph contains smaller micro particles (nm to μm) which may indicate the activated sites or surface functional groups of the carbon. All these features of the SEM make it a unique and potent instrument for studying the surface chemistry of activated carbons. The SEM images of the NAbIC show that the external surfaces for these carbons are full of cavities and it was observed that after reaction with fluoride, the surface morphology of NAbIC surface changed and smoothening of surface occurred, perhaps due to coverage by fluoride ions. The adsorption of fluoride may be due to the presence of pores or active groups on the surface of NAbIC and thus, SEM micrographs proved the fluoride adsorption.

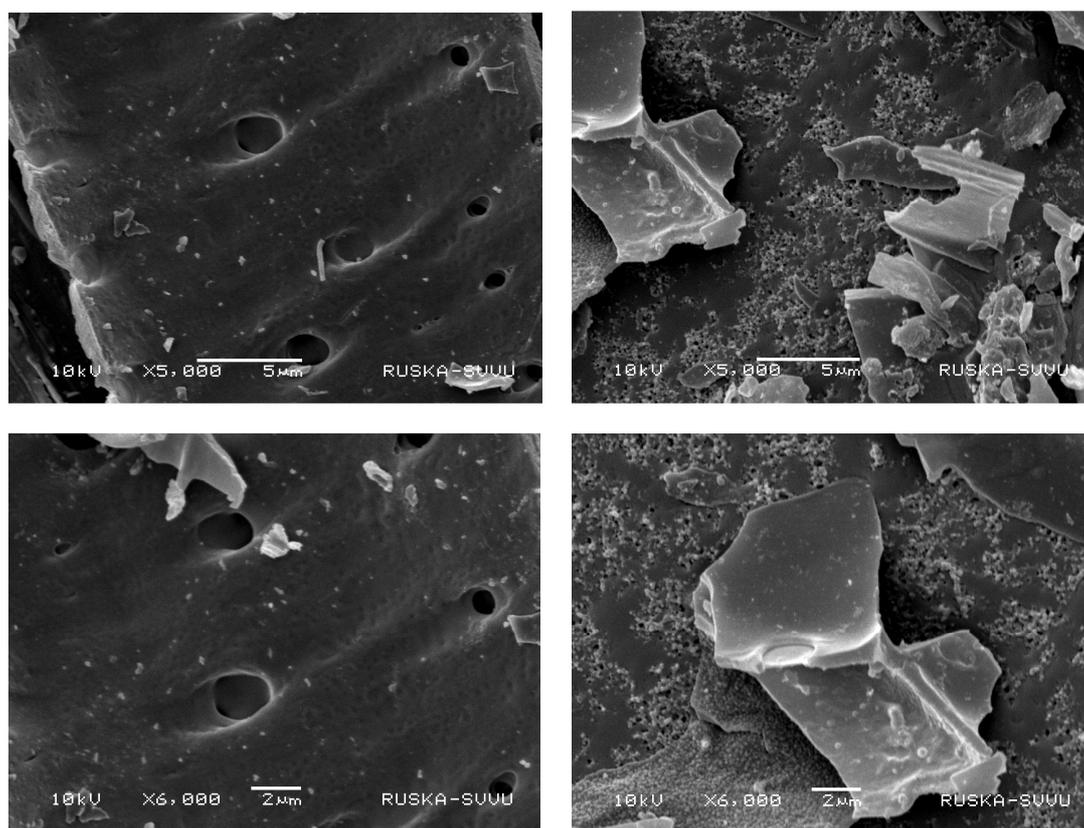


Fig.3: SEM analysis of NAbIC before (left) and after (right) defluoridation at X5000 and X6000 magnifications

3.1.3. EDX Elemental Analysis (Fig.4 & Table 3)

When SEM is equipped with energy-dispersive X-ray spectroscopy (EDX), it is possible to get information about the elemental composition on the surface of the activated carbon. Energy-dispersive analysis of X-rays was highlighted the presence of Carbon and Oxygen ions in untreated and fluoride treated sample as shown in Fig.4 and Nitrogen was present in small content other than the principal elements, Carbon and Oxygen and minor amount of

Nitrogen were due to the activation of prepared carbon with Nitric acid. It can clearly be concluded that the Oxygen element concentration has been reduced but simultaneously fluoride concentration is increased in the adsorbent after adsorption process and hence, the fluoride ion may replace the ion containing Oxygen atom (OH⁻) on the surface of adsorbent. EDX analysis provides direct evidence that fluoride has been adsorbed on the surface of NAbIC.

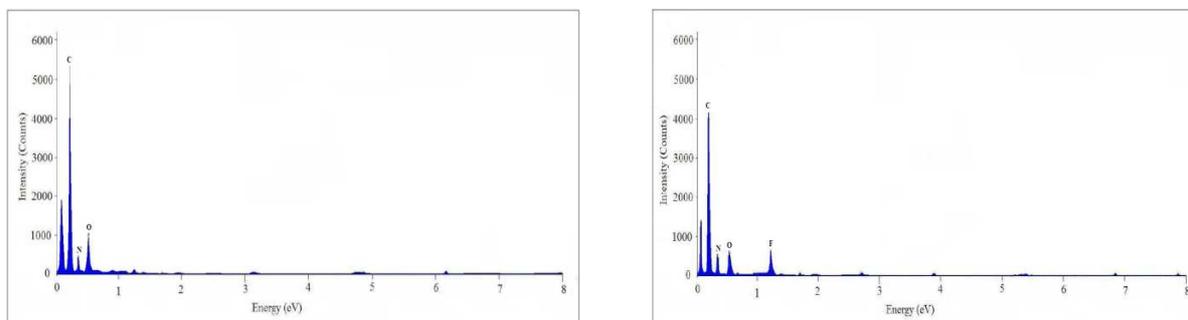


Fig.4: The EDX spectra of NAbIC before and after defluoridation

Table 3: Elemental analysis of NAbIC 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)	82.4	2.8	14.8	---	100	82.5	2.4	12.7	2.4	100
At% (Atomic percentages)	83.1	2.7	14.2	---	100	82.8	2.3	12.5	2.4	100

3.2 Effect of adsorbent dosage:

The effect of adsorbent dosage on the removal of fluoride ion from waste waters was studied at by varying the sorbent concentration from 1.0 to 9.0 g/lit at optimum conditions of pH:7, agitation time: 60 min, fluoride ion concentration: 5 mg/lit and constant temp of 30±1°C. The results obtained were presented in Fig.5

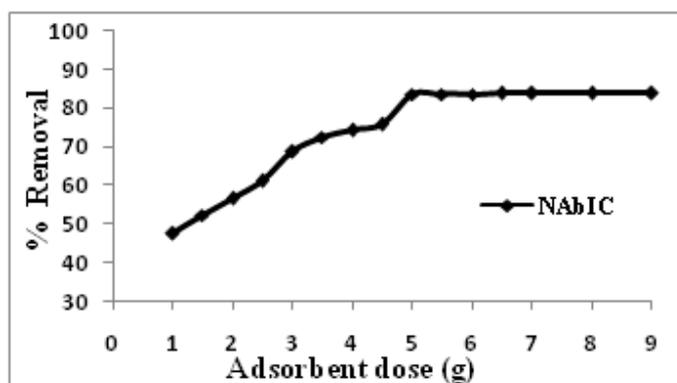


Fig. 5: Plot of percent removal of fluoride as a function of adsorbent dose

As is seen from the plot that the removal of fluoride ion increases with an increase in the adsorbent dose and attained maximum removal at 5.0 g/lit of NAbIC and then onwards, there is no further removal of fluoride with increase of the adsorbent dose.

3.3. Effect of pH

The sorption of fluoride was found to be pH sensitive and so, % removal of fluoride as the equilibrium pH changed from 2 to 11 was studied under optimum conditions of extraction namely: fluoride ion concentration: 5 mg/lit, agitation time: 60min, dose: 5.0g/lit and at a temperature of 30±1°C. The results obtained were plotted as percentage removal of fluoride ion Vs pH as shown in Fig.6

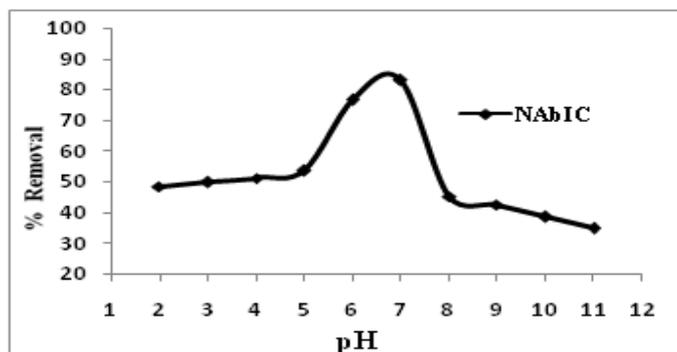


Fig. 6: Plot of percent removal of fluoride as a function of pH

It may be noted from the graph that the % removal of fluoride increases sharply in the pH range: 5.0-8.0 with maximum extraction at pH: 7.

As optimum pH: 7, is less than pH_{ZPC} : 9.56 (Table 1), the net positive charge is imported on surface of the NAbIC and it is attributed to adsorption of excess H^+ on the surface. This prevailing positive nature on the liquid-sorbent inter-surface causes thrust for anions on the inter-surface due to columbic interactions. So, the adsorption of the fluoride on the NAbIC surface is supposed to be favored in low pHs [124]. But another factor that affects the sorption process is nature of the species and the charge prevailing on the species. According to fluoride speciation, neutral hydro fluoride (HF) predominates at pH less than 3 and the specie being neutral, it has less affinity towards the positively charged surface of NAbIC adsorbent [125] and hence % removal is less at low pHs below 3. But at high pH values, the Fluoride exists as negative ion but at that pH, the surface of NAbIC loses positive charge and even functional groups like $-OH$ dissociates to import negative charge on the surface and so, the surface of the active carbon is no longer holds negatively charged fluoride ions and this results in the low % removal of fluoride at high pH values. Thus, the adsorption of fluoride is optimum when the species is negative and the surface has positive charge. As per the experimental data, it may be inferred that the optimum pH range is 5 to 8 with maximum removal at pH: 7.

3.4. Effect of contact time

The contact time between the sorbent and fluoride ion has been found to have profound effect on the % of removal of fluoride ion. The adsorption experiments were conducted at optimum conditions of pH: 7.0, fluoride concentration: 5 mg/lit, sorbent dosage: 5.0g/lit and at a temperature of $30 \pm 1^\circ C$ with varying the contact time from 10 to 100 min. The results obtained were plotted as percentage removal of fluoride ion Vs contact time (min) as shown in Fig.7

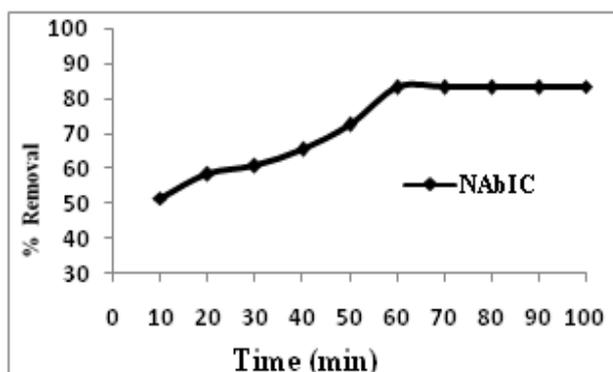


Fig. 7: Plot of percent removal of fluoride as a function of contact time (min)

It can be seen from the figure that the removal of fluoride increases rapidly with increase in time and it reaches maximum at 60 min and then onwards, the % of extraction remains constant i.e. an equilibrium state has been reached. At this steady state, rate of adsorption fluoride is equal to the rate of desorption fluoride on the inter-

surface. The rate of adsorption is found to be more initially but decreases with time and reaches study state after certain time. This is due to the fact that initially many active sites are available for the sorption process to occur and they are progressively used up with time and hence, rate of adsorption is decreased. But after a certain time, there will not be active sites on the sorbent surface for the adsorption process to take place i.e. a saturation station is reached and at this stage; there will not be further adsorption.

The decrease in the removal rate indicates the possible monolayer of fluoride ions on the outer surface and pores of the adsorbent leading to pore diffusion onto inner surface of adsorbent particles [34,126].

3.5. Effect of initial concentration

The effect of initial concentration of fluoride ion solution on extent of % removal of fluoride ion from aqueous solution was studied at optimum conditions of pH: 7.0, contact time: 60 min, sorbent dosage: 5.0g/lit and at a temperature: $30\pm 1^\circ\text{C}$ with varying concentration of fluoride ion solution from 1 to 12mg/lit. The results obtained were plotted as percentage removal of fluoride ion Vs concentration of fluoride ion solution as shown in Fig.8

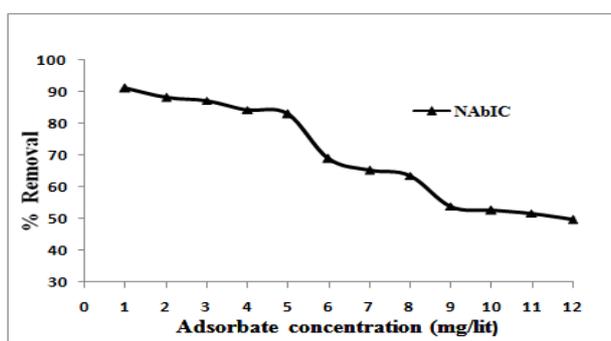


Fig.8: Plot of percent removal of fluoride as a function of concentration of fluoride ion solution

With increase in initial concentration of fluoride ion solution, the percentage removal of fluoride ion has been decreased due to the number of active adsorption sites are not enough to accommodate fluoride ions. At low concentrated solution of fluoride ions, the ratio of surface active sites to total fluoride ions is high, hence the fluoride ions could interact with the sorbent to occupy the active sites on the carbon surface sufficiently and be removed from the solution [127]. With an increase in initial concentration of fluoride ion solution from 1 to 12mg/lit, the percentage removal (%R) of fluoride ion decreased from 91.2 to 49.6% for NAbIC.

3.6. Effect of Particle Size

The effect of particle size on the % removal of Fluoride was explored by studying the % of removal with the change in the particle size from 45 to 150 μ mesh at optimum conditions of extraction namely, at pH : 7.0, contact time : 60 min, sorbent dosage : 5.0g/lit, concentration of fluoride ion solution : 5.0mg/lit, and at a temperature : $30\pm 1^\circ\text{C}$. The results obtained were plotted as percentage removal of fluoride ion Vs particle size as shown in fig.9.

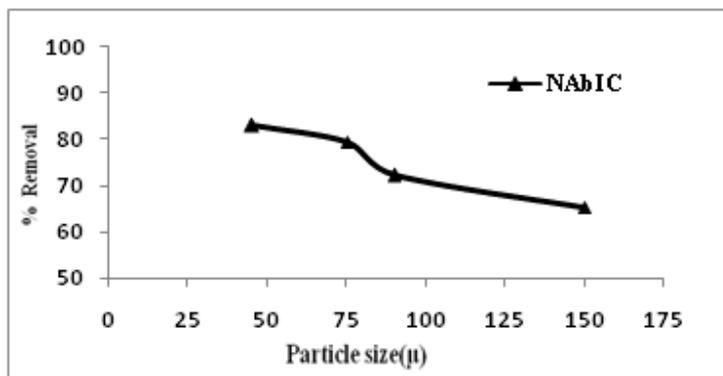


Fig.9: Plot of percent removal of fluoride as a function of particle size

It may be inferred from the graph that lesser the particle size more will be the surface area and more will be the number of active sites available and hence, the percentage removal of fluoride ion increases with decrease in particle size of the activated carbon adsorbent. But with large sized particles, there will be insufficient number of surface active sites available and hence, the percentage removal of fluoride ion has been decreased. The optimum size of the particles of activated carbon adsorbent was 45 μ .

3.7. Effect of co-ions on fluoride adsorption

The effect of co-ions on the % removal of fluoride by NAbIC was studied with 50 mg/lit concentration of co-ions commonly found in waters such as chloride, nitrate, sulphate, bicarbonate and phosphate under optimum conditions of extraction namely, pH: 7.0, contact time: 60 min, sorbent dosage: 5.0g/lit, concentration of fluoride ion solution: 5.0mg/lit, particles sized: 45 μ mesh and temperature: 30 \pm 1 $^{\circ}$ C. The results obtained were presented in Table 4 and plotted as shown in Fig.10.

Table 4: Effect of co-ions on fluoride ion removal from aqueous solution by the activated Carbon: NAbIC

S.No.	Adsorbent	Maximum Extractability at optimum conditions	Extractability of fluoride ion in presence of 50 mg/lit of interfering ions at optimum (pHs)				
			Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	HCO ₃ ⁻	PO ₄ ³⁻
1	NAbIC	83.0%, pH:7, 50 min.	81.8%, pH:7, 50 min.	80.3%, pH:7, 50 min.	76.5%, pH:7, 50 min.	71.3% pH:7, 50 min.	68.7%, pH:7, 50 min.

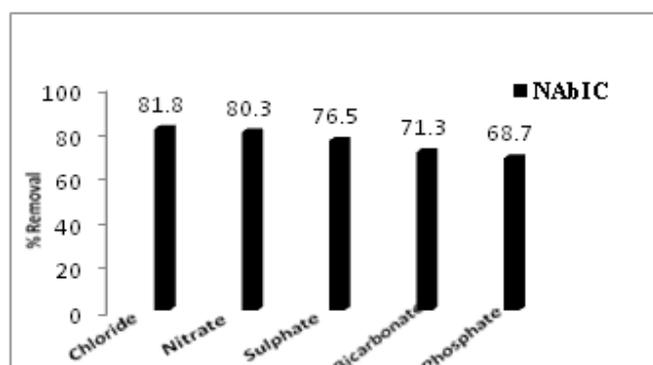


Fig. 10: Effect of co-ions on (%R) of fluoride ion onto NAbIC

It was observed that the co-ions affected the % removal of fluoride in the expected order: PO₄³⁻ > HCO₃⁻ > SO₄²⁻ > NO₃⁻ > Cl⁻. Anions being negative in charge will compete with fluoride ions for active sites on the active carbon and the extent of interference to the sorption of fluoride ions on the sorbent surface depends on various factors [65]. Previous research indicates that Chloride ions form outer-sphere surface complexes while Sulphate ions form both outer-sphere and inner-sphere surface complexes [65]. Hence, Chloride as well as Nitrate ions have less interference with fluoride removal. Sulphate has some significant effect on fluoride adsorption and it could be partly attributed to its higher negative charge compared to that of chloride or Nitrate ions. The presence of tenfold excess of Bicarbonate in the liquid, causes bicarbonate alkalinity which reduces the positive charge on the active sites of the active carbon and thereby, the affinity of fluoride towards the adsorbent surface is decreased and this results in the decrease in the % removal of fluoride.

Phosphate ion which is having high negative charge compared to the other anions needs three close surface groups for being adsorbed and it is adsorbed as inner-sphere surface complex. This inner-spherically adsorbing Phosphate ion [128-130] can significantly interfere with the fluoride ion and hence decrease in the percentage removal of fluoride ion from waters in presence of 10 fold excess of Phosphate co-ions.

3.8. Effect of Temperature

The effect of solution temperature on the % removal of fluoride was studied by conducting the extraction experiments at different temperatures 303, 313 and 323K and at optimum conditions of extraction: pH: 7.0; contact time: 60 min; sorbent dosage: 5.0g/lit; concentration of fluoride ion solution: 5.0mg/lit; particles size: 45 μ mesh and

the results obtained were plotted as $\ln K_d$ Vs $1/T$ as shown in Fig.11. Thermodynamic parameters of the adsorption process such as change in free energy (ΔG) (kJ/mole), change in enthalpy (ΔH) (kJ/mole) and change in entropy (ΔS) (J/K/mole) were determined at different temperatures by using the equations[131-133],

$$\Delta G = -RT \ln K_d$$

$$\ln K_d = \Delta S/R - \Delta H/RT$$

$$K_d = q_e/C_e \text{ and}$$

$$\Delta G = \Delta H - T\Delta S$$

Where K_d is the distribution coefficient for the adsorption,
 q_e is the amount of fluoride ion adsorbed on the activated carbon adsorbent per litre of solution at equilibrium,
 C_e is the equilibrium concentration of fluoride ion solution,
 T is the absolute temperature in Kelvin,
 R is the gas constant.
 ΔG is the change in free energy
 ΔH is the change in enthalpy
 ΔS is the change in entropy

The values of ΔH and ΔS were obtained from the slope and intercept of a plot between $\ln K_d$ and $1/T$ and ΔG values were obtained from the equation $\Delta G = \Delta H - T\Delta S$ and tabulated [134-135].

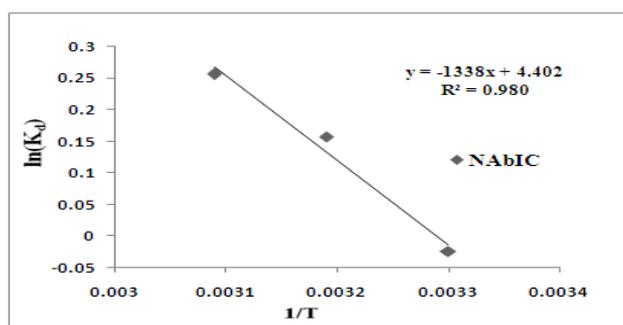


Fig. 11: Effect of temperature on (%R) of fluoride ion onto NAbIC

Table 5: Thermodynamic parameters of fluoride ion adsorption on NAbIC

Parameter	ΔH (kJ/mol)	ΔS (J/mol/K)	ΔG (kJ/mol)			R^2
Temperature(K)			303	313	323	
NAbIC	11.12	36.59	0.0332	-0.3327	-0.6986	0.980

It is observed that with increase in temperature from 303 to 323K (30 to 50°C), the percentage removal of fluoride ion increases from 83.0 to 88.5% for NAbIC.

As the temp increases, the thickness of outer surface of the activated carbon adsorbent decreases and kinetic energy of the fluoride ion increases and hence the rate of diffusion of fluoride ion increases across the external boundary layer and internal pores of the activated carbon adsorbent.

As can be inferred from the Table 5, the values of ΔH are positive, which indicates the physisorption and endothermic nature of adsorption [136]. The R^2 values close to one (0.984) also indicates that adsorption process is endothermic nature. The positive values of ΔS indicate the increased disorder and randomness at the solid solution interface of fluoride ion with the adsorbent [137]. The negative values of ΔG indicate the spontaneous nature of adsorption process i.e. the adsorptive forces are strong enough to overcome the potential barrier [138].

4. Adsorption Isotherms

Four well known adsorption isotherm models, Freundlich [139], Langmuir [140], Temkin [141] and Dubinin-Radushkevich [142] isotherms have been selected to evaluate the relation between the fluoride concentrations remaining in the bulk solution to the amount of fluoride adsorbed at the solid/solution interface at a constant temperature.

Linear form of Freundlich equation is $\log(q_e) = \log k_f + \left(\frac{1}{n}\right) \log C_e$

Linear form of Langmuir equation is $C_e/q_e = (a_L/k_L)C_e + 1/k_L$

According to Hall et al [143], the nature of the adsorption process is unfavorable ($R_L > 1$), linear ($R_L = 1$), favourable ($0 < R_L < 1$) and irreversible ($R_L = 0$) and the significant feature of the Langmuir isotherm model can be defined by the dimensionless separation factor,

$$R_L = 1 / (1 + a_L C_i)$$

The linear plots of these two adsorption isotherms were as shown in Fig.12 and isothermal constants along with the correlation coefficient values were presented in Table 6.

As the correlation coefficients (R^2 -values) is close to unity, it indicates the applicability of these two adsorption isotherms confirmed the heterogeneous surface of the adsorbent and the monolayer coverage of fluoride ion on the active carbon surface. The high correlation coefficient ($R^2=0.986$) value and dimensionless separation factor ($R_L=0.1096$) value which has been found to be fraction in the range of 0-1, indicate the favorability of the Langmuir isotherm than the Freundlich isotherm.

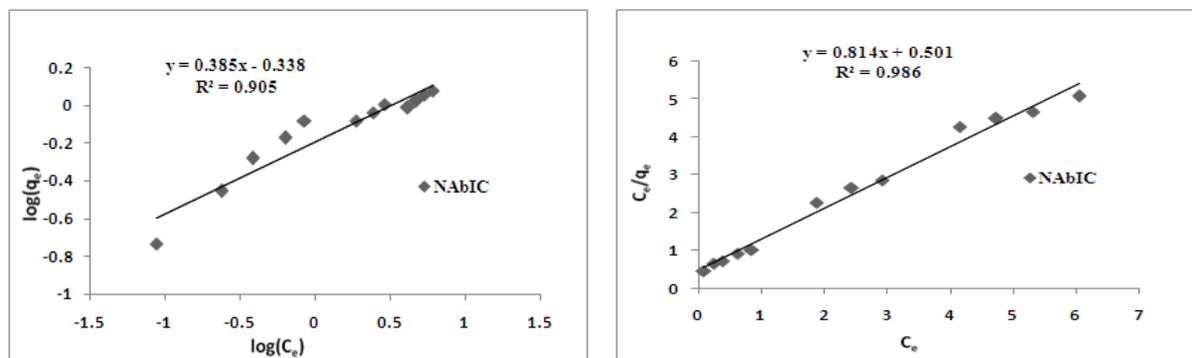


Fig. 12: Freundlich isotherm (Left), Langmuir isotherm (Right)

Table 6: Adsorption isothermal parameters of Freundlich and Langmuir plots

S.No:	Adsorption isotherms	Slope	Intercept	R^2
1	Freundlich Isotherm	0.385	-0.338	0.905
2	Langmuir isotherm	$R_L=0.1096$	0.814	0.986

Linear form of Temkin equation is $q_e = B \ln C_e + B \ln A$

where $RT/b = B$

Linear form of Dubinin-Radushkevich equation is $\ln q_e = -\beta \varepsilon^2 + \ln q_m$ where $\varepsilon = RT \ln(1+1/C_e)$

The linear plots of these two adsorption isotherms were as shown in Fig.13 and isothermal constants along with the correlation coefficient values were presented in Table 7.

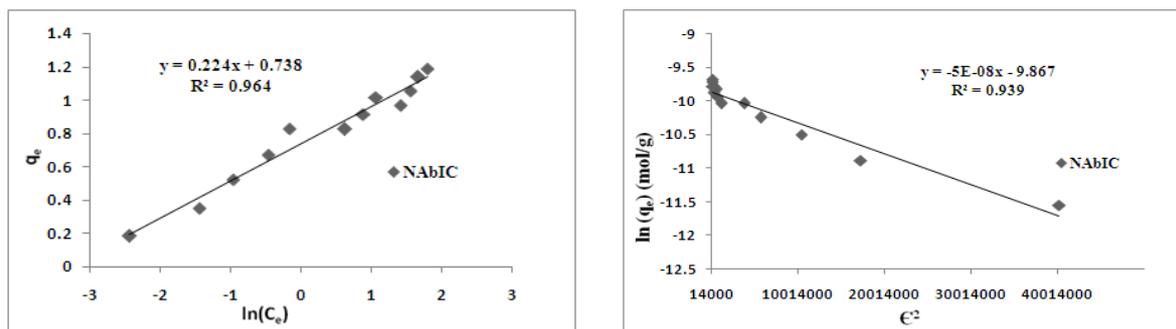


Fig. 13: Temkin Isotherm (Left), Dubinin-Radushkevich isotherm (Right)

Table 7: Adsorption isothermal parameters of Temkin and Dubinin-Radushkevich plots

S.No:	Adsorption isotherms		Slope	Intercept	R ²
1	Temkin Isotherm	B=0.224 J/mol	0.224	0.738	0.964
2	Dubinin-Radushkevich isotherm	E =3.16 kJ/mol	-5E-08	-9.867	0.939

As the correlation coefficients (R^2 -values) are close to unity, they have indicated the applicability of these two adsorption isotherms to the present extraction system and further confirmed the heterogeneous surface of the adsorbent.

The Temkin heat of sorption, $B=0.224$ J/mol was calculated from the slope of the Temkin linear plot [144-145], and the Dubinin-Radushkevich mean free energy, $E = 1/\sqrt{2}\beta$, [65] was found to be 3.16 kJ/mol for the activated carbon, NAbIC. As the $E < 8$ kJ/mol, it is an indication of ‘physisorption’ [146] dominating the chemisorptions and ion exchange etc. in the present extraction system of study. The ‘Physisorption’ is also called nonspecific adsorption which occurs as a result of long range weak Vander Waals forces between fluoride ions and adsorbent. According to Atkins [147], characteristics for ‘physisorption’ are the mean free energy (E) and also heats of sorption (B) values lower than 20kJ/mol. The B value of 0.224 J/mol for the present adsorbent system, further confirms the ‘physisorption’ nature.

5. Adsorption Kinetics

The rate and kinetics of adsorption of fluoride ion on to the activated carbon adsorbent NAbIC was studied with pseudo first-order model [125,148], pseudo second-order model [148-149], Weber and Morris intraparticle diffusion model [150], Bangham’s pore diffusion model[151] and Elovich equations[152-153].

The pseudo first-order equation is $\log(q_e - q_t) = \log q_e - k_1 t / 2.303$

The pseudo first-order equation is $t/q_t = 1/k_2 q_e^2 - (1/q_e) t$

Weber and Morris intraparticle diffusion equation is $q_t = k_{ip} t^{1/2} + c$

Bangham’s pore diffusion equation is $\log[\log(C_i/C_i - q_t/m)] = \log(k_o/2.303V) + a \log(t)$

Elovich equation is $q_t = 1/\beta \ln(\alpha\beta) + 1/\beta \ln(t)$

The linear plots of all these five kinetic models were as shown in Fig.14 and rate constants along with the correlation coefficient values were presented in Table 8.

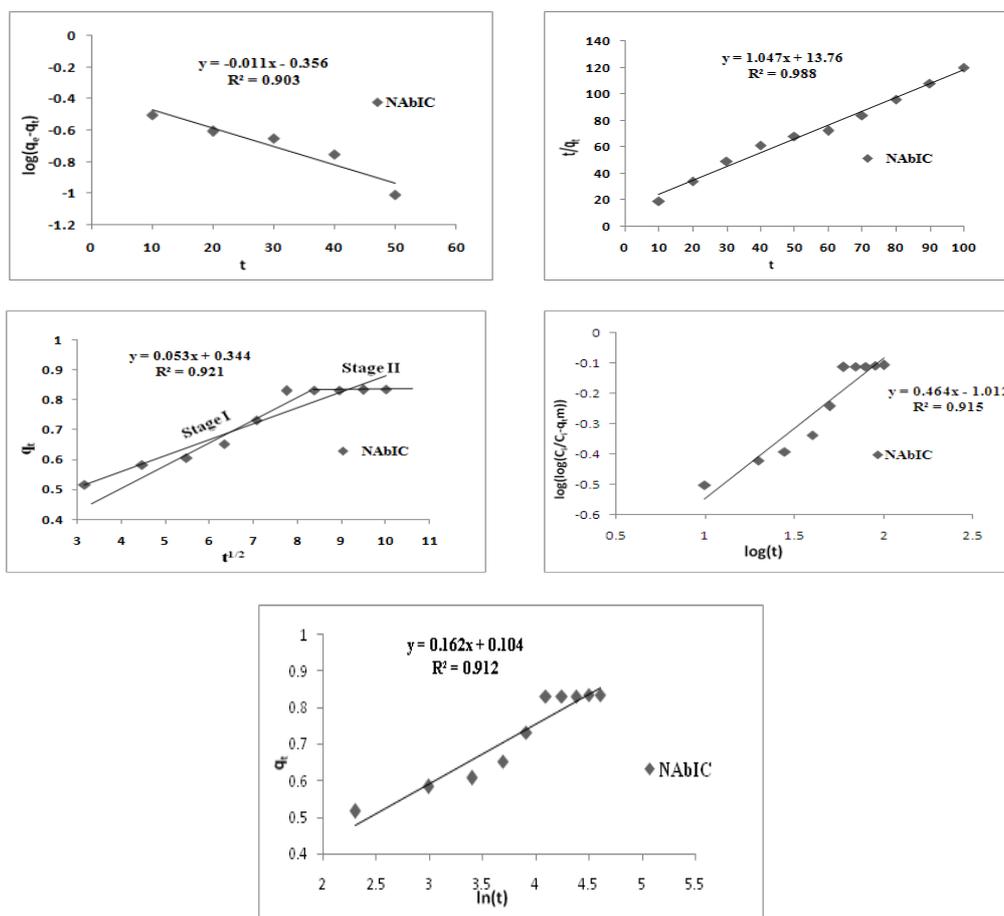


Fig.15: Pseudo first-order, Pseudo second-order, Weber and Morris intra particle diffusion, Bangham's pore diffusion, Elovich model (left to right)

Table 8: Kinetic parameters

S.No:	Adsorption Kinetics	Slope	Intercept	R ²
1	pseudo first-order	-0.011	-0.356	0.903
2	pseudo second-order	1.047	13.76	0.988
3	Weber and Morris intraparticle diffusion	0.053	0.344	0.921
4	Bangham's pore diffusion	0.464	-1.012	0.915
5	Elovich model	0.162	0.104	0.912

The applicability of the kinetic equations is compared from the correlation coefficient (R^2). Of these five kinetic models, the correlation coefficient value for the pseudo second-order model 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. Next best model is Weber and Morris intraparticle diffusion model ($R^2 = 0.921$) followed by Bangham's pore diffusion model ($R^2=0.915$), Elovich model ($R^2=0.912$), and least is pseudo first-order model ($R^2=0.903$).

4. APPLICATIONS

The methodology developed with the new active carbon, NAbIC for the removal of fluoride from waste waters was applied for real water samples collected from ground waters in fluoride affected areas in Vinukonda Mandal of Guntur District of Andhra Pradesh.

The samples were subjected to extraction for fluoride using NAbIC at optimum conditions of pH, equilibration time, particle size, temperature and sorbent concentration as cited above. The results obtained were presented in the Table 9.

Table 9: Fluoride ion concentration (before and after defluoridation) of ground water samples

S.No:	Village Name	C _i (mg/lit) (before defluoridation)	C _f (mg/lit) (after defluoridation)	% Removal
With NAbIC				
1	Sivapuram	3.75	0.806	78.5
2	Koppukonda	3.82	0.795	79.2
3	Thimmayapalem	3.56	0.726	79.6
4	Narasayapalem	3.48	0.689	80.2
5	Brahmanapalli	4.27	0.961	77.5
6	Mada manchipadu	3.88	0.830	78.6
7	Andugulapadu	3.69	0.760	79.4
8	Tsouta palem	4.09	0.793	80.6
9	Venkupalem	3.37	0.714	78.8
10	Nagulavaram	3.28	0.725	77.9
11	Peda kancherla	3.68	0.762	79.3
12	Narasarayani palem	3.52	0.662	81.2
13	Dondapadu	3.95	0.841	78.7
14	Vinukonda	3.62	0.731	79.8
15	Gokana konda	4.21	0.989	76.5
16	Enugupalem	3.69	0.838	77.3
17	Surepalli	3.45	0.759	78.0
18	Ummadivaram	3.59	0.779	78.3
19	Perumalla palli	4.12	0.849	79.4
20	Nayanipalem	3.68	0.701	80.7
21	Settupalli	3.72	0.714	80.8
22	Vithamrajupalli	3.43	0.792	76.9
23	Neelagangavaram	3.49	0.743	78.7

It can be seen from the Table 9: column: 3 that the concentration of fluoride in the water samples ranges from 3.37 to 4.27 mg/lit. The data indicates that the samples contain excess of fluoride beyond the permissible World Health Organization limit of 1.5 mg/lit [154-156] and their consumption in any form is detrimental to human beings and animals. These samples were subjected to extraction using the procedure developed in this work and the results were reported in the Table 9: column 4 and 5. It can be inferred that the methodology developed using NAbIC is effective in decreasing the fluoride content in ground water samples much below the permissible limits under optimum experimental conditions; more than 75% of extraction is observed.

CONCLUSION

An inexpensive activated carbon has been developed from stems of *Abutilon Indicum* plant for the removal of fluoride from waters in this study. The results indicated that the maximum fluoride adsorption takes place at the pH: 7.0, adsorbent dosage: 5.0g/lit; equilibrium time: 60 min, Particle size: 45 μ and temperature: 30 \pm 1 $^{\circ}$ C. It is observed that the adsorption process satisfactorily fitted with Langmuir adsorption isotherm which has good correlation coefficient value indicating monolayer adsorption. The Temkin heat of sorption, B=0.224 J/mol and the Dubinin-Radushkevich mean free energy, E = 3.16 kJ/mol for the activated carbon adsorbent NAbIC are an indication of 'physisorption' process. In the kinetic studies of de-fluoridation processes, pseudo-first-order, pseudo-second-order, Weber and Morris intraparticle diffusion, Bangham's pore diffusion and Elovich equations, have been applied to identify the rate and kinetics of adsorption process. It is found that the adsorption process has good correlation coefficient values with pseudo-second-order model. SEM-EDX data of the active carbon have shown a morphological change on the surface after adsorption and FTIR studies have indicated the involvement of some surface functional groups in fluoride adsorption. The methodologies developed in this work have been applied to real ground water samples contaminated with fluoride and found to be remarkably successful.

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