

# Removal of Aluminum(III) from Polluted Water Using Active Carbon Derived from Barks of *Ficus Racemosa* Plant

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Received July 11, 2017; revised and accepted November 16, 2017

**Abstract:** Nitric acid activated carbon is prepared from barks of *Ficus Racemosa* plant and it is characterized for various parameters to assess its suitability as adsorbent for the removal of Al (III) ions from polluted water. By adopting batch methods, the effect of various major parameters such as pH, contact time, initial Al(III) ion concentration, adsorbent dosage, particle size and temperature, on the affinity of the active carbon towards Al(III), is investigated and optimized for the maximum removal of Al(III) ions. The influence of co-ions on the extraction is investigated. Various adsorption isotherms such as Freundlich, Langmuir, Temkin and Dubinin-Radushkevich are analyzed and correlation coefficient ( $R^2 = 0.998$ ) and dimensionless separation factor ( $R_L = 0.0035174$ ) values, confirm that the sorption process obeys Langmuir adsorption, indicating monolayer formation. Further, the Temkin heat of sorption,  $B = 2.227$  J/mol and the Dubinin-Radushkevich mean free energy,  $E = 7.071$  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 are applied to identify the rate and kinetics of adsorption process. The adsorption process has good correlation coefficient values with pseudo-second-order model. FTIR studies indicate the involvement of some surface functional groups in Al(III) adsorption. The methodology developed is applied to real Al(III) contaminated water samples and found to be successful.

**Key words:** Al(III) ions, barks of *Ficus Racemosa* plant, adsorption, adsorption isotherms and kinetics, characterization studies, applications.

## Introduction

Aluminum and its compounds are commonly used in the manufacturing, construction of siding, aircrafts, motor vehicles and lightweight utensils because of its good strength and light weight. Dissolving aluminum compounds with acids produces aluminum salts, which are used widely in water treatment applications to facilitate coagulation of pollutants such as sediments,

nutrients, microbes and dissolved organic compounds (Water Quality Matters, 2001). Aluminum is known to dissolve in water at acidic and basic conditions (Water Quality Matters, 2001). Al(III) ions are toxic and effect the crop production in acid soils (Miller et al., 1994). Although water treatment processes by coagulation depend on the precipitation of aluminum (along with impurities) at neutral conditions, residual amounts of dissolved aluminum always remain in the treated

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water. The American Waste Water Association (AWWA) estimated that drinking water (including treated water) provides about 5% of overall aluminum in human diets (Water Quality Matters, 2001).

The Environmental Protection Agency (EPA) sets the secondary permissible standard for aluminum in drinking water as 0.05 – 0.20 mg/lit. When the aluminum concentration in drinking water exceeds this range, it causes encephalopathy (defect of the brain) and/or bone mineralization disorders, Parkinson and Alzheimer's disease (McClure and Smith, 1984), bone softening (Descotes, 1988), renal insufficiency, pulmonary fibrosis and microcytic anemia in human beings (Pesavento et al., 1998) and also harmful to fish (Campbell et al., 1983; Birchall et al., 1989; Haven and Heath, 1989), zooplankton (Haven, 1992; Pettersson et al., 1988), cyanobacteria (Gensemer, 1991), algae (Parker et al., 1989) and water weeds (Flaten, 2001). Aluminum ions act as neurotoxins when they are allowed to enter the bloodstream (Kochian, 1995). Therefore, it is necessary to remove the aluminum from water before being used as drinking water.

A number of techniques like chemical precipitation, ion exchange, reverse osmosis, electron deposition, adsorption, solvent extraction and flotation separation processes (Matus and Kubova, 2005, Singh and Pant, 2004; Paul et al., 1988) are developed for its control. Adsorption processes, which utilize natural adsorbents, are economical and they have an advantage over other removal methods for eliminating trace concentrations of pollutants. Our research group is working on these bio-adsorbents and developed methods for the removal of Cr(VI) (Hanumantha Rao et al., 2014; Hanumantha Rao and Ravindhranath, 2015; Krishna Veni and Ravindhranath, 2012; Sekhar et al., 2012; Sree Devi and Ravindhranath, 2012), Zn (II) (Papodu et al., 2014), Al(III) (Aruna Kumari and Ravindhranath, 2012 a, b, 2016). Fluoride (Hanumantha Rao et al., 2012 a, b; Sujitha Ravulapalli and Ravindhranath Kunta, 2017; Suneetha et al., 2014, 2015 a, b),  $\text{NO}_2^-$  (Suneetha and Ravindhranath, 2014, 2016, 2017).  $\text{NH}_3$  (Prameela Rani and Ravindhranath, 2014 a, b; Suneetha and Ravindhranath, 2012 a, b),  $\text{PO}_4^{3-}$  (Divya Jyothi et al., 2012 a, b; Hanumantha Rao and Ravindhranath, 2015) and dyes (Krishna Mohan et al., 2016 a, b; Srinivasa Reddy et al., 2012; Srinivasa Reddy and Ravindhranath, 2014, 2015). Various bio-adsorbents investigated for the removal of Al(III) are: starch (Choksi and Joshi, 2007), activated charcoal (Choksi and Joshi, 2007), wood charcoal (Choksi and Joshi, 2007), clay (Choksi and Joshi, 2007), algae (Lee et al., 2004) and various

sorbents derived from bio parts of *Acacia Melanoxylon* and *Eichhornia Crassipes* plants (Aruna Kumari and Ravindhranath, 2012 a), *Moryngea Millingtonia* and *Cygium Arjunum* plants (Aruna Kumari and Ravindhranath, 2012 b), *Withania Somnifera* plant (Aruna Kumari and Ravindhranath, 2016).

In the present work, a low-cost  $\text{HNO}_3$  activated carbon prepared from barks of *Ficus Racemosa* plant (NFRC) is investigated as an adsorbent for the removal of Al(III) ions from water. This sorbent has been characterized for various physicochemical parameters by using standard methods. The surface morphology is analyzed by using FTIR. The sorption nature of the active carbons towards Al(III) ions has been studied by varying pH, contact time, adsorbent dose, initial concentration of the Al(III) ions, temperature and co-ions and these conditions have been optimized for the effective removal of Al(III) ions from polluted waters. The adsorption process has been analyzed with Freundlich, Langmuir, Temkin and Dubinin-Radushkevich (D–R) isotherms and kinetics of adsorption process has 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 Al(III) ions.

## Materials and Methods

### 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. 75 ppm stock solution of Al(III) was prepared and was suitably diluted as per the need. Acetate buffer, Eriochrome Cyanine R and hydrogen peroxide solutions were prepared as per the literature (Jeffery et al., 1989).

### Plant Description

The activated carbon prepared from barks of *Ficus Racemosa* (NFRC) plant was used for Al(III) ions removal from polluted water. *Ficus racemosa* (syn. *Ficus glomerata* Roxb.) is a species of plant in the family Moraceae, popularly known as the Cluster Fig Tree, Indian Fig Tree or Goolar (Gular). This is native to Australia, Malaysia, South-East Asia and the Indian Subcontinent. The bark of this tree has healing power and hence the bark paste with water is applied over the skin which is afflicted by boils or mosquito bites.



**Figure 1:** *Ficus Racemosa* plant showing affinity towards Al(III) ions.

### Preparation of Nitric Acid Activated Carbon

Barks of *Ficus racemosa* tree were cut into small pieces, washed with double-distilled water and dried under sunlight for two days. In the absence of air at the optimum temperature of 500°C, the dried plant materials were carbonized for four hours (optimum) 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 0.1 N HNO<sub>3</sub> and boiled for three hours. Above this concentration of HCl and time of activation, there was no further improvement in the adsorption nature. 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. Thus obtained nitric acid activated carbon prepared from bark of *Ficus racemosa* tree was named as 'NFRC'.

### Characterization of the Nitric Acid Activated Carbon

#### Physicochemical Characteristics

By using standard methods, physicochemical characteristics of NFRC 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<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, 2006), Decolourizing power (Girgis and El-Hendawy, 2002; Rozada et al., 2005) and other parameters such as apparent density, moisture, ash,

water-soluble matter and acid soluble matter were analyzed by using standard test methods (ISI, 1989; Namasivayam and Kadirvelu, 1997). The Boehm titration method (Meldrum and Rochester, 1990 a, b, c; Bandosz et al., 1992; Boehm, 1994) was used to estimate the acidic and basic groups on the surface of active carbon adsorbent.

**Table 1:** Physicochemical characteristics of NFRC

S. No.	Physicochemical parameter	Value
1.	Apparent density (g/ml)	1.16
2.	Moisture content (%)	8.4
3.	Fixed carbon (%)	45.3
4.	Ash content (%)	2.4
5.	Volatile matter (%)	41.5
6.	Acid soluble matter (%)	0.61
7.	Water soluble matter (%)	0.5
8.	pH	8.0
9.	pH <sub>zpc</sub>	9.8
10.	Decolorizing power (mg/g)	373
11.	Iodine number (m <sup>2</sup> g <sup>-1</sup> )	632
12.	Particle size (μ)	45
13.	Surface functional groups (meq/g)- Boehm Titration	
	I Carboxyl	0.84
	II Lactonic	1.09
	III Phenolic	1.32
	IV Carbonyl	1.04
	V Total basic groups	6.29

#### FTIR Analysis

The surface functional groups on NFRC were examined using Fourier Transform Infrared spectroscopy (FTIR). The spectra measured from 4000 to 400 cm<sup>-1</sup> and recorded on a spectrum GX model spectrometer (Perkin-Elmer) having resolution 4 cm<sup>-1</sup> variable up to 0.125 cm<sup>-1</sup>.

### Removal of Aluminum Ions by Nitric Acid Activated Carbon (NFRC)

#### Experimental Procedure

For the removal of aluminum ions from wastewaters, batch adsorption studies were adopted. A solution of aluminum(III) of 5.0 mg/lit was used in all the experiments as the aluminum affected areas (in India) has the maximum concentration of 5.0 mg/



lit (Newcombe et al., 1993). 100 ml of 5.0 mg/lit of aluminum solution was taken into a 250 ml conical flask at room temperature  $\sim 30^{\circ}\text{C}$  and to it, a weighed quantity of the prepared NFRC adsorbent was added and then, the flask was shaken in horizontal shaker at 120 rpm. After the desired 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 aluminum concentration by Eriochrome cyanine R method using U.V-Visible Spectrophotometer (Model No: Elico U.V-2600) as described in Standard Methods of Water and Waste Water Analysis (APHA, 1985) at  $\lambda_{\text{max}}$  535 nm.

#### Aluminum Ion Analysis

The percentage removal of aluminum ion and amount adsorbed (in mg/g) were calculated using the 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 aluminum solution in mg/lit;  $C_e$  = Equilibrium concentration of the aluminum solution in mg/lit;  $m$  = Mass of the adsorbent in grams and  $V$  = Volume of test solution in liters.

The same procedure was adopted for the experiments carried out by varying physicochemical parameters namely, adsorbent dosage, pH of the solution, agitation time, initial concentration of aluminum solution, particle size, temperature and interference studies of co-ions.

## Results and Discussions

### Characteristic Nature of NFRC

The important features of various physicochemical properties of the active carbon, NFRC, are presented in Table 1. As  $\text{pH} < \text{pH}_{\text{ZPC}}$ , an anion adsorption is favoured on the adsorbent, NFRC. The functional groups of oxygen like phenol, carbonyl, hydroxyl and lactones were determined according to Boehm titration and from 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 (Garten and Weiss 1957 a, b), diketone or quinone groups (Leon y Leon and Radovic, 1994; Contescu et al., 1998) and pyrone-like groups (Voll and Boehm, 1971; Boehm, 1994). On the edges of the polyaromatic layers, the polycyclic pyrones 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

confirmed the presence of these groups. The observed basicity values were comparable with the activated carbon prepared from rice straw (Daifullah et al., 2007).

#### FT-IR Analysis (vide Figure 2 and Table 2)

Fourier transforms infrared (FT-IR) spectroscopy gives 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 NFRC (vide Table 2; Figure 2), before and after adsorption, confirmed the occurrence of aluminum adsorption on the active carbon as there were some changes like shifts and increase in the percentage of transmittance in the FT-IR spectra of the solid surface in the range  $4000\text{--}500\text{ cm}^{-1}$ . Band of O-H stretching vibrations were observed around  $3600\text{--}3200\text{ cm}^{-1}$  due to the existence of surface hydroxyl groups. Bands around  $2897.62\text{ cm}^{-1}$  are due to -C-H vibrations of aliphatic groups. As the carbon surface was subjected to oxidation by conc.  $\text{HNO}_3$ , the generation of quinone type carbon functional groups occurred and the presence of a band centered around  $1668.67\text{ cm}^{-1}$ , was attributed to the carbonyl (-C=O) stretching vibration of quinine or quinone or conjugated ketone (Biniak et al., 1997; Chang Yu et al., 2008; Ishizaki and Marti, 1981; Moreno-Castilla et al., 1998; Shin et al., 1997; Starsinic et al., 1983; Yongbin Ji et al., 2007; Zawadzki, 1989). 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 (Budinova et al., 2006). The stretching vibration bands of -O-H group and chemisorbed water (Daifullah et al., 2003; Ibrahim et al., 1980; Puziy et al., 2003; Yang and Lua, 2003), stretching (symmetric and asymmetric) vibrations of aliphatic -C-H group (Puziy et al., 2003; Yang and Lua, 2003), bending vibrations of -C-H of methylene group (Budinova et al., 2006; Gercel et al., 2007; Rajeshwari et al., 2001) and -C-O- stretching (Attia et al., 2006; Budinova et al., 2006; El-Hendawy, 2003; Figueiredo et al., 1999; Gercel et al., 2007; Gomez-Serrano et al., 1994; Lapuente et al., 1998; Rajeshwari et al., 2001; Park et al., 1997; Shin et al., 1997) were noted. Further, the peaks pertaining to the -C=O stretching in carbonyl and carboxyl groups and in lactones (Fanning and Vannice, 1993; Nageswara Rao et al., 2011; Painter et al., 1985; Zawadzki, 1989; Zhuang et al., 1994) and out of plane deformation vibrations of -C-H group in aromatic structures (Meldrum and Rochester, 1990 a,b,

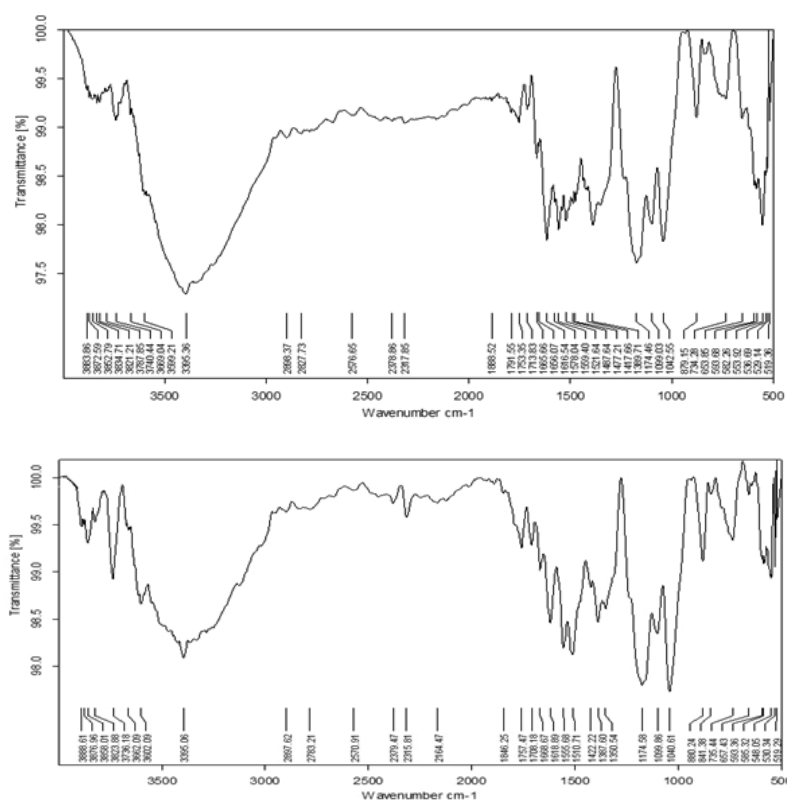


Figure 2: FTIR spectra of NFRC before (above) and after (below) adsorption.

Table 2: Bands assigned to the surface functional groups of NFRC before and after adsorption

S. No.	Wave number (cm <sup>-1</sup> )		
	NFRC (before)	NFRC (after)	Bond stretching
1	3883.86, 3872.59, 3852.79, 3834.71 3821.21, 3787.85 3740.44, 3669.04 3599.21, 3395.36	3888.61, 3876.96, 3858.01 3823.88, 3736.18, 3662.09 3602.09, 3395.06.	-O-H in alcohols, acids phenols and -N-H in amines and amides
2	2898.37, 2827.73, 2576.65, 2378.86, 2317.85,	2897.62, 2783.21, 2570.91 2379.47, 2315.81, 2164.47	-C-H in -CH <sub>3</sub> and -CH <sub>2</sub>
3	1888.52, 1791.55 1753.35, 1713.83	1846.25, 1757.47 1708.18	-C=O in carbonyl, carboxyl groups and lactones
4	1665.66, 1656.07	1668.67	-C=O in quinone or quinone
5	1616.54, 1578.04, 1559.40, 1521.64 1487.64, 1477.21 1417.66, 1389.71	1618.89, 1555.68 1510.71, 1422.22 1387.60, 1350.54	-C=C- in aromatic rings, -C=O in highly conjugated carbonyl groups and -C-H deformations in alkanes.
6	1174.46, 1099.03 1042.55	1174.58, 1099.86 1040.61	-C-O- in alcohols, phenols, ethers, esters, acids, epoxides, lactones and carboxylic anhydrides
7	879.15, 734.28 653.85, 593.68 582.26, 553.92 536.69, 519.36	880.24, 841.38 735.44, 657.43 593.36, 585.32 548.05, 530.34 519.29	-C-C- deformations and out of plane -C-H deformations in aromatic rings.

c; Nageswara Rao et al., 2011), have been, also observed in the IR spectra. The absence of specific peak pertains to -C-Al, suggested that the adsorption process was 'physisorption' but not chemisorption.

### Effect of Various Physicochemical Parameters on Aluminum Removal

#### Effect of Adsorbent Dosage

The effect of adsorbent dosage on the removal of aluminum ion from polluted waters was studied at by varying the sorbent concentration from 0.2 to 4.5 g/lit at optimum conditions of pH: 8, contact time: 120 min, aluminum ion concentration: 5 mg/lit and constant temp of  $\sim 30^\circ\text{C}$ . The results obtained are presented in Figure 3. From the plot, the percent removal of aluminum ion increases with an increase in the adsorbent dose and attained maximum at 3.0 g/lit of NFRC and then onwards, there is no further removal of aluminum with increase of the adsorbent dose.

As amount of adsorbent increases, number of active sites available for adsorption is also increased and this results in enhanced removal of Al(III) at low concentrations of NFRC. But after certain dosage, there is only marginal increase with further addition of the adsorbent and it may be due to overlapping or blocking of the active sites for being available for the adsorption process to occur.

#### Effect of pH

The sorption of aluminum was found to be pH sensitive and so, % removal of aluminum as the pH changed from 0.45 to 10, was studied under optimum conditions of extraction: aluminum ion concentration: 5 mg/lit, contact time: 120 min, adsorbent dose: 2.5 g/lit and at a temperature of  $\sim 30^\circ\text{C}$ . The results obtained were plotted as percentage of removal of aluminum(III) ion vs pH as shown in Figure 4.

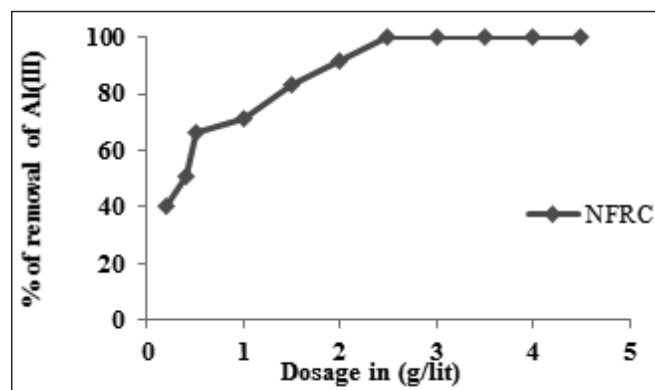


Figure 3: Plot of percent removal of aluminum as a function of adsorbent dose.

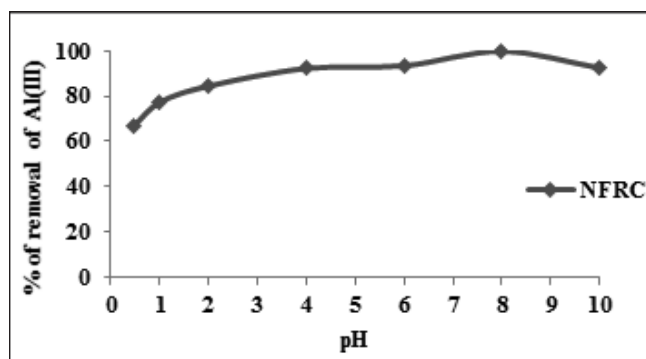


Figure 4: Plot of percent removal of aluminum as a function of pH.

It may be noted from the graph that substantial amounts of aluminum is removed in a wide range of initial pHs: 66.8% at pH: 0.45; 77.3% at pH: 1.0; 84.5% at pH: 2; 92.3% at pH: 4; 93.5% at pH: 6, 99.9% at pH: 8 and 92.5% at pH: 10. It is interesting to note that even in acidic pH values good removal is found. At low pH values (below 5), the surface is in its protinated form and Al(III) exists as hydrated cation,  $\text{Al}[(\text{H}_2\text{O})_6]^{3+}$ . The adsorption of  $\text{Al}^{3+}$  may be due to a sort of ion-exchange of  $\text{Al}^{3+}$  to  $\text{H}^+$ . As the pH is increased, hydrolysis species such as  $\text{Al}(\text{OH})^{2+}$ ,  $\text{Al}(\text{OH})_2^+$  and  $\text{Al}(\text{OH})_3$  are gradually formed and in basic pHs, aluminate anion is resulted. These species are also showing good tendency for adsorption and it may be due to the adsorption via hydrogen bonding as the surface is endowed with potential hydrogen bond forming groups such as -OH, -COOH, -N-H, -C=O etc. as is evident from the FTIR spectrum.

#### Effect of Contact Time

The contact time between the sorbent and aluminum ions was found to influence the % removal of aluminum ion. The adsorption experiments were conducted at optimum conditions of pH: 8.0, aluminum concentration: 5.0 mg/lit, sorbent dosage: 2.5 g/lit and at a temperature of  $\sim 30^\circ\text{C}$  and by varying the contact time from 10 to 180 min. The results obtained were plotted as '% removal of Al(III) vs contact time (min)', as shown in Figure 5.

From the figure, it can be inferred that the rate of adsorption is more initially but decreases with time and reaches steady state after 120 min. At this steady state, rate of adsorption of aluminum ions 'onto' the surface is equal to the rate of desorption of aluminum ions. 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 state is reached and at this stage, there will not be further adsorption. The decrease in the removal rate indicates the possible monolayer of aluminum ions on the outer surface and pores of the adsorbent leading to pore diffusion onto inner surface of adsorbent particles (Namasivayam and Kadirvelu, 1997, 1998; Yadav et al., 2006).

#### Effect of Initial Concentration

The effect of initial concentration of aluminum ion solution on % removal of aluminum ions from aqueous solution was studied at optimum conditions of pH: 8.0, contact time: 120 min, sorbent dosage: 2.5 g/lit and at a temperature:  $\sim 30^{\circ}\text{C}$  with varying concentrations of aluminum ion solution from 20 ppm to 100 ppm. The results obtained were plotted as percentage of removal of aluminum ion vs concentration of aluminum ion solution as shown in Figure 6.

With the increase in initial concentration of adsorbate i.e., aluminum ions, the percentage of removal of aluminum ions was found to be decreased. This is due to the number of active adsorption sites not being sufficient to accommodate aluminum ions. At low concentrations

of aluminum ions, the ratio of surface active sites to total aluminum ions is high and hence, the aluminum ions could interact with the sorbent to occupy the active sites on the carbon surface sufficiently and be removed from the solution (Montanher et al., 2005). For NFRC, with the increase in initial concentration of aluminum ion solution from 20 to 100 ppm, the percentage removal of aluminum ion is decreased from 99.9 to 72.1%.

#### Effect of Particle Size

The effect of particle size on the % removal of aluminum was explored by studying the % of removal with the change in the particle size from 45 to 150  $\mu$  mesh at optimum conditions of extraction namely, at pH: 8.0, contact time: 120 min, sorbent dosage: 2.5 g/lit, concentration of aluminum ion solution: 5.0 mg/lit and at a temperature:  $\sim 30^{\circ}\text{C}$ . The results obtained were plotted as percentage removal of aluminum ion vs particle size as shown in Figure 9.

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 aluminum 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 aluminum ion is decreased. The optimum size of the particles of activated carbon adsorbent is: 45 $\mu$ .

#### Effect of Co-ions on Aluminum Adsorption

The effect of co-ions on the % removal of aluminum by NFRC was studied with 50.0 mg/lit concentration of co-ions commonly found in waters particularly anions like chloride, nitrate, sulphate, bicarbonate and phosphate and cations like calcium, magnesium, zinc, copper and nickel, under optimum conditions of extraction namely,

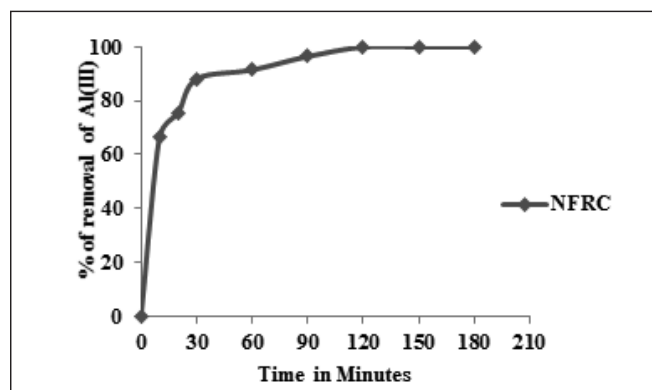


Figure 5: Plot of % removal of Al(III) as a function of contact time (min).

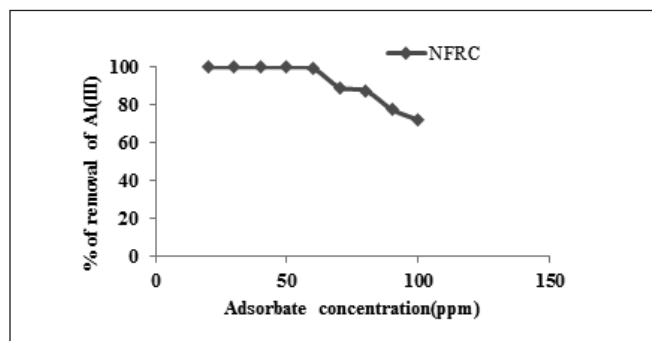


Figure 6: Plot of % removal of Al(III) as a function of initial concentration of Al(III) ions

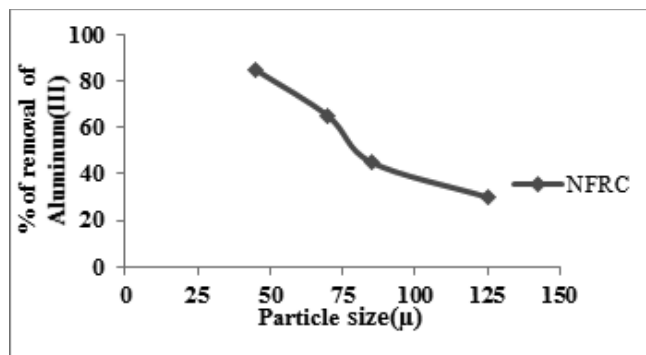


Figure 7: Plot of percent removal of aluminum as a function of particle size.



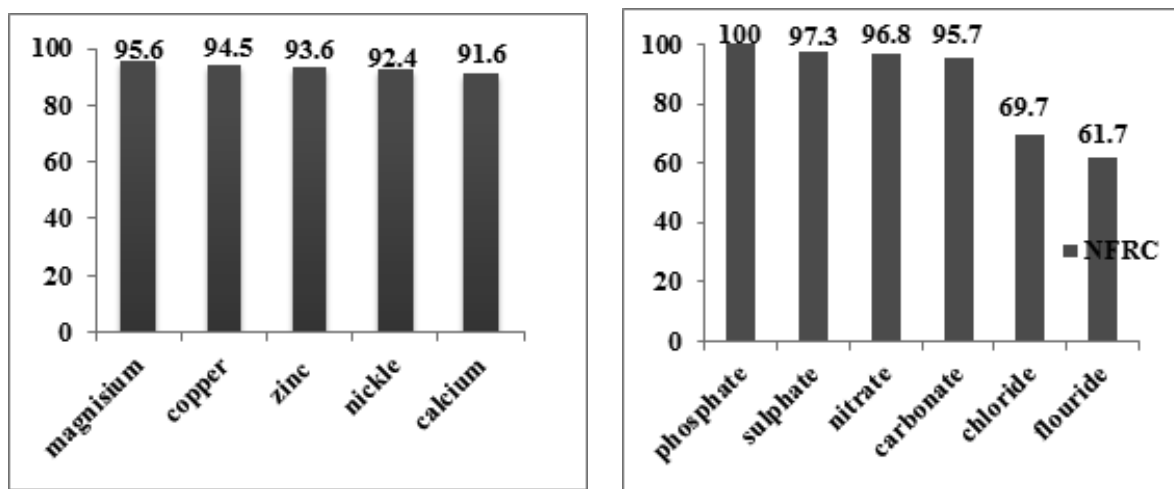


Figure 8: Effect of co-ions on % removal of aluminum(III) ion.

pH: 8.0, contact time: 120 min, sorbent dosage: 2.5 g/lit, concentration of aluminum ion solution: 5.0 mg/lit, particles sized: 45 $\mu$  mesh and temperature:  $\sim$ 30°C. The results obtained are presented in Figure 8.

The observations made with respect to the interfering ions are interesting to note. Sulphate, nitrate and carbonate seldom affect the extractability of Al(III) on the adsorbent while chloride and fluoride markedly decrease the extraction. This may be attributed to the fact that chloride and fluoride desorb the Al(III) from the adsorption sites of the sorbent (which are the weak cation exchange sites) by the formation of anionic complexes,  $\text{AlF}_4^-$  and  $\text{AlCl}_4^-$ . In presence of phosphate, the % removal of aluminum ions is enhanced and it may be due to the formation of sparingly soluble aluminum phosphate,  $\text{AlPO}_4$  which is gelatinous in nature and is trapped or occluded in the matrix of the sorbents and thus enhances the % of extractability of Al(III) species. The interference of the cations chosen for study on the extractability of Al(III) is minimal and it is of the order:  $\text{Ca}^{2+} > \text{Ni}^{2+} > \text{Cu}^{2+} > \text{Zn}^{2+} > \text{Mg}^{2+}$  (Jeffery et al., 1989). This order is as per the cation-exchange capabilities of cations on the cation-exchangers.

#### Effect of Temperature

The effect of solution temperature on the % removal of aluminum was studied by conducting the extraction experiments at different temperatures 303, 313 and 323K and at optimum conditions of extraction: pH: 8.0; contact time: 120 min; sorbent dosage: 2.5 g/lit; concentration of aluminum ion solution: 5.0 mg/lit; particles size: 45 $\mu$  mesh and the results obtained were plotted as  $\ln K_d$  vs  $1/T$  as shown in Figure 9. Thermodynamic parameters of the adsorption process

such as change in free energy ( $\Delta G$ ) (kJ/mole), change in enthalpy ( $\Delta H$ ) (kJ/mole) and change in entropy ( $\Delta S$ ) (J/K/mole) were determined at different temperatures by using the equations (Alagumuthu and Rajan, 2010; Karthikeyan and Siva Elango, 2007):  $\Delta G = -RT \ln K_d$ ;  $\ln K_d = \Delta S/R - \Delta H/RT$ ;  $K_d = q_e/C_e$  and  $\Delta G = \Delta H - T\Delta S$  where  $K_d$  is the distribution coefficient for the adsorption,  $q_e$  is the amount of aluminum ion adsorbed on the activated carbon adsorbent per litre of solution at equilibrium,  $C_e$  is the equilibrium concentration of aluminum ion solution,  $T$  is the absolute temperature in Kelvin,  $R$  is the gas constant.  $\Delta G$  is the change in free energy,  $\Delta H$  is the change in enthalpy,  $\Delta S$  is the change in entropy.

The values of  $\Delta H$  and  $\Delta S$  were obtained from the slope and intercept of a plot between  $\ln K_d$  and  $1/T$  and  $\Delta G$  values were obtained from the equation  $\Delta G = \Delta H - T\Delta S$  and presented in Table 3 (Hameed 2009; Nunes et al., 2009).

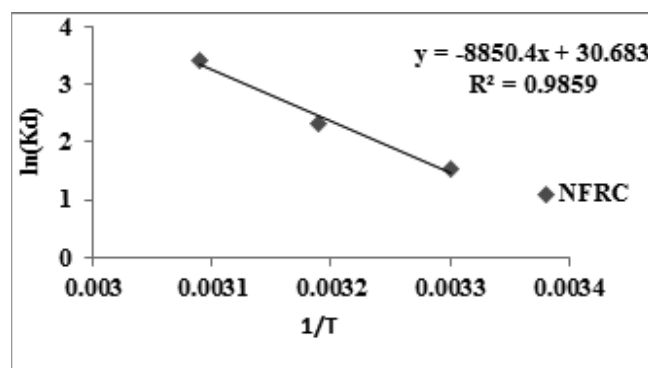


Figure 9: Effect of temperature on %R of aluminum(III) ion onto NFRC.



**Table 3: Thermodynamic parameters of aluminum(III) ion adsorption onto NFRC**

Parameter	$\Delta H$ (kJ/mol)	$\Delta S$ (J/mol/K)	$\Delta G$ (kJ/mol)			$R^2$
Temperature (K)			303	313	323	
NFRC	73.578	255.07	-3.708	-6.258	-8.809	0.985

It is observed that with increase in temperature from 303 to 323 K (30 to 50°C), the percentage removal of aluminum(III) ion increases from 83.0 to 88.5% for NFRC. As the temp increases, the thickness of outer surface of the activated carbon adsorbent decreases and kinetic energy of the aluminum ion increases and hence the rate of diffusion of aluminum ion increases across the external boundary layer and internal pores of the activated carbon adsorbent.

It is seen from Table 3, the values of  $\Delta H$  is positive, which indicates the 'physisorption' and endothermic nature of adsorption (Bouberka, 2005). The  $R^2$  value is close to one (0.985) also indicates that adsorption process is of endothermic nature. The positive values of  $\Delta S$  indicate the increased disorder and randomness at the solid solution interface of aluminum ion with the adsorbent (Sairam Sundaram, 2009). The negative values of  $\Delta G$  indicate the spontaneous nature of adsorption process at high temperatures, i.e. the adsorptive forces are strong enough to overcome the potential barrier (Chaturvedi, 1988).

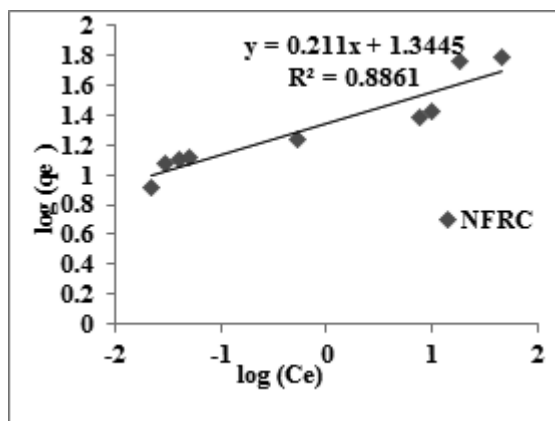
#### Adsorption Isotherms

Freundlich (1906), Langmuir (1918), Temkin (Temkin and Pyzhev, 1940) and Dubinin-Radushkevich (1947) isotherms were used to evaluate the relation between the aluminum concentrations remaining in the bulk solution to the amount of aluminum adsorbed at the solid/solution interface at a constant temperature.

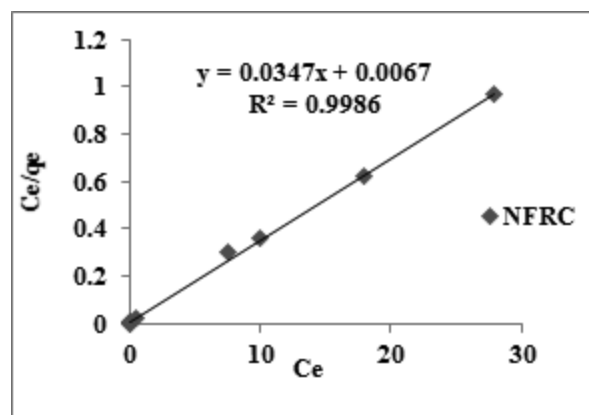
Linear form of Freundlich equation is  $\log(q_e) = \log k_F + (1/n) \log C_e$  and Linear form of Langmuir equation is  $C_e/q_e = (a_L/k_L) C_e + 1/k_L$ . According to Hall et al. (1966), the nature of the adsorption process is unfavourable ( $R_L > 1$ ), linear ( $R_L = 1$ ), favourable ( $0 < R_L < 1$ ) 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 are shown in Figure 10 and isothermal constants along with the correlation coefficient values are presented in Table 4.

As the correlation coefficients ( $R^2$ -values) is close to unity, it indicates the applicability of these two adsorption isotherms confirm the heterogeneous surface of the adsorbent and the monolayer coverage of aluminum ion on the active carbon surface. The high correlation coefficient ( $R^2 = 0.998$ ) value and dimensionless separation factor ( $R_L = 0.0035174$ ) value which are found to be fraction in the range of 0-1, indicate the favourability of the Langmuir isotherm than the Freundlich isotherm.

Linear form of Temkin equation is  $q_e = B \ln C_e + B \ln A$  where  $RT/b = B$  and 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 Figure 11 and isothermal constants along with the correlation coefficient values are presented in Table 5.



(a) Freundlich adsorption isotherm



(b) Langmuir adsorption isotherm

**Figure 10: Adsorption isotherms.**

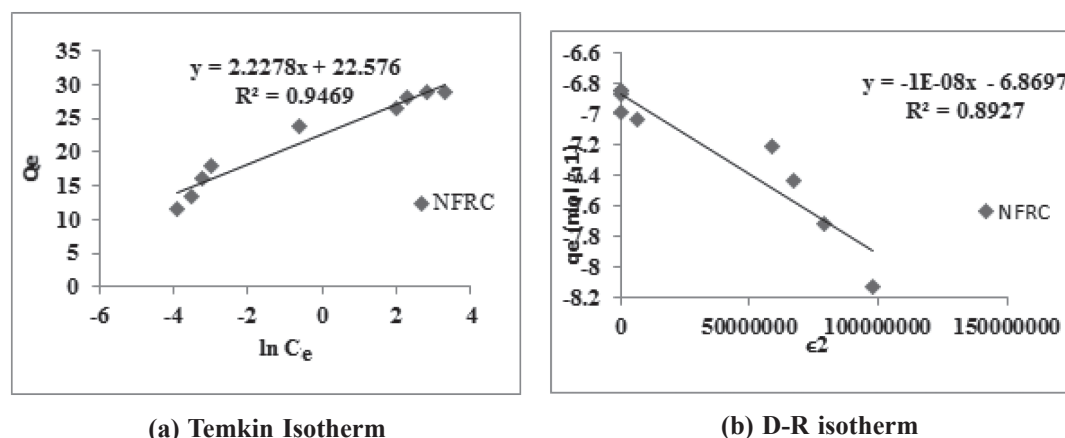


Figure 11: (a) Temkin and (b) D-R adsorption isotherms.

Table 4: Freundlich and Langmuir adsorption isothermal parameters

S. No.	Adsorption isotherms	Slope	Intercept	$R^2$
1	Freundlich isotherm	0.211	1.344	0.886
2	Langmuir isotherm	$R_L = 0.0035174$	0.006	0.998

Table 5: Temkin and Dubinin-Radushkevich isothermal parameters

S. No.	Adsorption isotherms	Slope	Intercept	$R^2$
1	Temkin isotherm	$B = 2.227 \text{ J/mol}$	22.57	0.946
2	Dubinin-Radushkevich isotherm	$E = 7.071 \text{ kJ/mol}$	-6.869	0.892

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,  $B = 2.227 \text{ J/mol}$  was calculated from the slope of the Temkin linear plot (Hameed, 2009; Nunes et al., 2009) and the Dubinin-Radushkevich mean free energy,  $E = 1/\sqrt{2}\beta$  (Onyango et al., 2004) was found to be  $7.071 \text{ kJ/mol}$  for NFRC. As the  $E < 8 \text{ kJ/mol}$ , it is an indication of 'physisorption' (Monika, 2009) dominating the chemisorption 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 Al(III) ions and adsorbent. According to Atkins (1999), characteristics for "physisorption" are the mean free energy ( $E$ ) and also heats of sorption ( $B$ ) values lower than  $20 \text{ kJ/mol}$ . The  $B$  value of  $2.227 \text{ J/mol}$  for the present adsorbent system, further confirms the 'physisorption' nature.

### Adsorption Kinetics

The rate and kinetics of adsorption of aluminum(III) ion 'onto' the NFRC was studied with pseudo first-order model (Ho and McKay, 1999), pseudo second-order model (Ho and McKay, 1999; Ho et al., 2000), Weber and Morris intra particle diffusion model (Weber and Morris, 1963), Bangham's pore diffusion model (Aharoni and Ungarish, 1977) and Elovich equations (Gerente et al., 2007; Ozacar and Sengil, 2005).

The pseudo first-order equation is:  $\log(q_e - q_t) = \log q_e - k_1 t/2.303$ ; the pseudo second-order equation is:  $t/q_t = 1/k_2 - (1/q_e) t$ ; Weber and Morris intraparticle diffusion equation is:  $q_t = k_{ip} t^{1/2} + c$ ; Bangham's pore diffusion equation is:  $\log[\log(C_i/C_i - q_m)] = \log(k_o/2.303 V) + \alpha \log(t)$ ; 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.12 and rate constants along with the correlation coefficient values are presented in Table 6.

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

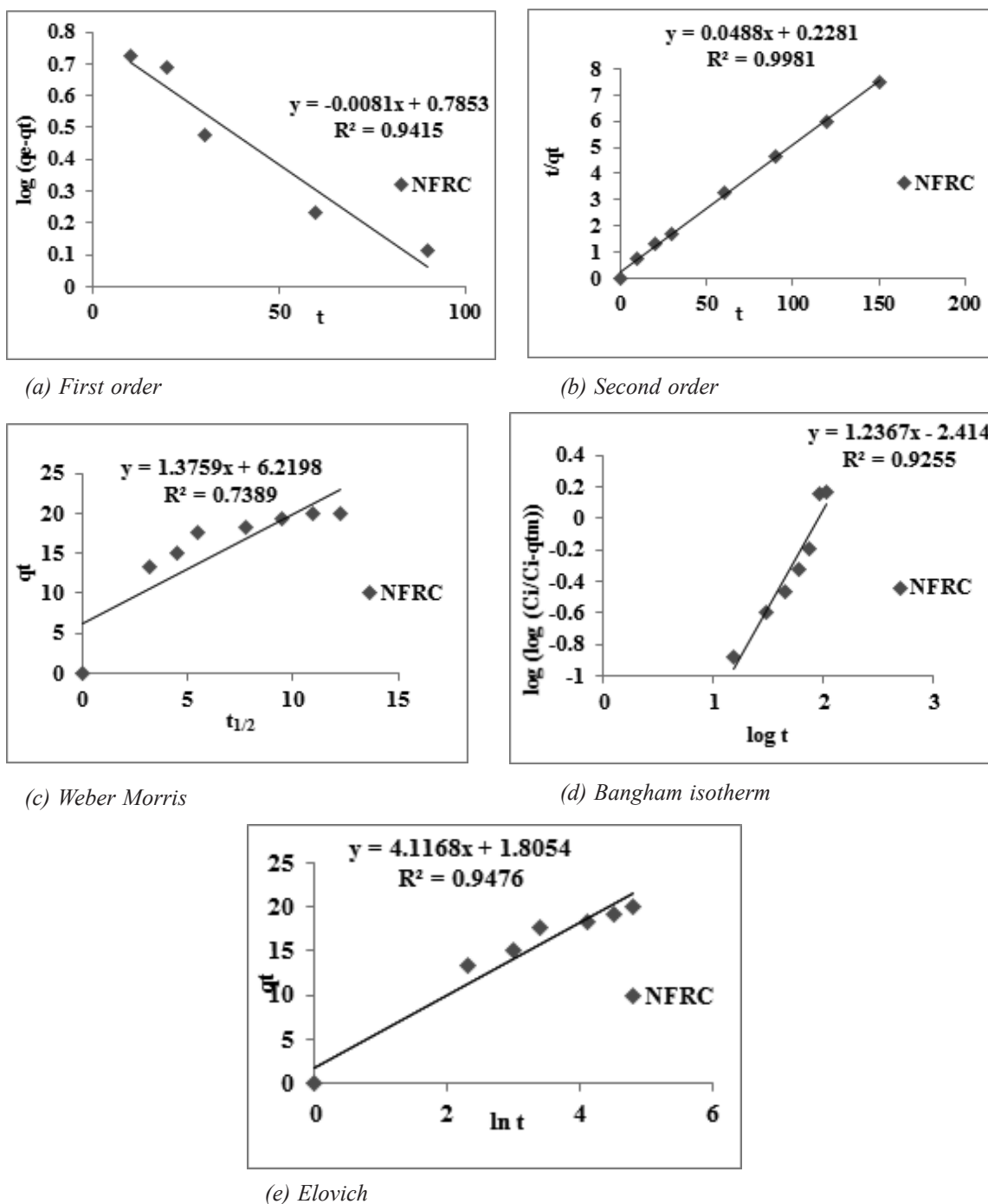


Figure 12: Linear plots of kinetic models: (a) First order; (b) Second order; (c) Weber Morris; (d) Bangham isotherm and (e) Elovich.

Table 6: Kinetic parameters for the adsorption of Al(III) onto to NFRC

S. No.	Adsorption kinetics	Slope	Intercept	$R^2$
1	Pseudo first-order	-0.008	0.785	0.941
2	Pseudo second-order	0.048	0.228	0.998
3	Weber and Morris intraparticle diffusion	1.375	6.219	0.738
4	Bangham's pore diffusion	1.236	-2.414	0.925
5	Elovich model	4.116	1.805	0.947

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 Elovich model ( $R^2 = 0.947$ ) followed by pseudo first-order model ( $R^2 = 0.941$ ), Bangham's pore diffusion model ( $R^2 = 0.925$ ) and least is Weber and Morris intraparticle diffusion ( $R^2 = 0.738$ ).

### Applications

The methodology developed in this work with the new bio-sorbent, NFRC, was adopted for the removal of Al(III) ions from real samples of diverse nature, collected from the sewages/effluents of aluminum-based industries and also in natural polluted lakes.

For this purpose, three samples were collected from alum manufacturing industries in Hyderabad and three from aluminum sulphate manufacturing industries in Chennai and three more natural samples from three polluted lakes at different places in Bapatla Mandal of Guntur Dist of Andhra Pradesh and all these samples were analyzed for the actual concentration of Al(III). Then these samples were subjected to the extraction of Al(III) using the NFRC developed in this work at optimum conditions of extraction of pH: 8, equilibration time: 120 min, particle size of NFRC: 45  $\mu$  and sorbent concentration of 2.5 g/lit and temperature:  $\sim 30^\circ\text{C}$  and the results obtained are presented in Table 7.

**Table 7: Initial concentration and maximum extraction of Al(III) using NFRC**

<i>Samples collected at different places</i>	<i>Initial concentration of Al(III) in the sample</i>	<i>% of removal (Average of three determinations of each sample and RSD ranging from 0.5 to 1.5%)</i>
<i>Alum manufacturing industrial effluents:</i>		
Sample 1	10.0 ppm	93.5
Sample 2	14.0 ppm	94.5
Sample 3	16.5 ppm	96.2
<i>Aluminum Sulphate manufacturing industrial effluents</i>		
Sample 1	15.5 ppm	95.7
Sample 2	17.5 ppm	94.5
Sample 3	19.0 ppm	96.2
<i>Natural polluted lake samples fed with known amounts of Al (III):</i>		
Sample 1	7.5 ppm	98.0
Sample 2	10.5 ppm	97.4
Sample 3	11.5 ppm	96.9

It can be inferred from the data that % removal of Al(III) is substantial and it has never come down below 93.5%. Thus the methodology developed in this research work using active carbon NFRC is remarkably successful.

### Conclusions

The batch methods of extractions with the adsorbent, NFRC, are successfully applied to the removal of Al(III) ions from simulated and real polluted waters. The optimum conditions of maximum extraction are pH: 8.0; adsorbent dosage: 2.5 g/lit; equilibrium time: 120 min; particle size: 45  $\mu$  and temperature:  $\sim 30^\circ\text{C}$ . Most of the common cations, even at tenfold excess, envisaged marginal effect on the % of extraction of Al(III) at optimum extraction conditions. Anions like sulphate, nitrate and carbonate have least affected the % of extraction while chlorides and fluorides markedly affected the % of extraction but Phosphates synergistically increased the % of extraction.

It is observed that the adsorption process satisfactorily fit with Langmuir adsorption isotherm which has good correlation coefficient value indicating monolayer adsorption. The Temkin heat of sorption,  $B = 2.227$  J/mol and the Dubinin-Radushkevich mean free energy,  $E = 7.071$  kJ/mol for the adsorbent, NFRC, indicate the 'physisorption' process. In the kinetic studies of the removal of aluminum(III) ions, 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. The methodologies developed in this work have been applied to real polluted water samples of industries contaminated with aluminum salts and found to be remarkably successful.

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