

Removal of fluoride by thermally activated carbon prepared from neem (*Azadirachta indica*) and kikar (*Acacia arabica*) leaves

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Abstract: The present investigation deals with fluoride removal from aqueous solution by thermally activated neem (*Azadirachta indica*) leaves carbon (ANC) and thermally activated kikar (*Acacia arabica*) leaves carbon (AKC) adsorbents. In this study, neem leaves carbon and kikar leaves carbon prepared by heating the leaves at 400°C in electric furnace was found to be useful for the removal of fluoride. The adsorbents of 0.3 mm and 1.0 mm sizes of neem and kikar leaves carbon was prepared by standard sieve. Batch experiments done to see the fluoride removal properties from synthetic solution of 5 ppm to study the influence of pH, adsorbent dose and contact time on adsorption efficiency. The optimum pH was found to be 6 for both adsorbents. The optimum dose was found to be 0.5g/100 ml for ANC (activated neem leaves carbon) and 0.7g/100 ml for AKC (activated kikar leaves carbon). The optimum time was found to be one hour for both the adsorbent. It was also found that adsorbent size of 0.3 mm was more efficient than the 1.0 mm size. The adsorption process obeyed Freundlich adsorption isotherm. The straight line of log (q_e-q) vs time at ambient temperature indicated the validity of Lagergren equation consequently first order nature of the process involved in the present study. Results indicate that besides intraparticle diffusion there may be other processes controlling the rate which may be operating simultaneously. All optimized conditions were applied for removal of fluoride from four natural water samples.

Key words: Activated carbon, Fluoride removal, Neem leaves, Kikar leaves, Adsorbent
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Introduction

Fluoride is a health affecting substance. The physiological effects of fluoride ingestion on human health have been studied extensively. The acceptable fluoride concentration in drinking water is generally in the range of 0.5 to 1.5 mg l⁻¹. Concentration higher than that affects the metabolism of elements such as Ca, P in human body and lead to dental and skeletal fluorosis. The fluoride content of soils varies from under 20 to several thousand ppm, the higher records being mostly from areas with bedded phosphate on fluoride deposits. Fluoride is present in the soil and rock formation in the form of fluorapatite, fluorospar, amphiboles and micas weathering rock-alkali contribute fluoride natural waters (Brewer, 1996; Elrashidi and Lindsay, 1986; Ward *et al.*, 1964; Bishnoi and Arora, 2007; Shailaja and Johnson, 2007). The fluoride present in these minerals is substituted by (OH⁻) ion under redox conditions resulting in the release of fluoride ions to the circulating waters.

India is among 23 nations in the world, where fluoride contaminated ground water is creating health problems. Sixty two million people including 6.0 million children in the country in 18 states are affected with dental, skeletal or non skeletal fluorosis (Chinoy, 1991; Susheela, 1993). In rural India, ground water (which contains high fluoride) remains the dominant source of drinking water. The contents of fluoride in ground water are increasing due to heavy withdrawal of water for agriculture purpose, poor recharging, low rainfalls and pollution from industrial effluents.

Industries which release significant quantities of fluoride in process waste to streams include fluorosilicone acid and fluoro carbon polymer synthesis, gasoline production, manufactures of coke, ceramic, cement, enamel, fiberglass, electronics, pesticides, fertilizer's, surface heating operation, metal itching (with hydrofluoric acid) and wood preservatives.

Several methods for defluoridation of drinking water have been developed. Most of these methods are based on principles of precipitation, such as the use of lime softening, alum and lime addition, activated alumina, bone char, synthetic calcium hydroxyl apatite (HA) bauxite, ion exchange resin, electrodialysis and reverse osmosis *etc.*

A large number of plants and their wastes have been used to remove heavy metals and other contamination from water all over the world (Axtell *et al.*, 2003). Recently, considerable attention has been devoted to develop better and suitable adsorbents for defluoridation purpose but adsorption process is the cheapest, simplest, easily available and accessible process for defluoridation in developing country like India (Kumar *et al.*, 2007). Materials like coconut shell carbon (Arulanantham *et al.*, 1992), activated carbon (Muthukumaran *et al.*, 1995; Mariappan *et al.*, 2002; Sivabalan *et al.*, 2002), activated alumina (Kumar, 1995; Li *et al.*, 2001), bone char (Killedar and Bhargava, 1993) and ion exchange resins (Shrivastava and Deshmukh, 1994) have been used as adsorbents. Activated carbon prepared from various raw materials exhibits good

capacity for removal of fluoride from drinking water. No reports on use of neem and kikar activated leaves have appeared for defluoridation.

In the present study, removal of fluoride by adsorption on to low cost material like thermally activated neem and kikar leaves carbon was investigated.

Materials and Methods

Preparation of activation carbon: The neem and kikar leaves were collected from the G.J. University campus, Hisar. They were washed with water to remove dust and other impurities. They were dried in the sun and then burnt in the thermal furnace at 400°C for half an hr. The neem and kikar leaves were ground to obtain small pieces. They were then washed with the 1% formaldehyde solution to remove the colour and then dried in oven maintained at temperature range of 120 - 140°C for a period of 12 hr. The dried material were ground and sieved through standard sieve (Sonar GSMS, Mumbai) to obtain particle of sizes up to 0.3 and 1.0 mm.

Characterization of adsorbents: Various characteristics of prepared adsorbents were studied by adopting the standard procedures (BIS, 1989).

Batch studies: Batch adsorption tests were conducted to investigate the effect of controlling parameters like pH, adsorbent dosage, size of adsorbent and contact time. All the experiments were conducted at room temperature of $27 \pm 1^\circ\text{C}$. All optimization experiments were performed with 100 ml. synthetic sample of 5 ppm fluoride. To study the effect of pH, adsorbent dose was 0.5 g/100 ml of ANC and 0.7 g/100 ml for AKC while time duration was kept 1 hr and pH was varied from 2 to 10. The experiment to study the effect of adsorbent dose was carried out at 1 hr contact time, pH 6.0 and ambient temperature. The effect of contact time studied at dose of adsorbent were taken as 0.5 g/100 ml for ANC and 0.7 g/100 ml for AKC, pH 6.0 for ANC and AKC and contact time was varied from 15 min to 120 min at ambient temperature.

After desired contact period, conical flasks were removed and allowed for two minutes to settle down the adsorbents. The solutions were filtered through sonar filter paper no. 1. The filtrate was then analyzed according to the SPANDS method as prescribed in standard methods of water and waste water analysis (APHA, 2005).

In batch process studies pH, adsorbent dose, contact time was optimized on synthetic sample of 5 ppm of fluoride. The effect of the initial concentration of fluoride was also studied. After optimization of these parameters the possible optimized conditions were applied on the ground water samples collected from Rohtak to check the suitability of the adsorbent for field condition.

Langergren's equation has been used to study the rate constant for adsorption of the fluoride by ANC and AKC of different sieve size of 0.3 mm and 1.0 mm.

$$\text{Log}(q_e - q) = \text{Log} q - \frac{K}{2.303} t$$

Where q_e = The amount of fluoride adsorbed at equilibrium (mg/g), q = Amount of fluoride adsorbed at time t (mg/g), K = Rate constant of adsorption (per minute), t = Time (minute)

Results and Discussion

The important characteristics of activated carbon are presented in Table 1. Characteristic of carbon reveals that activated neem leaves (ANC) was found basic while activated kikar leaves carbon (AKC) was found neutral. The adsorbent solubility in acid is more than water. The characteristics of carbon reveal that the ANC possessed less bulk density and particle density than the AKC. Fluoride removal by ANC and AKC was carried out to assess the suitability of ANC and AKC from aqueous solution. The effect of different parameters, viz. pH, adsorbent dose, and contact time were studied in batch experiments.

Effect of pH: Fig. 1 shows the effect of pH on fluoride removal by ANC and AKC (0.3 mm and 1.0 mm). It is evident that fluoride removal reached a maximum of 58% and 59.2% by particle size 0.3mm of ANC and AKC respectively at pH 6.0. Likewise, maximum percent fluoride removal by adsorbent size of 1.0 mm *i.e.* 46.4% and 44.8% by ANC and AKC was observed at pH 6.0. Initially it was observed that the percent fluoride removal increase as the pH increases from 2.0 to 6.0 then decreases above 6.0. Therefore, solution pH was maintained at 6.0 for further studies.

In the acidic pH range, the amount of fluoride adsorbed slightly decreased and this can be attributed to the formation of weak hydrofluoric acid. In the alkaline pH range there was sharp drop in adsorption which may be due to the competition of the hydroxyl ions with the fluoride for adsorption.

Effect of adsorbent dose: Fluoride uptake by both carbon, ANC and AKC at different dose of 0.2 g to 1.0 g particle sizes of 0.3 mm and 1.0 mm has been given in Fig. 2. The results showed that increase in adsorbent dosage increased the amount of fluoride removal. It is also found that as particle size increase there was decrease in defluoridation capacity. It is observed from the results that fluoride removal by 0.3 mm and 1 mm sizes adsorbent increases from 45.6% to 68.4% and 32.4 to 57.6% at 0.2 g to 1.0 g of ANC/100 ml. Likewise in case of AKC it was observed that fluoride removal by 0.3 mm and 1mm adsorbent sizes increases from 41.6% to 64.8% and 26% to 48.8% at 0.2 to 1.0 g/100 ml of AKC. The significant removal efficiency was reported at 0.5 g dose of ANC and 0.7 dose of AKC for both sizes (0.3 mm and 1.0 mm) beyond which further addition of carbon revealed fluoride removal at slower rate. So for further study 0.5 g of ANC/100 ml and 0.7 g of AKC/100 ml dose were taken.

As the particle size increases, surface area available per unit weight of the sorbent decreases. Moreover, as the particle size increases the time required for migration of the sorbate into inner pores also increases and this may result in longer time for equilibrium and a lower sorption capacity. A higher fluoride removal was observed by availability of more surface area (Sirmurali *et al.*, 1997).

Table - 1: Characterization of adsorbents

Parameters	ANC		AKC	
	0.3 mm	1.0 mm	0.3 mm	1.0 mm
pH	9.3	9.3	7.0	7.0
$\frac{e}{c} \frac{m}{m} \frac{h}{o} \frac{c}{m}^{-1}$	0.54	0.54	0.31	0.31
Bulk density gcm ⁻³	0.27	0.15	0.37	0.22
Particle density gcm ⁻³	0.31	0.19	0.49	0.37
Solubility in water (%)	6.2	5.9	5.7	5.3
Solubility in acid (%)	9.3	8.6	4.2	3.7
Moisture content (%)	8.92	7.32	6.68	7.54
Porosity(%)	12.9	21.05	24.48	40.54

Table - 2: Removal of fluoride from natural water sample by the adsorbents

Sample No.	Initial fluoride concentration	F- concentrations after treatment with adsorbents			
		ANC		AKC	
		0.3 mm	1.0 mm	0.3 mm	1.0 mm
1	1.18	0.48	0.6	0.44	0.58
2	1.88	0.75	1.02	0.68	0.96
3	2.6	1.02	1.16	0.94	1.18
4	4.7	2.22	2.65	2.1	2.82

Table - 3: Freundlich rate constants for different adsorbents

Adsorbents	K		1/n	
	0.3 mm	1.0 mm	0.3 mm	1.0 mm
ANC	1.1	1.52	2.24	1.97
AKC	1.01	4.37	2.01	2.57

Table - 4: Langergren and intraparticle diffusion rate constants for different adsorbents

Adsorbents	K_{ad} / min		K_i / min	
	0.3 mm	1.0 mm	0.3 mm	1.0 mm
ANC	-0.133	-0.0145	3.02	2.64
AKC	-0.126	-0.0111	3.3	2.94

It is also evident from the results that as adsorbent dose was increased, there was less commensurate increase in adsorption which may be due to lower adsorptive capacity utilization of sorbent and unit adsorption decreases significantly with increasing mass of sorbent per unit volume. This effect had been termed as "solid concentration effect" i.e. overcrowding of particles (Mehrotra *et al.*, 1999).

Effect of contact time: Fig. 3 exhibits the variation of fluoride removal from aqueous solution by ANC and AKC adsorbents sizes of 0.3 mm and 1.0 mm with respect to contact time. It has been revealed from the results that fluoride removal by ANC (0.3 mm and 1.0 mm) increases from 44.4% to 65.2% and 34.6% to 52.0%, respectively. Likewise, 46.4% to 68.8% and 30.4% to 51.6% fluoride removed by AKC sizes of 0.3 mm and 1.0 mm respectively at 15

min to 120 min was observed. There was slow removal (%) of fluoride after 60 min so this time period was taken as optimum time.

The perusal of results shows higher removal rate initially and slower rate after lapse of time. Vacant adsorption sites, high solute concentration gradient, electrostatic affinity and ion - exchange may attribute to the higher removal in the initial stages (Mariappan *et al.*, 2002).

Effect of adsorption on natural water sample: To explore the effect of different studied adsorbents on natural water samples, four natural water samples were collected from Azadgarh (Rohtak). The optimized conditions were applied during treatment to check the suitability of adsorbents and to study the after effect on water quality. The results have been shown in the Table 2.

The fluoride removal was slightly higher by AKC at 0.3 mm adsorbent size in comparison to ANC.

Adsorption isotherm: Experimental data on the adsorption of fluoride on activated carbon at room temperature under optimum conditions of contact time and dosage of adsorbent were found to obey Freundlich adsorption isotherm (Eq. 1) and the model was applied to the adsorption equilibria for both ANC and AKC.

$$\text{Log}(x/m) = \text{log } K + \frac{1}{n} \text{log } C_e \quad \dots\dots (1)$$

The results revealed that the adsorption of fluoride on ANC and AKC under optimum conditions at room temperature (27 ± 1°C) also obeyed the Freundlich adsorption isotherm. Freundlich adsorption isotherm relates fluoride adsorbed by per unit mass of the



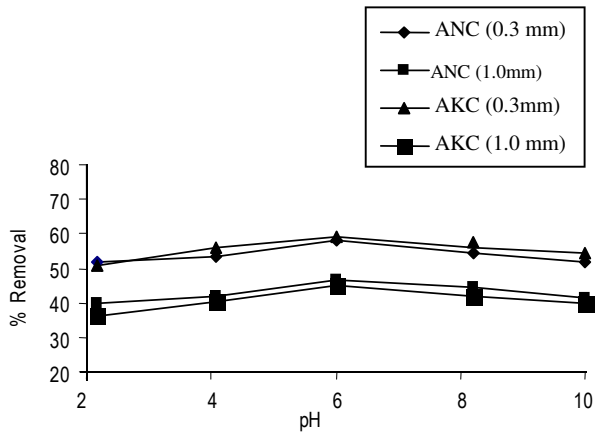


Fig. 1: Effect of pH on fluoride removal by ANC and AKC

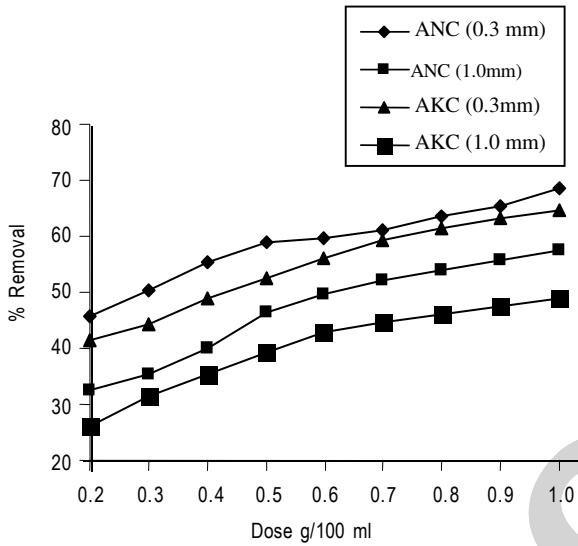


Fig. 2: Effect of dose on fluoride removal by ANC and AKC

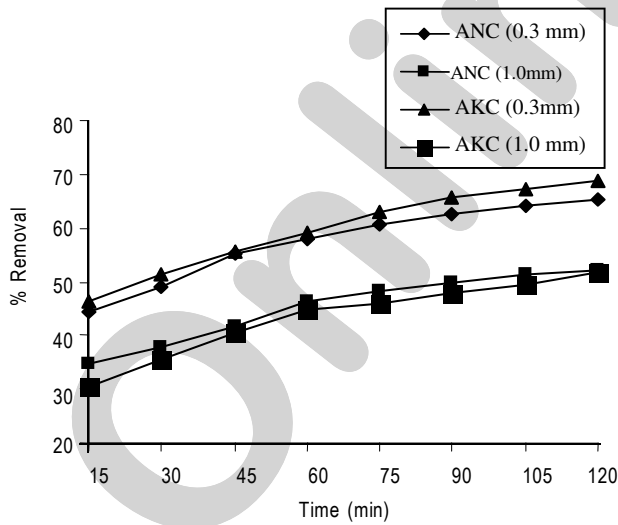


Fig. 3: Effect of time on fluoride removal by ANC and AKC

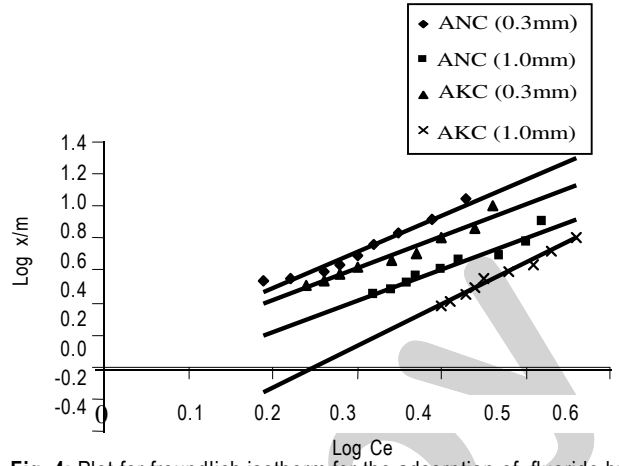


Fig. 4: Plot for freundlich isotherm for the adsorption of fluoride by ANC and AKC

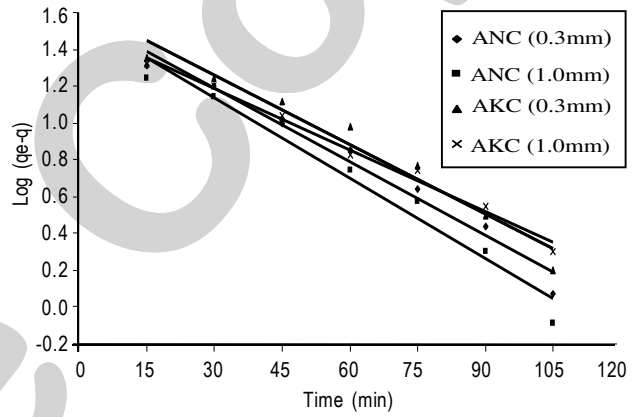


Fig. 5: Lagergren plot for fluoride by ANC and AKC (0.3 mm and 1.0 mm)

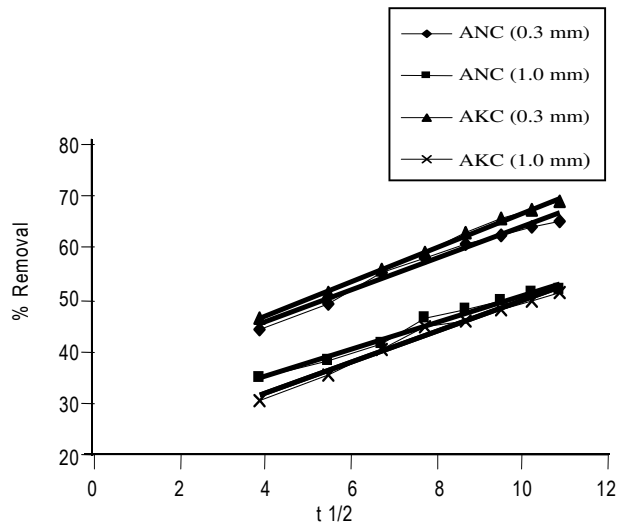


Fig. 6: Intraparticle diffusion plot for the adsorbent of fluoride by ANC and AKC (0.3 mm and 1.0 mm)



adsorbent x/m with fluoride at equilibrium (C_e). The constants K and n represent the adsorption capacity and intensity of the adsorption, respectively. The data obtained in this study gave good fits to the Freundlich adsorption isotherm. The plot of $\text{Log}(x/m)$ against $\text{Log}(C_e)$ was linear at various initial concentrations justifying the application of Freundlich adsorption isotherm (Fig. 4). The value of K 1.1 (0.3 mm) and 1.52 (1.0 mm) for ANC and 1.01 (0.3 mm) and 4.37 (1.0 mm) for AKC, indicated greater affinity for fluoride and the $1/n$ values, 2.24 (0.3 mm) and 1.97 (1.0 mm) for ANC and 2.01 (0.3 mm) and 2.57 (1.0 mm) for AKC respectively, showed the good adsorption character of the carbons (Table 3).

Langergren's studies: The straight line plots of $\text{Log}(q_e - q)$ vs time at ambient temperature indicated the validity of langergren equation, consequently first order nature of the process involved in the present study (Fig. 5). The value of K_{ad} at ambient temperature for ANC and AKC was calculated from the plots and shown in Table 4.

Intraparticle diffusion studies: Linear plots confirm intraparticle diffusion effects. Results are shown in Fig. 6. Rate constant for intraparticle diffusion were calculated from the slope of linear portion of respective plots. The value of slope calculated for each curve are given in Table 4 and were found to be widely divergent from the value of 0.5 which corresponds to the intraparticle diffusion being the rate determining step (Weber *et al.*, 1964). The divergence in values from 0.5 indicated besides intraparticle diffusion there may be other processes controlling the rate which may be operating simultaneously.

The ability of the activated carbon adsorbents prepared from various plant materials have been used to remove heavy metals, such as chromium(III) ions by coconut (*Cocos nucifera*) husk (Rashid *et al.*, 2005), toxic metal ions (iron and manganese) by palm fruit bunch and maize cob (Nassar *et al.*, 2004), Co(II) and Ni(II) ions from peanut hulls (Hashem *et al.*, 2005), mercury(II) ions from *Eichhornia crassipes* (Kadirvelu *et al.*, 2004), Zn (II) ions by almond husk (Hasar *et al.*, 2003) and organic pollutants through rice straw and water hyacinth (Rashwan and Girgis, 2004) from aqueous solution by adsorption was studied. Like the present study, the adsorption was pH, contact time, adsorbents concentration, temperatures and initial concentration of ions dependent. In all the above studies the equilibrium data were well fitted by the Langmuir and Freundlich adsorption models as reported in the present study also.

The present study indicates that removal of fluoride from aqueous solution depends on pH, contact time, particle size and dose of the adsorbent. The removal of fluoride is more for the finer-variety of carbon. The adsorption of fluoride from aqueous solution with ANC and AKC followed Freundlich, intraparticle diffusion and langergren absorption equation. The values of adsorption capacity (k) and intensity of adsorption ($1/n$) indicate greater affinity for fluoride. The kinetics of adsorption of fluoride with ANC and AKC followed first order kinetics. Thermally activated neem leaves carbon (ANC) was good adsorbent

and 0.3 mm size was more efficient than 1.0 mm. Removal efficiency of studied adsorbents is found $ANC > AKC/g$ dose.

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