

Fluoride removal by mixtures of activated carbon prepared from *Neem* (*Azadirachta indica*) and *Kikar* (*Acacia arabica*) leaves

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Fluoride removal from aqueous solution was investigated using activated carbon developed from mixture of *Neem* (*Azadirachta indica*) and *Kikar* (*Acacia arabica*) leaves. In this study, the mixture of sizes 0.3 mm and 1.0 mm (1:1, 2:1 and 1:2) adsorbent were prepared by mixing the thermally activated *Neem* (*Azadirachta indica*) leaves carbon and thermally activated *Kikar* (*Acacia arabica*) leaves carbon, according to their efficiency for fluoride removal. Batch type experiment was carried out for the adsorption of fluoride using mixture adsorbent. In the batch study influence of pH, adsorbent dose and contact time were investigated. Adsorption of fluoride was pH dependent and was found to be maximum at pH 6. Fluoride removal increased with increased dose of carbon. The adsorption process obeyed Freundlich adsorption isotherm, Langergren's equation and intraparticle diffusion. Fluoride removal increased with decreasing particle size of carbon. In mixture, adsorbent ratio 2:1 had slightly higher capacity than the 1:1 and 1:2.

Keywords: Fluoride, Adsorption, Thermally activated carbon, *Azadirachta indica*, *Acacia arabica*

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Sustainability of good health of living organisms depends upon the quality of water. It is constantly in motion in the hydrological cycle. Because of its inherent dissolution capacity, water picks up minerals and salts present in the earth crust during the runoff and percolation processes. Fluorine, the most abundant element in the earth crust, dissolves and contributes to fluoride in the water. Fluoride in drinking water may be beneficial or detrimental depending on its concentration and total amount ingested. The chronic and toxic effects of excessive intake of fluoride are usually observed as dental fluorosis, skeletal abnormalities that range from stiffness and rheumatism to a permanent crippling skeletal rigidity. It is a recommended essential substance in water for building healthy teeth when present upto 1 mg/L. It is beneficial particularly to infants and young children (< eight year) for calcification of dental enamel when present upto the permissible range of 1.0-1.5 mg/L, as the maximum acceptable level in drinking water is 1.5 mg/L¹. Many natural drinking water sources contain excess of fluoride requiring defluoridation to prevent the occurrence of fluorosis². Fluoride gets leached into

ground water from the igneous or sedimentary rocks in the earth's crust. The effluent from chemical processing industries like aluminium processing, electroplating, phosphate fertilizer, glass etc constitute another source of fluoride in water. Fluoride is present in excess of its limits in many parts of India including Andhra Pradesh, Haryana, Gujarat, Karnataka and Rajasthan states.

When fluoride concentration of the drinking water exceeds 1.5 mg/L, the fluoride removal becomes a technical challenge. Several methods have been adopted to remove the excess fluoride from drinking water viz. precipitation with calcium and aluminium salt^{3,4}, adsorption by activated alumina^{5,6}, charcoal^{7,8}, geomaterials⁹⁻¹¹, ion-exchange resins¹² and activated carbon^{1,13,14} prepared from various low cost materials. Activated carbon prepared from various raw materials exhibits good capacity for removal of fluoride from drinking water. Defluoridation is practised in India, Nalgonda technique (named after the village in India where the method was pioneered) being most common. Nalgonda technique involves addition of aluminum salt, lime and bleaching powder followed by rapid mixing, flocculation, sedimentation, filtration

and disinfection. The lime dose required to be added is empirically $1/20^{\text{th}}$ that of dose of aluminium salt. Lime facilitates forming denser floc or rapid settling. Alum a coagulant commonly used for water treatment is used to flocculate fluoride ion in the water. This technique requires careful control of *pH*, failing which the coagulation process will not be complete resulting into high residual levels in the product water. The quantity of alum and lime depend upon the quantity, alkalinity, *pH* and fluoride content of water. The amount of alum needed increases with alkalinity or initial fluoride concentration. Nalgonda technique is suitable only when the dissolved solids are below 1500 mg/L, total hardness is below 250 mg/L, alkalinity of the water is sufficient and raw water fluoride ranging from 2 to 20 mg/L. It is in this context that the novel adsorbent used here will be useful.

The removal of excess fluoride from drinking water is an uphill task and the search for a powerful fluoride adsorbing material, which can be employed to develop a user friendly, economically and technologically viable defluoridating method, is still continued. In the present study, naturally occurring tree leaves of *Neem* and *Kikar* have been studied as possible adsorbents for fluoride from synthetic solutions. The main objectives of this work was to evaluate the effectiveness of mixture of activated carbon prepared from *Neem* and *Kikar* leaves in adsorbing fluoride along with adsorption kinetics.

Experimental Procedure

Preparation of activated carbon

The *Neem* and *Kikar* leaves were collected from the G.J. University campus, Hisar, India. 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 hour. The *Neem* and *Kikar* leaves were ground to obtain small pieces. After this, they were washed with 1% formaldehyde solution to remove the colour and then were dried in an oven maintained at a temperature range of 120-140°C for a period of 12 h. The dried material was ground and sieved through standard sieve (Sonar GSMS, Mumbai) to obtain particle of sizes up to 0.3 and 1.0 mm.

Preparation of mixtures of adsorbents

The mixtures of adsorbents were prepared by mixing the activated *Neem* leaves carbon and

activated *Kikar* leaves carbon according to their efficiency for fluoride removal. The adsorbent dose which removed maximum fluoride from synthetic solution was considered as the most efficient dose. For mixture adsorbent preparation *Neem* and *Kikar* leaves adsorbent were mixed in three ratios i.e. 1:1, 2:1 and 1:2. The mixtures adsorbents were tested for removal of fluoride by batch process.

Characterization of adsorbents

Various characteristics of prepared adsorbents were studied by adopting the standard procedures¹⁵. The important characteristics of activated carbon presented in Table 1 revealed that activated *Neem* carbon (ANC) was found basic whereas activated *Kikar* carbon (AKC) was found neutral. Electrical conductivity of ANC and AKC was 0.54 and 0.31 m mho respectively. The adsorbent sizes of ANC were 0.3 and 1.0 mm and their bulk density were found to be 0.27 and 0.15 g/cm³ respectively. Likewise, the adsorbent sizes of AKC were 0.3 and 1.0 mm and bulk density was found to be 0.37 and 0.22 g/cm³ respectively. Moisture content of adsorbent was found 6.9% for 0.3 mm size and 7.3% for 1.0 mm size. The moisture content was found 6.6% for 0.3 mm size and 7.5 for 1.0 mm size for AKC adsorbent. The particle density of ANC was noted 0.19 and 0.31 g/cm³ for 1.0 and 0.3 mm sizes respectively. It was 0.37 and 0.49 g/cm³ for AKC by 1.0 and 0.3 mm size respectively. The adsorbent solubility in acid was more than in water.

Batch studies

Batch adsorption tests were conducted to investigate the effect of controlling parameters like *pH*, adsorbent dosage, size of adsorbent and contact

(Parameters)	ANC		AKC	
	0.3 MM	1.0 MM	0.3 MM	1.0 MM
<i>pH</i>	9.3	9.3	7	7
EC m	0.54	0.54	0.31	0.31
mho/cm				
Bulk density g/cm ³	0.27	0.15	0.37	0.22
Particle density g/cm 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

time. All the experiments were conducted at room temperature of $27\pm 1^\circ\text{C}$. The 100 mL of the test fluoride solution (5 mg F/L) was taken in a reagent bottle.

After desired contact period, conical flasks were removed and adsorbents were allowed to settle down for two minutes. The solutions were filtered through Sonar Filter Paper No.1, then filtrate was analyzed according to the SPANDS method, as prescribed in Standard Method of Water and Waste Water Analysis¹⁶. The SPANDS method is based on reaction between fluoride and zirconium dye-lake and formation of colourless complex anion and the dye takes place. As the amount of fluoride increases, the colour produced becomes progressively lighter. Fluoride standard curve was prepared. SPANDS and zirconil acid reagent each 5.0 mL is mixed to each standard and spectrophotometer is set to zero observance with the reference solution. Absorbance is measured spectrophotometrically at 570 nm. Fluorides in water samples were determined with the help of the standard curve.

In batch process studies, pH, adsorbent dose, contact times were optimized on synthetic sample of fluoride. The effect of the initial concentration 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 conditions. The underground water samples were collected from hand pumps in colourless polythene bottles of 1 liter capacity. The bottles were rinsed out two or three times with water to be examined before being finally filled. In taking the sample from hand pumps, water was allowed to be wasted for few minutes before filling the container. The container was completely filled with water and after replacing the stopper/cap, sample were labeled and brought to the laboratory.

Results and Discussion

The characteristics of carbon reveal that the ANC possessed less bulk density and particle density than the AKC. The effect of pH, dosage of adsorbent and contact time, was studied in batch experiments. Fluoride removed 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, contact time was studied in batch experiments.

Effect of adsorbent dose

Fluoride uptake by mixture of ANC and AKC (1:1, 2:1 and 1:2) at different doses of 0.2 to 1.0 g particle sizes of 0.3 mm and 1.0 mm has been given in Fig. 1. The experiment was conducted at initial fluoride concentration of 5.0 ppm of the test solution, 1 h contact time, pH 6.0 and at ambient temperature. The results showed that increase in adsorbent dosage increased, the amount of fluoride removal. It was also found that as the particle size increased, there was decrease in defluoridation capacity. It was observed from the results that the fluoride removal by adsorbent mixture (ANC and AKC) in the ratio of 1:1, 2:1 and 1:2, increasing from 42.8 to 66.0%, 44.0 to 67.8% and 42.0 to 65.2% at 0.3 mm adsorbent size and fluoride removal was 42.8 to 53.2%, 30.8 to 55.2% and 27.2 to 49.2% at 1.0 mm size from 0.2 to 1.0 g/100 mL of mixture adsorbents dose.

As the particle size increased, surface area available per unit weight of the adsorbent decreased. Moreover, as the particle size increased the time required for migration of the sorbate into inner pores also increased and this might have resulted in longer time for equilibrium and a lower sorption capacity. More fluoride removal was observed due to the availability of more surface area with decrease in particle size which might be responsible for more fluoride removal¹⁴. It is also evident from the results that as adsorbent dose was increased, there was less commensurate increase in adsorption which might be due to lower adsorptive capacity utilization of sorbent and unit adsorption decrease significantly with increasing mass of sorbent per unit volume. This effect had been termed as "solid concentration effect" *i.e.* overcrowding of particles¹⁷.

Effect of contact time

Figure 2 exhibits the variation of fluoride removal from aqueous solution by adsorbent mixture (ANC and AKC) ratio of 1:1, 2:1 and 1:2 at sizes 0.3 mm

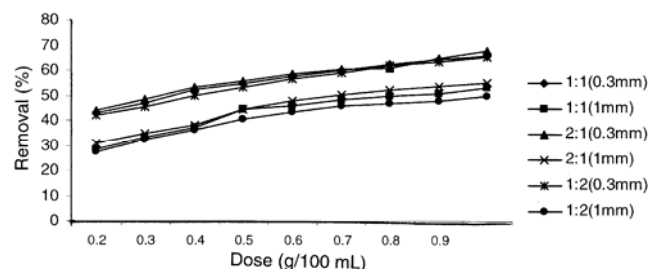


Fig. 1—Effect of dose on fluoride removal by mixtures (1:1, 2:1 and 1:2).

and 1.0 mm with respect to contact time. The study was conducted at initial fluoride concentration of 5.0 ppm, dose of adsorbent were taken as 0.5 g/100 mL, pH 6.0 for adsorbent mixture and contact time was varied from 15 to 120 min at ambient temperature. It has been revealed from the results that fluoride removal by adsorbent mixture of ANC and AKC in ratio of 1:1, 2:1 and 1:2 (size up to 0.3 mm) increased from 43.2 to 61.6%, 44.0 to 63.6% and 40.4 to 61.2% respectively, while it was 29.4 to 48.2%, 33.6 to 51.2% and 27.2 to 47.6% for 0.3 to 1.0 mm size adsorbent mixture at 15 to 120 min contact 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 stages¹⁸.

Effect of pH

Figure 3 shows the effect of pH on fluoride removal in the ratio of 1:1, 1:2 and 2:1 mixture of ANC and AKC adsorbents (0.3 and 1.0 mm sizes). The initial fluoride concentration was kept constant at 5.0 ppm, adsorbent dose was 0.5 g/100 mL while time duration was kept 1 h and pH was varied from 2 to 10. It is evident that fluoride removal reached at maximum level of 58.3, 58.6 and 53.2% at particle size of 0.3 mm at 1:1, 2:1 and 1:2 mixtures respectively, at pH 6.0. Likewise, maximum percent fluoride removal was 45.6, 45.8 and 40.4% at particle size of 1.0 mm at 1:1, 2:1 and 1:2 of mixtures respectively at pH 6.0. Initially it was observed, that, the percent fluoride removal increased as the pH increased from 2.0 to 6.0 then decreased above 6.0. Therefore, solution pH was maintained at 6.0 for further studies.

In the acidic pH range, the amount of fluoride adsorbed is slightly decreased and this can be attributed to the formation of weak hydrofluoric acid. HF is present below pH 5 at concentrations used in the experiments. In the alkaline pH range there is sharp drop in adsorption which may be due to the competition of the hydroxyl ions with the fluoride for adsorption¹⁰.

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. The four natural

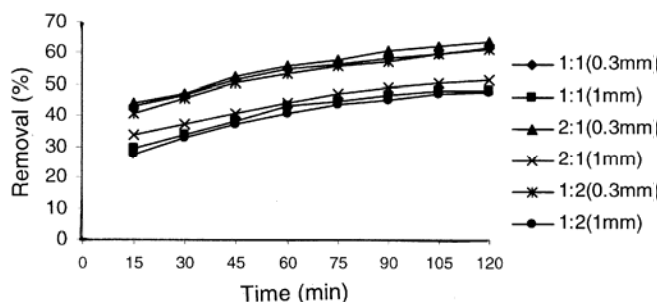


Fig. 2—Effect of time on fluoride removal by mixtures (1:1, 2:1 and 1:2).

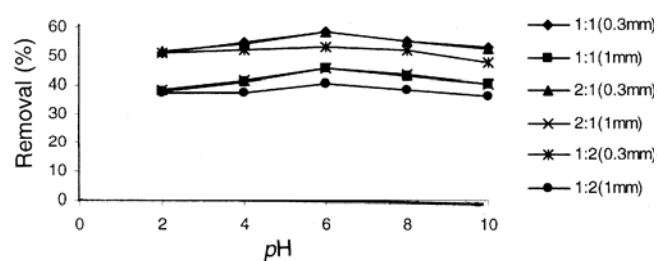


Fig. 3—Effect of pH on fluoride removal by mixtures (1:1, 2:1 and 1:2).

water samples having fluoride contents 1.18, 1.88, 2.60 and 4.70 mg/L were analyzed at 0.3 mm adsorbent size. In the first water sample the level of fluoride were decreased to 0.46, 0.47 and 0.44 mg/L in the adsorbent mixture with ratio of 1:1, 2:1, and 1:2 respectively. The second water sample showed the fluoride level 0.71, 0.73 and 0.69 mg/L in the adsorbent mixture with ratio of 1:1, 2:1, and 1:2 respectively. The third water sample showed the fluoride level 0.98, 1.0 and 0.96 mg/L in the adsorbent mixture with ratio of 1:1, 2:1, and 1:2 respectively. The fourth water sample showed the decrease in fluoride level to 2.16, 2.20 and 2.12 mg/L treated with the adsorbent mixture in the ratio of 1:1, 2:1, and 1:2 respectively.

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 isotherm¹⁹ (Eq. 1) and the model was applied to the adsorption equilibria for adsorbent mixture (ANC and AKC) in the ratio of 1:1, 2:1 and 1:2.

$$\log (x/m) = \log K_f + 1/n \log C_e \quad \dots (1)$$

where x is the amount adsorbed (mg), m is the weight of the adsorbent used (g), K_f is the Freundlich

constant related to sorption capacity and n is a constant related to energy or intensity of adsorption. This gives an expression encompassing the surface heterogeneity and the exponential distribution of active sites and their energies. This isotherm does not predict any saturation of adsorbent surface. The Freundlich exponents K_f and n can be determined from their linear plot of $\log(x/m)$ versus $\log C_e$ (Fig. 4). The results revealed that the adsorption of fluoride on adsorbent mixture (ANC and AKC) in ratio of 1:1, 2:1 and 1:2 under optimum conditions at room temperature ($27 \pm 1^\circ\text{C}$) also obeyed the Freundlich adsorption isotherm.

The value of K_f 1.03 (0.3 mm) and 2.38 (1.0 mm) for 1:1 (ANC and AKC) and 1.03 (0.3 mm) and 1.38 (1.0 mm) for 2:1 (ANC and AKC), and 1.04 (0.3 mm) and 4.56 (1.0 mm) for 1:2 (ANC and AKC), indicated greater affinity for fluoride and the $1/n$ values, 2.2 (0.3 mm) and 2.17 (1.0 mm) for 1:1 (ANC and AKC) and 2.19 (0.3 mm) and 2.16 (1.0 mm) for 2:1 (ANC and AKC), and 2.11 (0.3 mm) and 2.6 (1.0 mm) for 1:2 (ANC and AKC) respectively, showed the good adsorption character of the carbons (Table 2).

Langergren's studies

Langergren's equation²⁰ has been used to study the rate constant for adsorption of the fluoride by mixture adsorbents (ANC and AKC) in the ratio of 1:1, 2:1, and 1:2 of different sieve size of 0.3 mm and 1.0 mm.

$$\text{Log}(q_e - q) = \text{Log} q \frac{K}{2.303} t \quad \dots (2)$$

where q_e is 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 min), t = time (min). The straight line plots of $\log(q_e - q)$ versus time at ambient temperature, indicated the validity of langergren equation, consequently first order nature of the process is involved in the present study (Fig. 5). The value of K_{ad} at ambient temperature for adsorbent mixture (ANC and AKC) in the ratio of 1:1, 2:1 and 1:2 was calculated from the plots and is shown in Table 2.

Intraparticle diffusion studies

Results of intraparticle diffusion studies have been shown in Fig. 6. Rate constant for intraparticle diffusion were calculated from the slope of linear portion of respective plots. Linear plots confirm intraparticle diffusion effects²¹. The value of slope

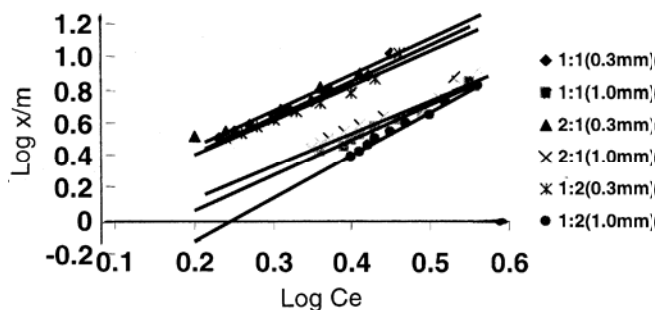


Fig. 4—Plot for Freundlich isotherm for the adsorption of fluoride by mixtures (1:1, 2:1 and 1:2).

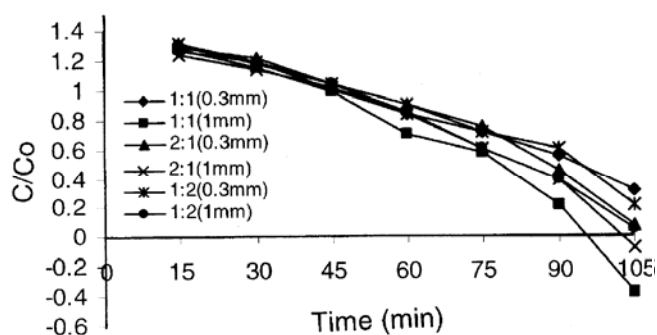


Fig. 5—Langergren plot for fluoride by mixtures (1:1, 2:1 and 1:2).

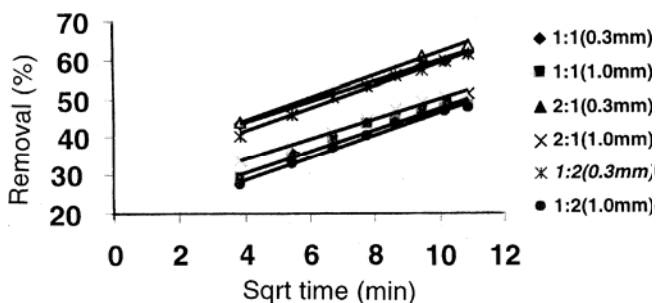


Fig. 6—Intraparticle diffusion plot for the adsorption of fluoride by mixtures (1:1, 2:1 and 1:2).

calculated for each curve are given in Table 2 and were found to be widely divergent from the value of 0.5, which corresponds to the intraparticle diffusion being the rate-determining step²². The divergence in values from 0.5 indicated that besides intraparticle diffusion there might be other processes controlling the rate which might be operating simultaneously.

Although, the most likely fluoride removal mechanism is adsorption, other mechanism such as absorption and precipitation may occur. Adsorption is the phenomenon whereby molecules adhere to a surface with which they come into contact due to

Table 2—Freundlich, Langergren and intraparticle diffusion rate constants for different adsorbents

Adsorbents	Freundlich rate constants				Langergren		Intraparticle diffusion	
	K_f		$1/n$		$K_{ad} - \text{min}$		$K_i < \text{min}$	
	0.3 mm	1.0 mm	0.3 mm	1.0 mm	0.3 mm	1.0 mm	0.3 mm	1.0 mm
1:1 (ANC & AKC)	1.03	2.38	2.2	2.17	-0.01	-0.017	3.38	2.81
2:1 (ANC & AKC)	1.03	1.38	2.19	2.16	-0.031	-0.014	2.92	2.65
1:2 (ANC & AKC)	1.04	4.56	2.11	2.6	-0.0115	-0.0138	2.04	2.97

forces of attraction at the surface. Adsorption is set to occur in three basic steps. These are film diffusion, pore diffusion and adhesion of the solute molecules to the carbon surfaces. The fact that activated carbon has an extremely large surface area per unit weight makes it an extremely efficient adsorptive material. The activation of carbon and its manufacture produces many pores within the particles and it is the vast area of the wall within these pores that accounts for most of the total surface area of the carbon. Activated carbon when contacted with water, removes the components selectively by a combination of adsorption of the less polar molecules, filtration of the large particles and partial deposition of colloidal materials on the exterior surface of the activated carbon. The extent of removal of fluoride by adsorption depends on the diffusion of the particle to the external surface of the carbon and diffusion within the porous adsorbent. For all types of adsorbents and background solutions, the optimum pH for fluoride removal was near neutral, thus the aquo and hydroxyl group on the surface of the adsorbents may be responsible for the adsorption of fluoride. The presence of other co-ions in the water decreases the fluoride adsorption²³.

Adsorption takes place on the surface as well as through intraparticle diffusion pattern of adsorbent material. SEM studies revealed the morphological characteristics of the untreated sorbents as well as changes in the treated sorbents. X-ray diffraction studies also confirmed the deposition of fluoride on the surface of activated carbon. FTIR studies showed the involvement of hydroxyl group present on the surface in the adsorption interaction²⁴.

Conclusion

Activated carbon prepared from mixture of *Neem* and *Kikar* leaves are capable of removing fluoride effectively in the synthetic and ground water. The study indicates that removal of fluoride from aqueous solution depends on 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 adsorbent mixture (ANC and AKC) in the ratio of 1:1, 2:1 and 1:2 followed Freundlich isotherm 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 adsorbent mixture (ANC and AKC) in the ratio of 1:1, 2:1 and 1:2 follow first order kinetics. Thermally activated adsorbent mixture (ANC and AKC) with ratio 2:1 is good adsorbent and 0.3 mm size is more efficient than 1.0 mm. Removal efficiency of studied adsorbents is found to be 2:1 (ANC and AKC) > 1:1 (ANC and AKC) > 1:2 (ANC and AKC)/g dose.

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