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Comparative Studies of Fluoride Removal from Groundwater by Calcium Carbonate, Activated Alumina and Activated *Punica granatum* Ash

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This study investigates the comparative feasibility of three low-cost adsorbents namely calcium carbonate, activated alumina and activated *Punica granatum* ash (APGA) for the removal of fluoride ions by adsorption from groundwater of Raebareli district of India. The effect of various process parameters like pH, contact time, adsorbent dose, *etc*. have been investigated by batch adsorption technique. Experimental results revealed that fluoride adsorption increases with increasing adsorbent dose. Fluoride adsorption increased with increasing contact time and reached equilibrium at 100 min for all the three adsorbents. The maximum fluoride adsorptions occurred at 4.7, 1.03 and 3.34 mg/g of calcium carbonate, activated alumina and activated *Punica granatum* ash, respectively. All the adsorption experimental data of calcium carbonate, activated alumina and activated *Punica granatum* ash were fitted well with the Langmuir isotherm and followed pseudo-second-order kinetics.

Keywords: Fluoride adsorption, *Punica granatum* ash, Calcium carbonate, Activated carbon, Langmuir isotherm.

INTRODUCTION

Fluoride contamination of groundwater is a serious problem of the whole world as ingestion of excess fluoride through contaminated groundwater causes fluorosis. High level of fluoride intake through drinking water causes dental caries, skeletal fluorosis and decreases growth and intelligence [1]. It is estimated that about 80 % of diseases in the world are attributed to poor quality of drinking water and fluoride contamination in drinking water is responsible for 65 % cases of endemic fluorosis [2]. The permissible level of fluoride in drinking water for general good health set by WHO is considered to be 1.5 mg/L [3]. It has been reported that geological and anthropogenic factors are mainly responsible for fluoride contamination in groundwater [4]. Physiological conditions of rock like decomposition, dissociation and subsequent dissolution along with long residence time may be the responsible factors for fluoride leaching [5]. Further, various anthropogenic factors such as industrialization, urbanization and improper use of water resources are the main cause for enhancing the fluoride content of ground water in the developing countries.

Various technologies such as precipitation [6], ion exchange [7], reverse osmosis [8], electro-dialysis [9] and adsorption [10] have been employed for fluoride removal from groundwater. Among these methods, adsorption is a common technique used for fluoride removal from aqueous solution due to its universal, inexpensive, easy handling and applicable for the removal of pollutants even at low concentration. Large numbers of adsorbents have been investigated for fluoride removal from water based on activated alumina [11], charcoal [12], alum sludge [13], calcite [14], chitosan beads [15], zeolite [16], activated carbon [17] and spent bleaching earth [18]. These adsorbents have shown a certain degree of fluoride adsorption capacities but some of them only can work at extreme pH range, which is not suitable in natural conditions [19].

There is a plethora of research for defluoridation process of groundwater based on calcium adsorbents. It is because of the fact that calcium possesses a strong affinity with fluoride. In addition, it has low cost and biocompatible with the human body [20]. It is reported by Yang *et al.* [14] that fluoride level in groundwater could be reduced *via* precipitation of fluoride as fluorite (CaF_2) in the presence of calcite ($CaCO_3$). Further, some other adsorbents such as limestone (LS) and aluminium hydroxide impregnated limestone (AILS) can also be used for removal of fluoride in batch mode. It has been observed experimentally that the maximum fluoride removal capacity of limestone (LS) and aluminium hydroxide impregnated limestone (AILS) is 43.10 and 84.03 mg/g, respectively [21]. Nath and

Dutta have critically reviewed the defluoridation capabilities of calcium containing materials [22]. Furthermore, there are some other calcium based adsorbents for defluoridation such as calcium hydroxyapatite (HAP), quick lime, slack lime, calcium chloride, limestone or calcium carbonate, calcium hydroxide, calcium phosphate, calcium nitrate, calcium sulfate, bleaching powder, plaster of Paris, cement paste, hydrated cement, *etc*. [22]. However, the materials mentioned above are always associated with certain advantages and disadvantages. A novel approach for defluoridation of water has been prelude [23]. In this method, it has been revealed that the addition of dilute phosphoric acid (PA) to the influent water before the limestone treatment renders the characteristic of defluoridation of water. Moreover, the consumed adsorbent can be easily regenerated by simple scrubbing and rinsing with lime or sodium hydroxide [23].

Activated alumina showed good adsorption characteristics during removal of fluoride from natural water [11]. Most of the available materials for defluoridation are expensive and technically non-feasible for rural areas. Activated alumina is known to be a very good adsorbent due to its high surface area, crystalline form and activation process [24]. However, the working of activated alumina is considerably effective at pH < 6 [25]. The fluoride adsorption capacity of activated alumina has been studied [26] under varying conditions.

In addition to calcium carbonate and activated alumina, activated carbon can also be used for the defluoridation purposes. Activated carbon has high percentage of fixed carbon and is widely known as activated charcoals. It is carbonaceous material that differs from elemental carbon and can be produced by the oxidation of entire carbon atoms [27]. It has been reported by Karthikeyan and Rajan [28] that activated carbon obtained by burning and carbonization of the Morringa indica bark entails appreciable efficacy of defluoridation. Alagumuthu *et al.* [29] have investigated the potentiality of zirconium impregnated cashew nut shell carbon and compared its performance with normal cashew nut shell carbon for fluoride removal from aqueous solutions. Further, Alagumuthu *et al.* [30] has examined the defluoridation capability of Cynodon dactylon and stated its appreciable performance.

There is plethora of research work comparing the performance of defluoridation technique of calcium carbonate, activated alumina and activated carbons. Yadava *et al.* [31] studied the removal of fluoride from aqueous solution and groundwater by three low-cost agricultural biomass based adsorbents; wheat straw (WSR), sawdust (SDR) and activated bagasse carbon (ABC) of sugarcane. Performance of these adsorbents was compared with commercially available activated carbon (CAC). Mondal *et al.* [32] compared easily available and low cost adsorbents like calcium carbonate, activated alumina and activated sugarcane ash with the aim of fluoride ion removal from aqueous environment.

Indeed, the perpetual fluoride content of groundwater is a major issue in the global arena and in India as well. In India, this problem is prevalent in many states such as Andhra Pradesh, Tamilnadu, Karnataka, Kerala, Rajasthan, Gujarat, Uttar Pradesh, Punjab, Orissa as well as Jammu and Kashmir [33]. It is pertinent to mention that many districts of Uttar Pradesh including Unnao, Agra, Mathura, Ghaziabad, Pratapgarh and Aligarh are facing the problem of inland salinity and excessive fluoride in groundwater [34,35].

Raebareli is a district of Uttar Pradesh state in India. The land area of this district is traversed by two rivers namely Ganga and Sai. The groundwater of this district is not safe because it is contaminated with fluoride, arsenic and coliform bacteria. The fluoride level in some of the villages of Raebareli District is as high as 4.2 mg/L and it implicates that the villagers are at high risk of developing severe, adverse health effects [36]. Arsenic content in groundwater of this district is also beyond the permissible limit (0.01 ppb) specified by WHO. Even few places of this district have arsenic contamination more than 0.05 ppb. The Homemade bio-sand filter is one of the options for the removal of fluoride, arsenic and coliform bacteria and this is also economical to construct, operate and maintain [37].

In this paper authors have compared the defluoridation capacity of calcium carbonate, activated alumina and activated carbon obtained from *Punica granatum* for Raebareli district. Perhaps, no such work has ever conducted in this district and this is the first endeavour of the authors in this pursuit.

EXPERIMENTAL

All the reagents used were of GR grade from E. Merck Ltd. (India). The specifications of the synthetic adsorbents are shown in Table-1.

TABLE-1
SPECIFICATIONS OF SYNTHETIC ADSORBENT

Calcium carbonate [Ref. 38]		Activated alumina (Al_2O_3) [Ref. 39]	
m.w. (g/mol)	100.09	m.w. (g/mol)	101.96
Assay ($CaCO_3$)	≥ 98.5 %	Content of $CaSO_4$	10.0 %
Solubility in HCl	≤ 0.05	pH of suspense	7.5
Particle size	150 µm	Particle size	150 µm
Maximum limit of impurities			
Chloride	≤ 0.05	Chloride	0.02
Sulphate	≤ 0.5	Iron	0.02
Lead	≤ 0.005		
Iron	≤ 0.05		

Preparation of activated *Punica granatum* ash (APGA): *Punica granatum* seed (powdered sample), common name, pomegranate was purchased from market. It was washed several times with double distilled water and dried up in sunlight. It was burned in muffle furnace at 773 K for 1 h. The ash was collected from the furnace and treated with 4 N HCl and 4 N NaOH. Ash was again washed with distilled water until the pH of the ash fell down to 7. The resultant product is considered as APGA. The composition of this adsorbent is shown in Table-2.

Batch study: Fluoride solution was prepared by dissolving 0.221 g of sodium fluoride in double distilled water and preparing a solution of 1 L. The solution contains 100 mg/L of fluoride. By diluting this solution with double distilled water, synthetic fluoride contaminated water solution was prepared. 100 mL fluoride solution was taken into conical flasks (250 mL) containing 0.8 g of different adsorbents *viz*. calcium carbonate, activated alumina and APGA. Adsorption experiments were carried out for the determination of pH, adsorbent dose varia-

TABLE-2
PHYSICO-CHEMICAL PROPERTIES OF ACTIVATED *Punica granatum* ASH (APGA) [Ref. 40]

Parameter	Value
Surface area	6.42 $m^2 g^{-1}$
Density	1.18 g cm^{-1}
Particle size	150 µm
Specific volume	0.92 $dm^3 kg^{-1}$
Moisture	25.76 % mass
Ash content	28.6 % mass

tion, equilibrium time and kinetics, selection of an isotherm, effect of temperature. The contents were kept at constant shaking at 600 rpm for 60 min in a temperature controlled magnetic stirrer at 298 K and the solids were separated through filtration. The solutions were collected for analysis and fluoride concentration in the solution was determined by using ion selective electrode. Each experiment was conducted three times and average values are reported.

The amount of fluoride adsorbed per unit adsorbent was calculated according to a mass balance on the fluoride concentration using eqn. 1:

$$q_e = \frac{(C_o - C_e)v}{m} \quad (1)$$

where v (L) is the volume of fluoride solution, C_o (mg/L) is the initial concentration of fluoride, C_e (mg/L) is the concentration of fluoride at equilibrium and m (g) is the dry weight of the adsorbent.

The percent removal (%) of fluoride was calculated using eqn. 2:

$$\text{Fluoride removal } (\%) = \frac{(C_o - C_e)}{C_o} \times 100 \quad (2)$$

RESULTS AND DISCUSSION

Effect of pH: The pH of solution has been recognized as one of the most important factors influencing the kinetic study of adsorption. Present results demonstrate that calcium carbonate, activated alumina and APGA removed 74, 70 and 73 % of fluoride at pH 2.0, respectively (Fig. 1). These results also suggest that with decrease in pH, the adsorption efficiency increases under these experimental conditions. At lower pH the surface of APGA may get positively charged, which enhances the negatively charged fluoride ion through electrostatic force of attraction. At higher pH values, the reduction of adsorption may be possible due to abundance of OH^- ions causing increased hindrance to diffusion of fluoride ions.

Effect of adsorbent dose: The effect of adsorbent dosage on adsorption of fluoride at pH 2 and contact time of 60 min for the considered adsorbents were studied. The results are presented as % fluoride adsorption *versus* function of adsorbent dosage in Fig. 2. Fluoride adsorption was studied with the variation of adsorbent dose from 0.1 to 3.0 g/L at fixed pH 2. From figure, it is clear that removal of fluoride increases with increasing adsorbent dose. However, initially the removal increased gradually with increasing adsorbent dose, but after certain dose (about 2.0 g/L) no increase in removal was observed. This may be due to aggregation among the available active

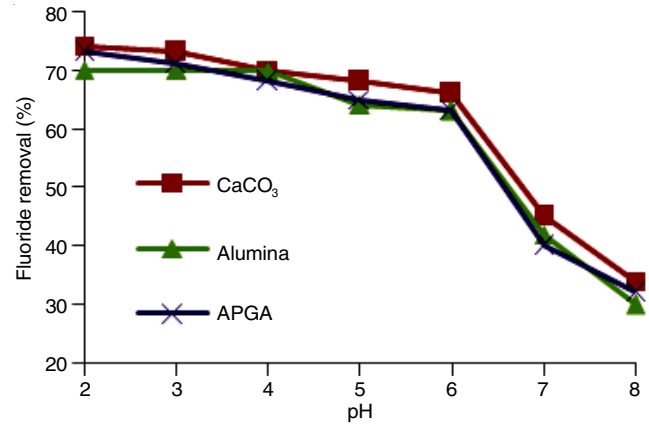

Fig. 1. Effect of pH on the removal of fluoride by three adsorbents

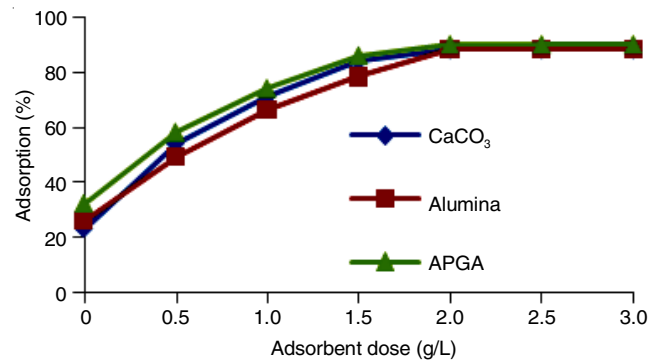

Fig. 2. Effect of adsorbent dose on the adsorption of fluoride by three adsorbents

binding sites, which may act for less adsorption of fluoride at higher doses.

Effect of contact time: The sorption of fluoride ion on calcium carbonate, activated alumina, APGA has been investigated as a function of contact time in the range of 20-120 min with 3 mg/L as initial fluoride concentration at room temperature. Fig. 3 illustrates the percentage of fluoride removal as a function of contact time in the range of 20-120 min at room temperature. As the contact time increased, the removal of fluoride increased rapidly, but after the time of 100 min, it gradually approached a constant value denoting attainment of equilibrium. At this contact time, maximum fluoride removals were found as 92.0, 88.0 and 93.0 % for calcium carbonate, alumina, APGA respectively (Fig. 3). The fast adsorption rate at the initial stage may be explained by the increase of availability in the number of active binding sites on the adsorbent surface.

Effect of initial fluoride concentration: Various initial fluoride concentrations (*i.e.*, 3.0, 5.0, 15.0, 20.0 and 25.0 mg/L) were tested in this study at the optimum pH, adsorbent dose and contact time. Fig. 4 presents the percentages of fluoride removal for calcium carbonate, activated alumina and APGA to be 92, 90, 92 % at 5 mg/L and 75, 72, 77 % at 25 mg/L, respectively. This is probably due to the fact that for a given adsorbent dose, the total available adsorption sites are limited; thereby adsorbing almost the same amount of fluoride.

Adsorption isotherm analysis: The isotherm models of Langmuir (1916) and Freundlich (1906) were used to fit the experimental adsorption equilibrium data of fluoride on different adsorbent. These models are represented mathematically as follows:

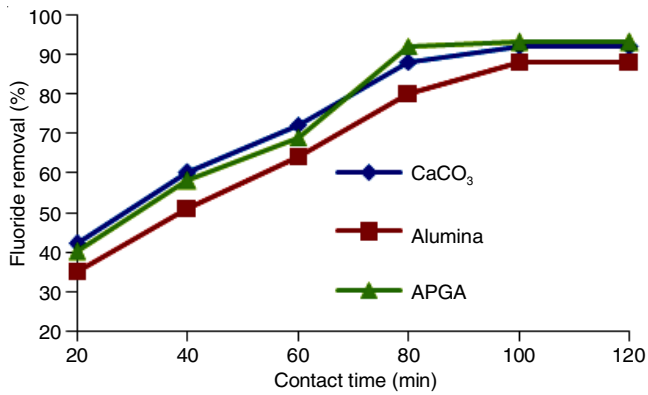

Fig. 3. Effect of contact time on the adsorption of fluoride by three adsorbents

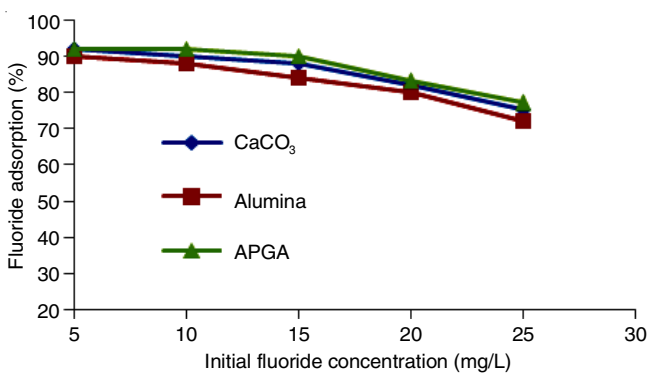

Fig. 4. Effect of initial fluoride concentration on the adsorption of fluoride by three adsorbents

Langmuir isotherm:

$$\frac{C_e}{q_e} = \frac{1}{q_m} C_e + \frac{1}{K_a q_m} \quad (3)$$

where C_e is the equilibrium concentration of adsorbate (mg/L), q_e denotes the amount of adsorbate (mg) adsorbed per gram of the adsorbent at equilibrium (mg/g), K_a is the Langmuir isotherm constant (L/mg) and q_m is the maximum adsorption capacity (mg/g) of the adsorbent.

Freundlich isotherm:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (4)$$

where K_f is the Freundlich isotherm constant $mg^{1-(1/n)} L^{1/n} g^{-1}$, n represents the adsorption intensity, C_e indicates the equilibrium concentration of adsorbate (mg/L) and q_e is the amount adsorbed per gram of the adsorbent at equilibrium (mg/g). As shown in Table-3, the Langmuir isotherm better fits the experimental equilibrium adsorption data than the other model for all the adsorbents. It was also seen from Table-3 that the Langmuir adsorption capacities (q_m) are 4.7, 1.03, 3.34 mg/g for calcium carbonate, activated alumina and APGA, respectively. These results imply that fluoride adsorption onto different adsorbents are homogeneous in nature. The Freundlich constant K_f and n value are also shown in Table-3. The value of n between 1 and 0 represents favourable adsorption.

Adsorption kinetic studies: Adsorption kinetics is one of the most important characteristics representing the adsorption efficiency. The adsorption rate of fluoride on the surface of the three adsorbents, as a function of time has been shown in Fig. 3.

TABLE-3
COMPARATIVE ANALYSES OF ISOTHERM MODEL PARAMETERS OF DIFFERENT ISOTHERM MODELS IN CASE OF DIFFERENT ADSORBENT

Isotherm model	Calcium carbonate	Activated alumina	APGA
Langmuir			
q_m	4.7	1.037	3.344
K_a	1.77	0.544	0.359
R^2	0.99	0.97	0.98
Freundlich			
K_f	3.20	0.5	0.893
1/n	0.18	0.23	0.588
R^2	0.96	0.88	0.959

The pseudo-first-order rate (Lagergren 1898) equation is represented by eqn. 5:

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (5)$$

where q_t and q_e are the amount of fluoride adsorbed (mg/g) at contact time t and at equilibrium respectively and k_1 is the pseudo-first-order rate constant (min^{-1}). The pseudo first- order rate constant k_1 and the equilibrium adsorption capacity q_e were determined from the slope and intercept of the plots of log (q_e-q_t) *versus* t and are listed in Table-4 along with the correlation coefficient (R^2).

TABLE-4
COMPARATIVE ANALYSIS OF KINETIC MODEL PARAMETERS IN CASE OF DIFFERENT ADSORBENT

Parameters	Calcium carbonate	Activated alumina	APGA
Pseudo-first-order			
K_1	0.018	0.02	0.021
q_e	0.08	0.06	0.06
R^2	0.22	0.19	0.12
Pseudo-second-order			
K_2	2.48	0.074	0.072
q_e	0.065	2.42	2.45
R^2	0.99	0.98	0.99

The pseudo-second-order kinetic model (eqn. 6) is the rate-determining step and can be expressed as:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e 2} + \frac{t}{q_e} \quad (6)$$

where k_2 is the rate of adsorption (g/mg/min), q_t is the amount of fluoride adsorbed at any time (mg/g) and q_e is equilibrium adsorption capacity (mg/g). The pseudo-second-order model constants were determined from the slope and intercept of the plot of t/q_t *versus* t. From the kinetic data in Table-4, a large difference between theoretical and experimental equilibrium adsorption capacity, q_e, indicates a poor fit of the pseudo-first-order equation to the experimental data for all three adsorbents. Furthermore, the calculated q_e values from pseudo second-order were found to be quite close to the experimental q_e values for all adsorbents. So, it was inferred that the adsorption of fluoride onto different adsorbents followed pseudo second-order kinetics.

Comparative analysis of bio-adsorbents: Comparison of various biomass based adsorbents is given in Table-5. Calcium

TABLE-5
COMPARISON OF THE DEFLUORIDATION CAPACITIES OF DIFFERENT BIOMASS BASED ADSORBENTS

Adsorbent	pH	Adsorption capacity (mg/g)	Ref.
Biomass carbon produced at 300 °C	5.8	0.52	[41]
Rice husk ash (RHA) with $Al(OH)_3$	5.0	9-10	[42]
Activated carbon derived from rice straw	2.0	15.90	[43]
Moringa indica based activated carbon	2.0	0.23	[28]
Cynodon dactylon-based activated carbon	7.0	4.617	[30]
Activated silica gel	-	0.244	[44]
Carbonized *Punica granatum* ash	-	1.68	[40]
Sugarcane charcoal	2.0	7.33	[45]
Activated bagasse carbon, sawdust raw, commercial activated carbon and wheat straw raw (WSR)	6.0	4.0	[31]
Calcium carbonate, activated alumina and activated sugarcane ash	2.0	2.0	[32]

carbonate, activated alumina and APGA used in this study showed Langmuir adsorption capacity of fluoride in the order of 4.7, 1.03 and 3.34 mg/g, respectively. Other adsorbents listed in Table-5 performed in different pH range and showed variable adsorption capacity. The performance of adsorbents used in this study may be further enhanced by different methods of adsorbent preparation.

Conclusions

In the present study, calcium carbonate, activated alumina and activated *Punica granatum* ash (APGA) were studied for removal of fluoride from groundwater sample. The conclusions drawn from this study are given below:

• The calcium carbonate, activated alumina and APGA removed 74, 70 and 73 % respectively from an aqueous solution of 5 mg/L fluoride at pH 2.0, with the contact time of 60 min and a dose of 0.8 g/L.

• Activated carbon from APGA showed intermediate fluoride adsorption capacity compared to calcium carbonate and activated alumina. However, APGA was well fitted Langmuir adsorption isotherms.

• Adsorption of fluoride on all studied adsorbents from aqueous solution followed pseudo-second order reaction and the mechanism of fluoride removal on adsorbents was found to be complex.

• A significant amount of fluoride can be adsorbed in the pH range of 2-6 by using these adsorbents, which makes them suitable for drinking purpose.

Activated *Punica granatum* ash can effectively remove fluoride, which makes it suitable for drinking water treatment, especially in rural areas where minimum facilities are available.

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