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Comparative Study of Powdered Activated Alumina with Granular Polymer-Agglomerated Alumina in Fluoride Removal from Drinking Water

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The characteristics of commercially available powdered activated alumina for defluoridation of drinking water in batch process have been investigated. The powdered form of activated alumina possesses enhanced defluoridation capacity compared to granular form but could not be used in column process as it is reported to cause pressure drop in column operations. To overcome this drawback powdered activated alumina was agglomerated with neutral and nontoxic polymer poly(vinyl acetate) to get the granular polymer-agglomerated alumina. Using synthetic fluoride solution the effect of pH, adsorbent dose, kinetics of adsorption process and adsorption isotherm for fluoride removal by granular polymer-agglomerated alumina were investigated in batch experiments and compared with that of powdered activated alumina. Column experiments were performed using granular polymer-agglomerated alumina to find out the effect of co-existing anions in water and the suitability of the adsorbent for repeated cycles after regeneration.

Key Words: Defluoridation, Granular polymer-agglomerated alumina, Powdered activated alumina, Isotherm, Kinetics.

INTRODUCTION

Widespread occurrence of fluoride above the prescribed limit in water meant for human consumption has caused detrimental effects on health[1]. The recommended limits of concentration of fluoride vary among countries. WHO[2] has set a limit range between 0.5 and 1 mg/L and Bureau of Indian standards[3] has prescribed a permissible limit of 0.6-1.2 mg/L. The methods reported for the removal of excess fluoride from drinking water include chemical treatment[4], ion exchange[5], electrodialysis[6], adsorption[7], membrane separations[8], electrolytic defluoridation[9] and Nalgonda technique[10].

Among various treatment methods available, defluoridation using granular activated alumina has been found to be effective[11]. Granular activated alumina of various grades ranging from 0.3-0.6 mm to 1-2 mm sizes were used for operational requirements.

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Attrition loss during repeated cycles after recharging has also been reported. It has been reported that it is difficult to prepare granular activated alumina of uniform size and shape with desired product density/crush strength[12]. During crushing and sieving of alumina to desired sizes, occurrence of wasteful high fine dust is common. The powdered activated alumina (PAA) possessed high internal active surface and exhibited increased fluoride removal capacity. However, the powdered material is not useful in column operations as it caused pressure drop and hence reduced the efficiency of treatment processes.

The increase in adsorption characteristics of powdered material can be profitably utilized if it could be converted into granular form by combining it with a neutral and non-toxic binding material without the loss of its adsorption characteristics and increasing its attritional characteristics.

In the present study, powdered activated alumina was agglomerated with poly(vinyl acetate) to granular form and its potential for the removal of fluoride from aqueous solution has been studied and compared with that of plain powdered activated alumina. The effect of pH, adsorbent dose, kinetics of adsorption and adsorption isotherm were also investigated in the batch studies and compared. The effect of other ions on fluoride removal by granular polymer-agglomerated alumina (GPAA) and regeneration of exhausted bed of GPAA using aluminum sulphate solution have also been investigated in column experiments.

EXPERIMENTAL

Defluoridation materials: Commercially available powdered activated alumina (acidic) of > 500 mesh size (S.D. Fine Chemicals Ltd.) was used for batch studies.

Granular polymer-agglomerated alumina (GPAA) was prepared by thoroughly mixing one part by weight of poly(vinyl acetate) in minimum quantity of acetone and 2.5 parts by weight of finely powdered activated alumina till a semi-solid mass was obtained. Large volume of water was poured into it in one lot with vigorous stirring. It was found that this approach was effective to cover the aluminium oxide powder by polymer. The agglomerated product was separated and pressed between two glass plates into a sheet of 2-3 mm thickness. The sheet was washed with water dried at room temperature overnight and then cut to 20-50 mesh size for detailed examination. The characteristics of the adsorbents are presented in Table-1.

TABLE-1
CHARACTERISTICS OF POWDERED ACTIVATED ALUMINA (PAA) AND GRANULAR POLYMER-AGGLOMERATED ALUMINA (GPAA)

Parameter	PAA	GPAA
Bulk density (g/cc)	0.97	0.53
Attrition loss (%)	1	5
Swelling (%)	5	111.78
pH	4.5	4.5
Particle size (mesh size)	>500	20-50

Fluoride stock solutions were prepared by dissolving 2.21 g of anhydrous sodium fluoride (99.0 % S.D. Fine Chemicals Ltd.) in 1000 mL distilled water in volumetric flask and all working solutions were prepared by appropriate dilution of stock solution with distilled water. The total ionic strength adjustment buffer (TISAB) was prepared according to a recommended procedure.

Fluoride ion was estimated by Orion Ion meter (EA 920 model). The method of direct potentiometry was used where the concentration can be read directly. The fluoride ion selective electrode was calibrated prior to each experiment in order to determine the slope and intercept of the electrode. The pH was measured with pH meter (Elico LI 120) using pH glass electrode. The meter was calibrated whenever the measurements were made using pH calibration buffers.

Batch studies: Batch adsorption experiments were carried out by shaking predetermined quantity of PAA and GPAA with 100 mL of aqueous fluoride solution of desired initial concentration taken in polythene bottles of 300 mL capacity. After equilibration in a mechanical shaker for predetermined period, the filtrate was analyzed for residual fluoride concentration.

To find out the effect of pH, experiments were carried out by varying the solution pH at initial fluoride concentration of 10 mg/L and adsorbent dose of 10 g/L. The effect of adsorbent dose was also studied by varying adsorbent doses (2, 4, 6, 8, 10, 12 and 14 g/L) at initial fluoride concentration of 10 mg/L and at optimum pH.

Equilibrium adsorption isotherm was drawn for fixed adsorbent dose and varying fluoride concentration from 10 to 80 mg/L for 24 h contact time, at pH 6.0. The kinetic studies were carried out using constant adsorbent dose of 2.0 g/L of PAA and GPAA for the initial fluoride concentrations of 10, 15 and 20 mg/L, respectively at optimum pH.

Column experiments: Column experiments were carried out using 1.5 cm dia. Teflon column packed with the materials under study, GPAA, to a predetermined height. Solutions containing 5 mg/L of fluoride adjusted to pH 7.5 were allowed to percolate through the column at known rates. Each lot of 1000 mL was separately collected and analyzed for fluoride content using Orion ion meter. Percolation of fluoride solution was stopped when the concentration of fluoride in the effluent exceeded the permissible limit of 1.2 mg/L.

RESULTS AND DISCUSSION

Effect of pH: The pH controls the adsorption at the water-adsorbent interfaces. Fig. 1 shows the effect of pH on the removal of fluoride by PAA and GPAA. It is evident that the removal was complete for both the adsorbents at pH 1.0. However it was found the removal of fluoride is around 98 % by both PAA and GPAA in the pH range 2 to 7. It is also observed that the fluoride removal was drastically reduced to 93 and 65 % at pH 8 and 9, respectively for both PAA and GPAA. The progressive decrease of fluoride uptake at pH greater than 7 is possibly due to the electrostatic repulsion of fluoride ion to the negatively charged surface and competition for active sites by excessive amount of hydroxyl ions[13]. There is no significant difference in the effect of pH on the removal of fluoride by PAA and GPAA. Hence, an optimum pH of 6 was maintained for further studies.

Effect of adsorbent dose: The removal of fluoride as a function of adsorbent dose is shown in Fig. 2. It is evident that the fluoride removal increased with increase in the adsorbent dose and for maximum removal of fluoride the minimum adsorbent dose was found to be 10 g/L for PAA and 14 g/L for GPAA.

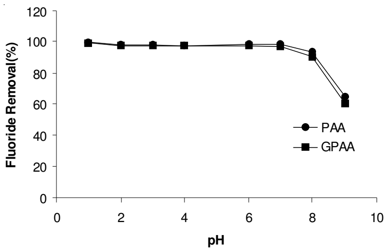

Fig. 1. Effect of pH

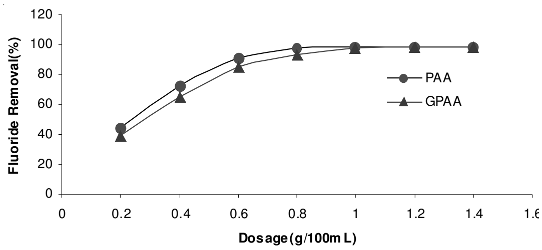

Fig. 2. Effect of adsorbent dose

Regeneration of adsorbents: Regeneration studies were tried with dilute HCl, H_2SO_4 and $Al_2(SO_4)_3$ solutions. Aluminium sulphate solution was found to be effective for complete regeneration of the adsorbents[14]. Regeneration studies were carried out using $Al_2(SO_4)_3$ solutions of concentration ranging from 0.05-5.00 %. From the study, it was concluded that both 1.0 g PAA and 1.4 g of GPAA regained their original fluoride removal capacity after regeneration with 100 mL of 0.25 % $Al_2(SO_4)_3$ solution.

Adsorption isotherm: Freundlich adsorption isotherm model is widely used[15]. The adsorption values plotted in Fig. 3 were calculated using the Freundlich equation:

$$\log(q_e) = \log K + \frac{1}{n}\log C_e \tag{1}$$

where q_e is the amount of fluoride adsorbed per unit weight of the adsorbent (mg/g), K the minimum sorption capacity (mg/g) and 1/n is the adsorption intensity. C_e is the equilibrium concentration of fluoride (mg/L).

The straight line nature of the graph indicates that the adsorption confirms to Freundlich adsorption model and they fitted with a correlation co-efficient greater than 0.97.

The values of 1/n and Freundlich constant K were respectively obtained from the slope and intercept of the plot between log q_e and log C_e (Fig. 3). These values are reported in Table-2.

The slope values were comparable suggesting that identical processes were occurring on the surfaces of both PAA and GPAA.

Kinetic study: It was found that for the fixed adsorbent dose the uptake of fluoride increased with respect to time. The adsorption of fluoride was rapid in the first 1.5 h after which the rate slowed down as the equilibrium approached.

TABLE-2
ADSORPTION ISOTHERM CONSTANTS FOR FLUORIDE ON PAA AND GPAA

	Freundlich constants		
	K (mg/g)	1/n	R^2
PAA	1.3362	0.1605	0.9843
GPAA	0.9326	0.1511	0.9763

The adsorption kinetic data of fluoride were first analyzed using the Lagergren first order rate equation[16]:

$$\log(q_e - q) = \log(q_e) - \frac{k_1}{2.303} \cdot t \tag{2}$$

where q_e and q are the amount of fluoride adsorbed (mg/g) at equilibrium and time t (min), respectively and k_1 is the Lagergren rate constant (min^{-1}).

The plots of log (q_e-q) *vs.* t are shown in Fig. 4 for GPAA and in Fig. 6 for PAA. The sorption data were further processed to find the rate constant k_1 and correlation co-efficient R^2 for Lagergren plots. The second order kinetic model[17] can be represented as:

$$\frac{t}{q} = \frac{1}{(k_2 q_e^2)} + \frac{t}{q_e} \tag{3}$$

where k_2 is the equilibrium rate constant (g mg^{-1} min^{-1}) of pseudo-second order adsorption, k_2, can be determined by plotting t/q against t of eqn. 3. Fig. 5 and 7 are the plots of pseudo second order kinetics for GPAA and PAA, respectively. The larger the k_2 value the slower the adsorption rate (1.94×10^{-2} for PAA and 3.0×10^{-3} for GPAA).

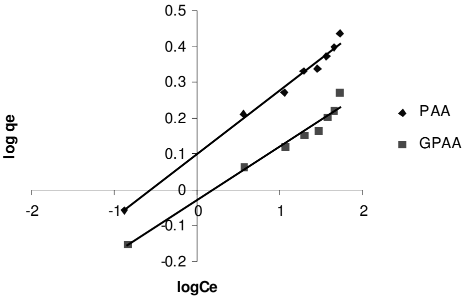

Fig. 3. Freundlich plot for adsorption of fluoride on both PAA and GPAA

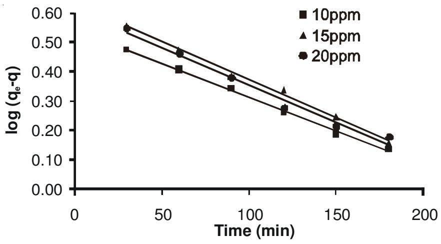

Fig. 4. Lagergren plot for adsorption of fluoride on GPAA at different initial concentration for the dose of 2 g/L

The adsorption rate k_2, the correlation co-efficient R^2 were found as near to unity for the different initial fluoride concentrations (Table-3). These values indicated favourable adsorption and the results show that the adsorption were in the second-order reaction. A similar phenomenon has been observed for removal of fluoride using alum residue as an adsorbent[13].

TABLE-3
COMPARISON OF CORRELATION COEFFICIENT FOR THE FIRST AND SECOND ORDER ADSORPTION

R^2	PAA		GPAA	
	1st	2nd	1st	2nd
10 ppm	0.9575	0.9961	0.9749	0.9990
15 ppm	0.9805	0.9986	0.9737	0.9957
20 ppm	0.9882	0.9948	0.9504	0.9982

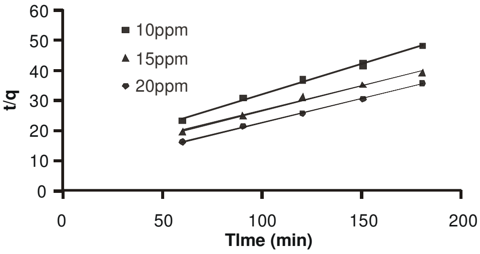

Fig. 5. Plots of the pseudo-second-order kinetics for GPAA at different initial concentration for the dose of 2 g/L

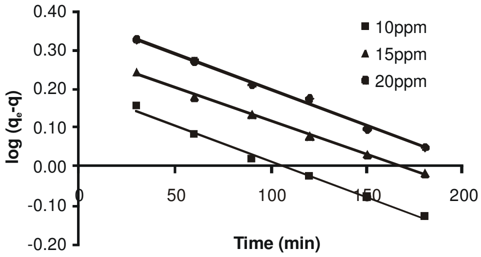

Fig. 6. Lagergren plot for adsorption of fluoride on PAA at different initial concentration for the dose of 2 g/L

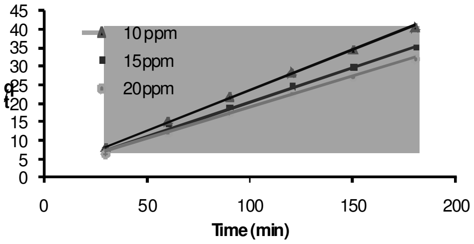

Fig. 7. Plots of the pseudo-second-order kinetics for PAA at different initial concentration for the dose of 2 g/L

Column studies: Column studies were conducted using 20-50 mesh polymer-agglomerated activated alumina only, as the 500 mesh plain powdered activated alumina developed pressure drop in the course of column experiments. As the fluoride concentration of untreated drinking water usually lies below 5 mg/L and pH remaining in the range of 6.5 to 8.5, it was decided to maintain the fluoride concentration of the influent solution at the maximum level of 5 mg/L and pH at 7.5.

Influence of flow rate: In order to find out the optimum flow rate, the fluoride solutions were allowed to flow through the column of constant bed height 25 cm (20 g) at separate flow rates from 7, 10, 12 and 15 mL/min. The effluent was analyzed until breakthrough has occurred and the capacity of GPAA in each instance was established. The results indicate that the capacity of GPAA remained almost constant for flow rates upto 12 mL/min. At higher flow rates there was a rapid fall in the capacity of GPAA for fluoride. Therefore, in all subsequent experiments, a flow rate of 10 mL/min was employed.

Influence of bed height: In order to find out the optimum bed height for maximum removal of fluoride, experiments were conducted using varying amount of GPAA under study over the range of 15 g (19 cm), 20 g (25 cm), 25 g (31 cm) and 30 g (37 cm) at the flow rate of 10 mL/min. After breakthrough has occurred the capacity of GPAA was established. The capacity for unit weight of GPAA remained almost constant for the heights above 25 cm. Hence, an optimum bed height of 31 cm was maintained for further experiments.

It was established that under the optimum conditions of flow rate 10 mL/min and bed height 31 cm (25 g) GPAA is capable of removing 52.84 mg of fluoride. Therefore the capacity can be reported as 1.948 mg of F^-/g of GPAA.

Regeneration studies: Regeneration of the column was done by percolating sufficient volume of 0.25 % solution of aluminium sulphate through the saturated bed of GPAA. The volume of aluminium sulphate solution used was measured in terms of number of bed volumes. Since the fluoride removal from the GPAA bed was a slow process, after washing the exhausted column with three bed volumes of aluminium sulphate solution at a flow rate of 5 mL/min, one bed volume of aluminium sulphate solution was left in contact with GPAA for 12 h. The solution was then drained out and the column was washed thoroughly with water to render it free from aluminium(III). The capacity of the regenerated GPAA was established after conducting the defluoridation experiments under optimum conditions. It was established that regeneration was completed. The cyclic defluoridation and subsequent regeneration experiments indicated that the potential usefulness of the GPAA for nearly 8 cycles without significant loss of sorption capacity. After 8 cycles, the GPAA was withdrawn from the column, washed and air dried and weighed to find out the loss of the adsorbent. It was established that there was no significant loss of the adsorbent.

Effect of co-existing anions: The effect of co-existing anions (Cl^-, SO_4^{2-} and HCO_3^-) on fluoride adsorption efficiency of the adsorbent was also studied using column experiments with fluoride solution of 5 mg/L by varying anions concentration from 100 to 500 mg/L. The selection of the anion concentrations was based on their availability in ground water used for drinking purposes.

The presence of HCO_3^- at higher concentration (100-300 mg/L)[18] was found to decrease the fluoride removal efficiency while other anions (Cl^- and SO_4^{2-}) have no significant effect within the concentration range tested.

Conclusion

PAA and GPAA were found to be a suitable adsorbent for the removal of fluoride from water. The adsorption was strongly dependent on pH and adsorbent dose. A maximum of about 98 % fluoride removal could be achieved at pH 6 for both PAA and GPAA.

Defluoridation by batch-studies showed that 1.0 g of PAA and 1.4 g of GPAA are the optimum quantities required for the removal of over 98 % of fluoride from 100 mL of 10 mg/L fluoride solution.It is evident that 1.4 g of GPAA contains 1.0 g of powdered activated alumina and no loss in adsorption capacity is observed due to agglomeration of powdered activated alumina by the polymer polyvinyl acetate.

Adsorption of fluoride is fairly rapid in first 20 min and increased slowly to reach the equilibrium in *ca.* 1 h for both the PAA and GPAA. The calculated average equilibrium rate constant k_2 for the adsorbent GPAA is smaller than that of PAA indicating that the adsorption may be slightly faster in the case of GPAA. The adsorption process followed pseudo second order reaction. The regression analysis of equilibrium data fitted into Freundlich adsorption isotherm. The adsorbents fluoride removal efficiency was affected significantly by bicarbonate ion and the effect was little with sulphate ion and there was no effect with chlorides. Column studies indicated practical utility of GPAA for the removal of fluoride. This advantage is not available with PAA. For an optimum bed height of 31 cm in 1.5 cm dia column and flow rate of 10 mL/min the capacity was 1.948 mg of F^-/g of GPAA. Regeneration studies revealed that exhausted GPAA may be regenerated and used for nearly 8 cycles without significant loss of sorption capacity indicating that GPAA possesses good attritional characteristics.

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