



# Removal of fluoride from drinking water using aluminum hydroxide coated rice husk ash

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## ABSTRACT

Fluoride content in groundwater that is greater than the WHO limit of 1.5 mg/L, causes dental and skeletal fluorosis. In India, several states are affected with excess fluoride in groundwater. The problem is aggravated due to the lack of appropriate and user friendly defluoridation technology. Several fluoride removal techniques are reported in the literature amongst which the Nalgonda technique and use of activated alumina have been studied extensively. However a simple, efficient and cost effective technology is not available for widespread use in many affected regions. In this paper, we present a novel cost effective defluoridation method that is based on surface modification of rice husk ash (RHA) by coating aluminum hydroxide. RHA is obtained by burning rice/paddy husk which is an abundantly available and is an inexpensive raw material. The results showed excellent fluoride removal efficiency and the adsorption capacity was found to be between 9 and 10 mg/g.

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## 1. Introduction

The prolonged intake of high concentrations of fluoride (more than 1.5 mg/L) in drinking water causes serious health problems such as dental and skeletal fluorosis. The physiological effects of fluoride ingestion on human health have been extensively studied. The acceptable fluoride concentration in drinking water is generally in the range of 0.5–1.5 mg/L (ppm). The presence of fluoride concentrations higher than this in the drinking water affects the metabolism of elements such as calcium and phosphorus within the human body. These elevated levels can lead to dental and skeletal fluorosis. In affected areas, the fluoride content of soils varies from less than 20 mg/L to an occasionally high level of 3000 mg/L [1,2]. Fluoride is present in soil and rock formations in the form of fluorapatite, fluorspar, amphiboles and micas [1–4]. The fluoride present in these soil/rock/minerals is substituted by (OH<sup>-</sup>) ions under redox conditions, resulting in the release of fluoride ions to the circulating water. In groundwater, the natural concentration of fluoride depends on the geological, chemical and physical characteristics of the aquifer, the porosity and acidity of the soil and rocks, the temperature, the action of other chemical elements, and the depth of well. Due to the large number of variables, the fluoride concentration in groundwater can range from well under 1 mg/L to more than 35 mg/L [5]. High fluoride concentrations are expected in ground water from calcium-poor aquifers and in areas

where fluoride-bearing minerals are common. Fluoride concentrations may also increase in ground water in which cation exchange of sodium for calcium occurs [5].

Fluorosis endemic is prevalent in at least 25 countries across the globe and 62 million people are affected with fluorosis in the world [6]. In China, endemic fluorosis has been reported in all 28 provinces, autonomous regions and municipalities except Shanghai. Both shallow and deeper ground water are affected; in general the deeper groundwater has the higher concentrations. In Sri Lanka, Dissanayake [7] found concentrations of fluoride ions up to 10 mg/L in ground water in the dry zone. India is one of the worst affected countries due to presence of excess fluoride in underground water. In India, 19 states have been reported with high levels of fluoride in drinking water [8]. Over 6 million children in India are affected with dental, skeletal and non-skeletal fluorosis [9,10]. Recent national figures can be obtained from various compendia of environmental and water supply statistics [11]. In many parts of rural India, the ground water (with high fluoride concentrations) remains the main source of drinking water.

The fluoride content in ground water tends to increase due to heavy withdrawal of water for agriculture purpose, poor recharging, low rainfalls and pollution from industrial effluents. India has declared fluorosis as an epidemic and has banned the use of water for drinking and cooking if the fluoride content is more than 1.5 mg/L. Latest guidelines from the Bureau of Indian Standards (BIS) suggest [12] that the fluoride limit in ground water used for drinking and cooking purposes should not be greater than 1 mg/L.

Fluorosis can be prevented by the removal of excess fluoride from drinking water by chemical treatment which is a difficult task and requires favorable socio-economical conditions of knowledge,

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motivation, prioritization, technical and organizational set-ups. Most of these methods are based on principles of precipitation, such as the use of lime softening, alum-lime addition and adsorption/ion exchange methods using materials such as activated alumina, bone char, synthetic calcium hydroxyl apatite and bauxite. In addition ion exchange, electro dialysis and reverse osmosis techniques have also been attempted to remove fluoride. However, due to lack of favorable conditions (like low fluoride removal capacity, high treatment cost, lack of user friendly technologies and government initiatives etc), many initiatives on defluoridation of water have resulted in failures and frustrations listed by Heidweiller [13]. Therefore, in any attempt to mitigate the fluoride problem for an affected community, the provision of safe low fluoride water from alternative sources (like surface water) must be investigated as the first option and then defluoridation methods should be investigated. This depends on the materials and methods used in defluoridation. Some of the attributes desirable in the standard defluoridation devices are (i) modest investment, (ii) low maintenance cost, (iii) simple design, (iv) easy to operate methodologies (v) ability to reduce fluoride content, e.g. from 5 to 0.5 mg/L, (vi) improved water quality in general and (vii) ingredients maintainable for acceptable period [13].

One of the simplest and most efficient methods for the defluoridation of drinking water is the use of aluminum sulfate. The hydrolysis of aluminum sulfate in an alkaline medium produces polyhydroxy alumino precipitate which complexes with fluoride ions. The most common and widely used precipitation method is the Nalgonda technique [14,15]. In this method, alum (aluminum sulfate) and lime are added to form a precipitate of fluoride-aluminum complex which is separated to produce fluoride of less than 1.5 mg/L in the treated water. Another commonly used and well studied adsorption method is based on activated alumina [16,17]. In activated alumina adsorption method, the fluoride adsorbs on active sites present on the surface of alumina. Another method which combines the chemical treatment (using sodium dihydrogen phosphate and calcium chloride) and adsorption (using fish bone charcoal) method known as contact precipitation has also been reported by Dahi et al. [18].

Since, adsorption was found to be one of the preferred methods for the remediation of fluoride, over the years considerable attention has been devoted to the development of better adsorbents. Defluoridation by adsorption process is the cheapest, simplest, easy to implement for a developing country like India [19]. Materials like coconut shell carbon [20], activated carbon [21–23], activated alumina [24,25], bone char [26], ion exchange resins [27], zeolites [28], manganese dioxide-coated activated alumina [29] and hydrous alumina [30] have been used as adsorbents. In addition various low cost materials as adsorbents for fluoride removal have been studied by Srimurlai et al. [31]. Activated carbon prepared from various raw materials exhibits good adsorption capacity for the removal of fluoride from drinking water [31].

The above discussed methods have disadvantages such as high treatment cost, limited efficiency, unnoticeable breakthrough and disposal of sludge. Due to these disadvantages, most of the existing defluoridation methods turn out to be unsustainable under the given socio-economical and practical conditions. To the best of our knowledge, not a single defluoridation device (based on the precipitation or adsorption techniques) under working condition are reported in India [13,32,33]. Hence there is a need of simple, efficient, free from residual aluminum and cost effective defluoridation device.

In this paper we report a novel and inexpensive patented technique [34] based on aluminum hydroxide (AH) coating on the rice husk ash (RHA) surface. This work is aimed at overcoming some of the typical problems associated with regular defluoridation techniques as discussed above. It is well known that most of

the defluoridation techniques involve the use of aluminum compounds because of the similarities of the charges of the fluoride ( $F^-$ ) ions with that of hydroxyl ions ( $OH^-$ ) and the ease of replacement of the  $F^-$  ions with that of  $OH^-$  ions to form fluoride aluminum hydroxide complex. RHA has been used as a filtration medium for the removal of bacteria and suspended particles [35]. RHA has typically a crystalline-amorphous porous structure with a high surface area in the range of 70–100  $m^2/g$ . It contains 85–95% silica, 4–12% carbon and the remainder residues are metal oxides. The bulk density of RHA is 0.25–0.3  $g/cm^3$  and its water holding capacity is twice that of its weight. These properties make RHA a good filter material. Taking advantage of the efficient filtering characteristics of RHA, water purifiers were fabricated using a mixture of RHA, pebbles and ordinary Portland cement. The pebble matrix – RHA filter provides a zigzag path for the water to flow and hence trap the bacteria present in drinking water [35].

In the present work, we have utilized the filtering characteristics of RHA by coating aluminum hydroxide on RHA substrate to obtain a composite material. This novel composite material was used for the removal of fluoride ions from drinking water. There have been studies reported in the literature for the removal of fluoride and arsenic from water using metal hydroxides coated sand, but these metal hydroxides coated sand are limited with low adsorption capacity [36]. This limitation was overcome by replacing sand with RHA. The use of RHA as substrate for coating of metal hydroxides has distinct advantages over sand as RHA is 9–10 times lighter and its specific surface area 20–30 times higher than that of sand. Besides this RHA is an inexpensive raw material obtained by burning rice/paddy husk, which is available abundantly in tropical countries like India and China. The AH coated RHA has bulk properties of the RHA and the surface properties of aluminum hydroxide. This makes the perfect combination of a filtering media with an excellent fluoride adsorbing composite material. The process of AH coating on RHA surface was optimized as a function of various process parameters to obtain best fluoride removing capacity. The resultant adsorbent material showed superior fluoride removal capacity compared to other adsorbents such as activated alumina [33], bone charcoal [26] and activated charcoal [24].

Furthermore, in the present work, removal of fluoride ions using AH coated RHA was studied in batch systems and continuous operations. The performance of the fluoride removal column was investigated as a function of the flow rate of the fluoride spiked tap water, initial fluoride concentration and amount of adsorbent.

## 2. Experimental

### 2.1. Chemicals and materials

All chemical reagents used in this work were of analytical grade (AR). Aluminum sulfate [ $Al_2(SO_4)_3 \cdot 16H_2O$ ], sodium hydroxide (NaOH), aluminum hydroxide [ $Al(OH)_3$ ] and sodium fluoride (NaF) were purchased from Sigma–Aldrich Chemicals, India.

Rice husk ash was produced by burning rice husks in a step grate furnace with tube-in-basket (TiB) burner, or obtained from boilers and brick kiln etc. The ash was free of unburnt husk and wood tars, grit, stones and fused lumps of silica. The RHA was sieved through 425  $\mu m$  size sieve, washed with dilute hydrochloric acid and washed several times with water.

### 2.2. Method of coating of aluminum hydroxide on RHA

The process flow chart (Fig. 1) shows the use of a stirred tank reactor with stirrer, a vacuum/pressure filter and oven/drier. 500 mL of 0.6 M aluminum salt solution is first added to the stirred reactor tank, followed by slow addition of 100 g RHA to the stirred

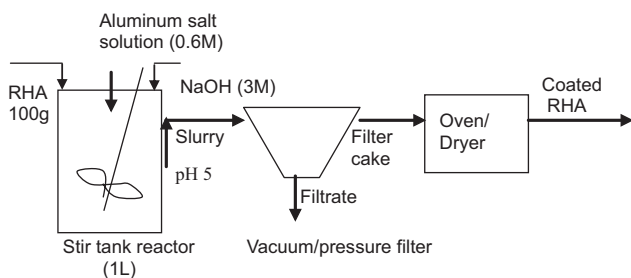


Fig. 1. Process flow sheet of aluminum hydroxide coating on RHA.

reactor tank with proper mixing to ensure the complete soaking of RHA in aluminum sulfate solution. Thereafter, sodium hydroxide solution (five times the concentration of the aluminum sulfate) is slowly added to the reactor while stirring at 180–200 rpm. Sodium hydroxide reacts with aluminum sulfate to produce precipitate of aluminum hydroxide, which gets deposited on RHA surface. The addition of the sodium hydroxide is controlled by pH; once the pH of the reaction mixture reaches the desired value of 5–7, the sodium hydroxide addition is stopped. The resultant slurry mixture consists of aluminum hydroxide coated RHA and sodium salt. This slurry is filtered using a vacuum or pressure filter to produce a filter cake of aluminum hydroxide (AH) coated RHA. This filter cake is then dried in the oven at 110 °C to get the aluminum hydroxide coated RHA. For further experiments, the coated RHA is washed thoroughly with distilled water to remove sodium sulfate salt. The washing is done till the output water shows less than 1 mg/L of sulfate ions. Then washed AH coated RHA is again dried in an oven at 100 °C for 3–4 h. This washed and dried AH coated RHA is characterized and used for the column and adsorption studies.

### 2.3. Characterization of RHA and AH coated RHA

The particle size of RHA and AH coated RHA were determined using a laser particle size analyzer (Horiba LA-910<sup>®</sup>, Japan). X-ray powder diffractometer (XRD, PANalytical<sup>®</sup>, Netherlands) was used to analyze the phases/structures of RHA and AH coated RHA. The scanning rate was 10°/min in the 2 $\theta$  diffraction angle between 10° and 80°. The specific surface areas of adsorbents were determined by the BET method with N<sub>2</sub> gas (Micromeritics<sup>®</sup>, Norcross, GA). Chemical analysis of RHA and AH coated RHA was carried out using standard methods.

### 2.4. Fluoride measurements

Fluoride measurements were conducted using the Orion<sup>®</sup> selective ion electrode. The fluoride electrode was calibrated for 1, 10, 100 mg/L fluoride solutions using the total ionic strength absorbing buffer (TISAB). TISAB is prepared by dissolving 4 g CDTA (cyclohexylene dinitrilo tetra acetate), 58 g sodium chloride and 57 mL glacial acetic acid in about 500 mL of distilled water, and pH adjusted to 5.5 by adding 5 M NaOH and diluted to 1 L with distilled water. The calibrated electrode was used for measuring fluoride concentrations of all water samples.

### 2.5. Column studies

A column made of polyethylene (35 mm diameter and 200 mm height) was used for evaluating the performance of the aluminum hydroxide coated RHA adsorbent for the removal of fluoride from water. The column consisted of several layers of different materials as shown in Fig. 2. About 20 g of washed and dried AH coated RHA is placed in between bottom and top layer of sand (Fig. 2). The bottom and top sand layers provide support to AH coated RHA. Tap

water spiked with a known fluoride concentration is prepared and stored in the reservoir and then passed through column containing aluminum hydroxide coated RHA. The filtered water drawn from the bottom the column is collected in a storage vessel at regular intervals (Fig. 2). The water flow rate flowing through the column is regulated by a stop cock.

### 2.6. Adsorption studies

The adsorption isotherm experiments were conducted with initial fluoride concentrations in range of 10–60 mg/L using batch procedure at 27 ± 1 °C. 0.1 g of AH coated RHA (washed and dried) was added to 100 mL of fluoride solution of known initial fluoride concentration (10–60 mg/L). The pH value of the initial fluoride solution was adjusted to about 7 ± 0.2 with acid/base. All of the equilibrium experiments were carried out at 27 ± 1 °C in waterbath with stirring for 1 h. After 1 h, 10 mL reaction mixture was withdrawn by a micropipette and analyzed for residual fluoride ions.

The time-dependent adsorption reactions were conducted by agitating the reaction mixture at 100 rpm that was placed in shaker with water bath at 27 ± 1 °C. Herein, 0.5 g of AH coated RHA was thoroughly mixed with 500 mL of a fluoride solution with fixed initial fluoride concentrations (10 and 20 mg/L). At a fixed pre-selected time interval from 0.1 to 210 min, 5 mL reaction mixture was withdrawn by a micropipette and analyzed for residual fluoride.

## 3. Results and discussion

Several parameters were found to affect the capacity and performance of the AH coated RHA for fluoride removal. For example, the concentration of aluminum salt and the pH of the reaction mixture slurry were found to be directly influencing the coating process. The effect of flow rate and the input fluoride concentration on the fluoride removal efficiency were also evaluated. These are discussed in this section.

### 3.1. Characterization of RHA and AH coated RHA

The specific (BET) surface areas of RHA and AH coated RHA are determined to be 62.8 m<sup>2</sup>/g and 50.4 m<sup>2</sup>/g, respectively. As

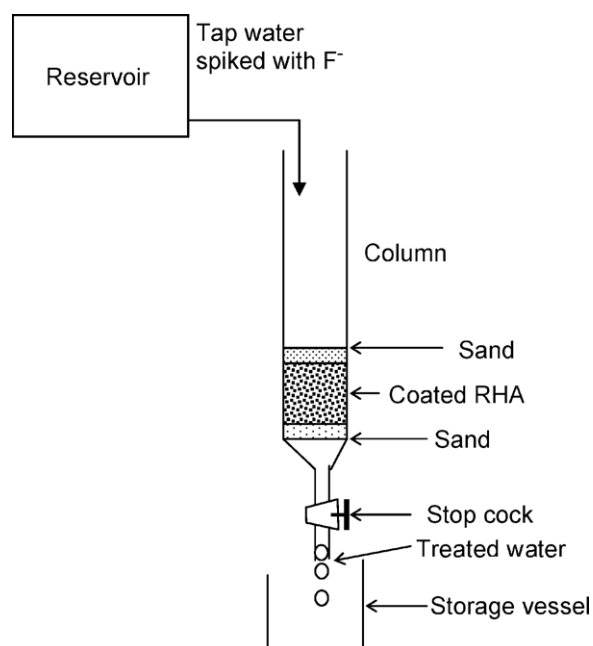


Fig. 2. Schematic of column experiments for fluoride removal.

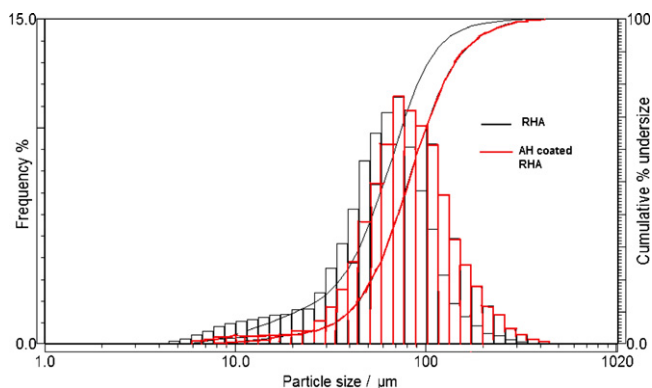


Fig. 3. Particle size distribution of RHA and AH coated RHA.

expected, there is a lowering of the specific surface area of AH coated RHA compared to the uncoated RHA. The bulk density of RHA is  $0.24 \text{ g/cm}^3$  which increased to  $0.33 \text{ g/cm}^3$  for AH coated RHA due to coating of aluminum hydroxide on RHA surface.

The particle size distribution for RHA and AH coated RHA is shown in Fig. 3. The particle sizes are in the range of 5–400  $\mu\text{m}$ . The results show that for the AH coated RHA the mean particle size is 108  $\mu\text{m}$  compared to 92  $\mu\text{m}$  obtained for the uncoated RHA sample. Increase in particle size due to coating of AH on RHA surface is however expected.

XRD diffractograms of RHA and AH coated RHA (Fig. 4) showed strong broad peaks between  $22^\circ$  and  $27^\circ$  ( $2\theta$ ). These strong broad peaks are characteristic of amorphous silica ( $\text{SiO}_2$ ) for RHA and amorphous aluminosilicates ( $\text{Al}_2\text{O}_3\text{--SiO}_2$ ) for AH coated RHA. No specific peak of alumina ( $\text{Al}_2\text{O}_3$ ) is observed for AH coated RHA. This confirms that the amorphous aluminum hydroxide is coated on RHA.

The chemical analysis of AH coated RHA and RHA are presented in Table 1. The silica content of AH coated RHA was found to be 60% as compared to 85% of RHA, alumina and moisture content of AH coated RHA was found to increase from 0.2% to 21% and 0.9% to 9%, respectively. This shows that around 35–40% of  $\text{Al}(\text{OH})_3$  (AH) is coated on the RHA surface.

### 3.2. Effect of aluminum concentration for coating of AH on RHA

To investigate the role of aluminum sulfate concentration in the coating process and its subsequent efficacy, the initial aluminum sulfate concentrations were varied from 0.1 to 0.7 M. As described in the coating procedure, sodium hydroxide solution (five times the

**Table 1**  
Chemical composition of typical RHA and AH coated RHA.

Parameters	%Composition	
	RHA	AH coated RHA*
Silica ( $\text{SiO}_2$ )	84.73	59.46
Alumina ( $\text{Al}_2\text{O}_3$ )	0.21	21.74
Lime ( $\text{CaO}$ )	0.539	0.378
Magnesium oxide ( $\text{MgO}$ )	0.185	0.130
Potassium oxide ( $\text{K}_2\text{O}$ )	0.42	0.295
Iron oxide ( $\text{Fe}_2\text{O}_3$ )	0.25	0.175
Loss on Ignition (LOI)	13.08	9.201
Moisture ( $\text{H}_2\text{O}$ )	0.979	8.92

\* AH coated RHA using 0.6 M aluminum salt.

**Table 2**  
Chemical composition of typical tap water spiked with fluoride.

Parameters	Typical value in tap water
Chloride (mg/L)	30–35
Hardness (mg/L)	70–80
TDS (mg/L)	160–180
Alkalinity (mg/L)	75–85
pH	7–7.5
Conductivity (mho/cm)	180–200

concentration of the aluminum sulfate) was prepared and slowly added to the aluminum salt solution with gentle stirring. The addition was continued until the pH of the reaction mixture slurry reached around pH 5.

Tap water (composition is given in Table 2.) spiked with 10 mg/L fluoride was passed through the column. The results are depicted in Fig. 5. For the sake of clarity, the results of 0.5, 0.6 and 0.7 M aluminum sulfate concentrations are shown in Fig. 5. The results show that with increase in the initial concentration of aluminum sulfate, there was a corresponding increase in the fluoride removal capacity of the coated RHA. This is attributed to the increased amount of aluminum hydroxide on RHA surface with the increase in initial aluminum sulfate concentrations. Table 3 shows the results for the different aluminum sulfate concentrations with corresponding aluminum hydroxide formation and the resultant fluoride removal capacity based on volume of fluoride spiked tap water treated. Further increase in the aluminum sulfate concentration renders great difficulty for the coating process, as it is difficult to dewater the aluminum hydroxide and RHA slurry. Thus, the concentration of the initial aluminum sulfate was optimized at 0.6 M to address the fluoride removal capacity and ease of coating process.

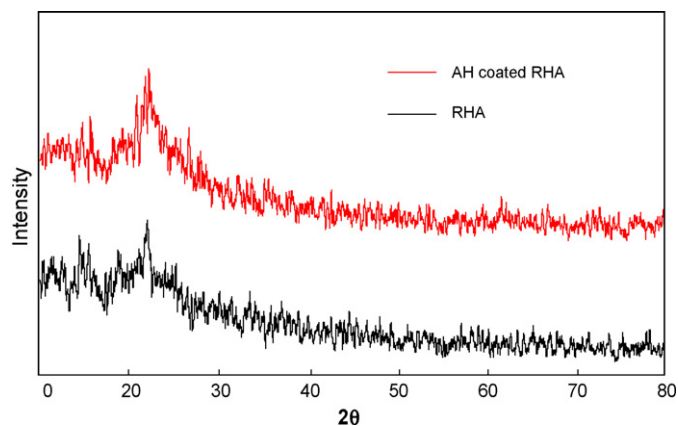


Fig. 4. X-ray powder diffractometer (XRD) for AH coated RHA and RHA.

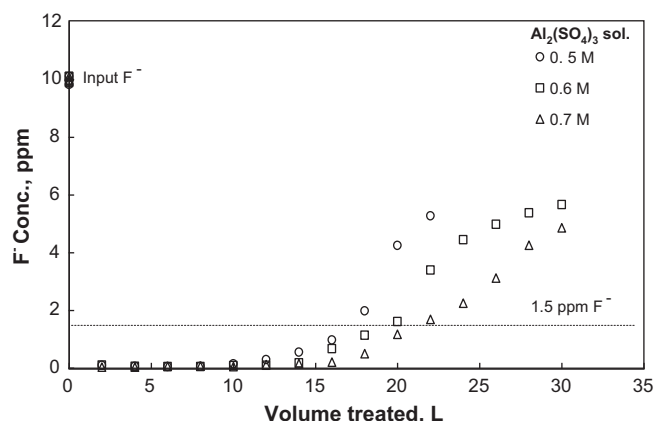


Fig. 5. Effect of aluminum salt concentration on fluoride removal of AH coated RHA.

**Table 3**  
Effect of aluminum salt concentration on fluoride removal capacity.

Initial conc. of aluminum salt solution (M)	Weight of aluminum hydroxide (g/g of RHA)	Volume of 10 ppm F <sup>-</sup> spiked tap water treated (L)	Fluoride removing capacity (mg/g of AH coated RHA)
0.1	0.071	3	1.5
0.2	0.142	6	3
0.3	0.213	9	4.5
0.4	0.284	12	6
0.5	0.35	16	8
0.6	0.436	19	9.5
0.7	0.496	21	10.5

### 3.3. Effect of pH of the AH coating on the RHA surface on the fluoride removal

The AH coating on RHA surface was carried out as a function of the pH. The pH of the reaction mixture is controlled by addition of sodium hydroxide into slurry of RHA soaked in aluminum sulfate solution. Based on the above result (see Section 3.2) the initial concentration of aluminum sulfate was fixed at 0.6 M. The formation of aluminum hydroxide precipitate on the RHA surface is controlled with the final pH of reaction mixture. Tap water (composition is given in Table 2.) spiked with 10 mg/L fluoride was passed through the column. Effect of pH on AH coating on the RHA surface showed that the fluoride removing capacity decreases when the pH of slurry is 7 or higher, the maximum fluoride removal was observed when the pH of the coating conditions was maintained to be in the acidic pH range, pH 4.5 (Fig. 6).

Based on the above results, the final coating conditions were fixed at 0.6 M aluminum sulfate concentration and pH of coating at 5. Coatings prepared under these conditions were henceforth used for further evaluation studies.

### 3.4. Effect of input fluoride concentration on fluoride removal capacity

Experiments were conducted to evaluate the effect of fluoride removal capacity of AH coated RHA with variable input concentrations (2–20 mg/L) of fluoride in the spiked tap water on a 10 g AH coated RHA. From Fig. 7 it is observed that average fluoride adsorbing capacity per gram of AH coated RHA was around 9.5 mg/g, irrespective of input fluoride concentration upto 20 mg/L.

### 3.5. Scale up experiments of fluoride removal by coated RHA

Scale up experiments were conducted by passing fluoride spiked tap water of fixed concentration (5 mg/L) through various amounts of coated RHA (for example 10, 20, 30 and 50 g of aluminum hydrox-

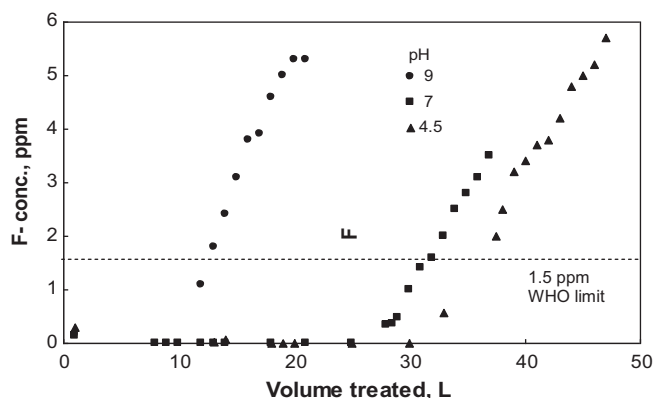


Fig. 6. Effect of pH on the coating of RHA.

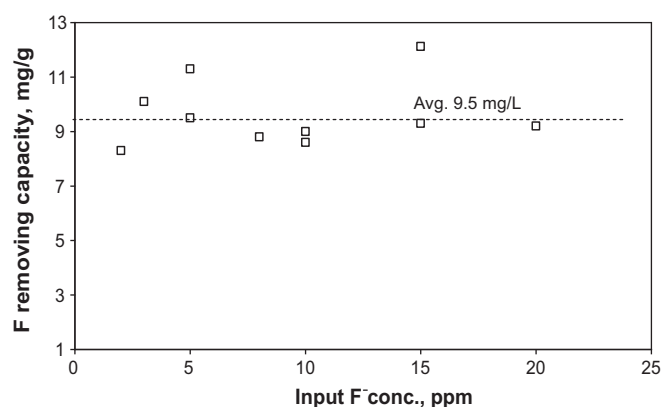


Fig. 7. Effect of input fluoride concentration on trapping capacity of AH coated RHA.

ide coated RHA). It may be observed from Fig. 8 that there is a linear increase in the fluoride removal with increase in the amount of coated RHA. The adsorption capacity of AH coated RHA is calculated based on volume of 5 mg/L fluoride spiked tap water treated and amount of AH coated RHA used (10–50 g). For example, for 10 g of AH coated RHA, 20 L of 5 mg/L fluoride spiked tap water is treated while for 50 g of AH coated RHA, 95 L of 5 mg/L fluoride spiked tap water is treated (Fig. 8) and average fluoride adsorption capacity of AH coated RHA is found to be 9–10 mg/g. The scale up experiments, thus, indeed show the consistency in fluoride adsorption capacity of 9.5 mg/g of AH coated RHA.

### 3.6. Laboratory study of the filter

Having established the key parameters that have a direct influence on the adsorption of fluoride on AH coated RHA through controlled column experiments, it was decided to test the efficacy of the AH coated RHA through an appropriate filtering device.

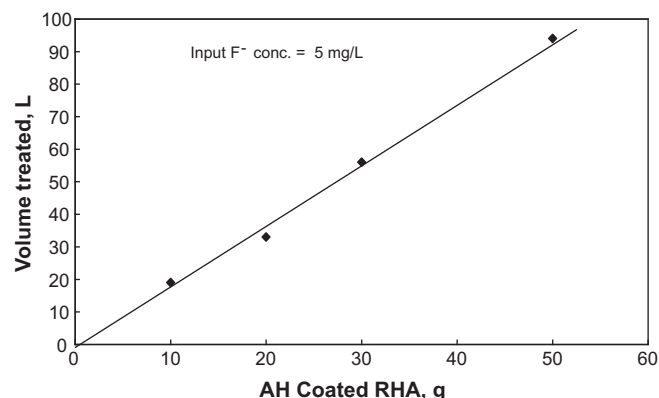


Fig. 8. Effect of input fluoride on trapping efficiency of fluoride.

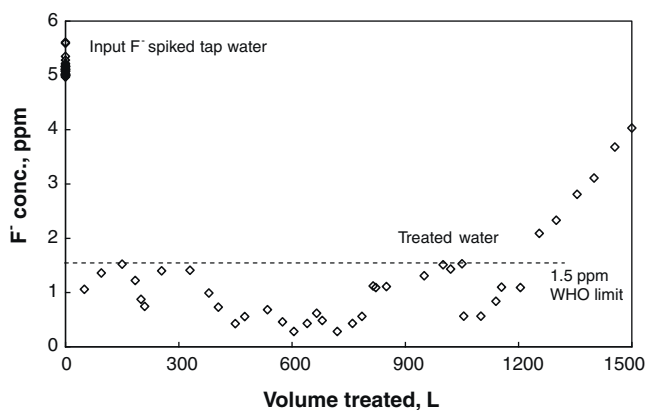


Fig. 9. Fluoride removal filter made of coated RHA using 0.6 M Aluminum salt.

Accordingly, filters were fabricated using standard operating procedure by Prasad [37]. The filter used for the testing purposes contained 750 g of AH coated RHA. An influent concentration of 5 mg/L fluoride in spiked tap water and flow rate of 5 L/h was maintained during the course of this investigation. It was found that 1250 L of 5 mg/L of fluoride spiked tap water could be treated to obtain water in the permissible range of 1.5 mg/L fluoride (Fig. 9). In this study, the adsorption density of the coated RHA was found to be 9 mg/g which was consistent with our results obtained from the column experiments. Thus, the coated RHA filter was found to be scalable (20 g in the column tests or 750 g in an actual filter, the adsorption capacities are comparable).

### 3.7. Adsorption isotherms

Adsorption equilibrium study was performed for analyzing the performance and adsorption behavior of AR grade aluminum hydroxide [Al(OH)<sub>3</sub>] and AH coated RHA as adsorbents for fluoride ions. Experimental data on the adsorption of fluoride on coated RHA at room temperature (27 ± 1 °C), at pH of 5, under optimum conditions of contact time and dosage of adsorbent were generated for AR grade Al(OH)<sub>3</sub> and AH coated RHA, the results are shown in Fig. 10. The adsorption capacity of Al(OH)<sub>3</sub> and AH coated RHA reached an equilibrium value of 25 mg/g and 15 mg/g, respectively.

Experimental data for fluoride adsorption were plotted (Fig. 11) as log of fluoride adsorbent ( $x/m$ ) vs. log of equilibrium concentrations ( $C_e$ ). It can be seen from Fig. 11 that adsorption of fluoride on pure Al(OH)<sub>3</sub> and AH coated RHA under optimum conditions at room temperature (27 ± 1 °C) obeyed the Freundlich adsorption

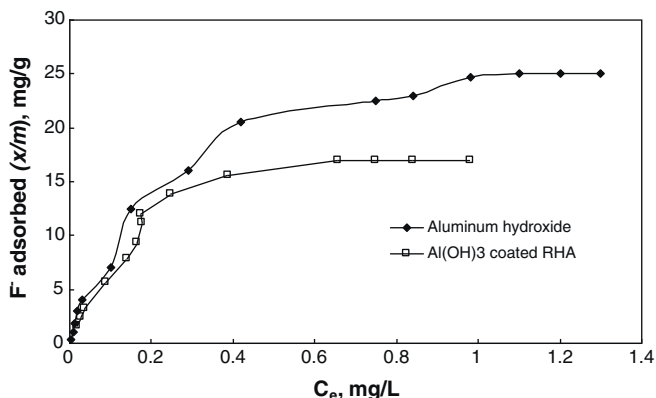


Fig. 10. Adsorption isotherms for fluoride adsorbed on Al(OH)<sub>3</sub> and AH coated RHA.

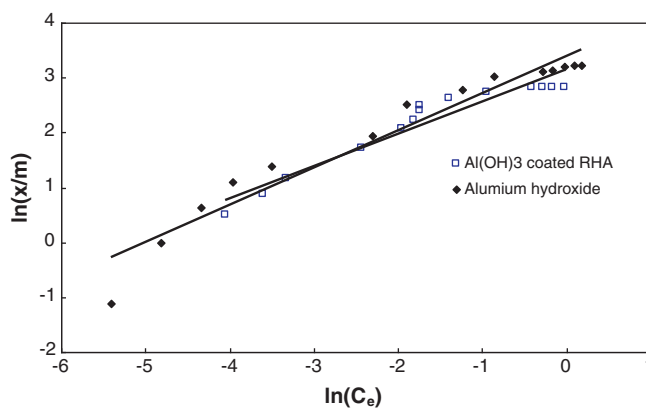


Fig. 11. Freundlich isotherms for fluoride adsorption on AH coated RHA and Al(OH)<sub>3</sub>.

isotherm as described by Eq. (1):

$$\ln\left(\frac{x}{m}\right) = \ln K + \frac{1}{n} \ln(C_e) \quad (1)$$

The Freundlich adsorption isotherm relates mass of fluoride adsorbed ( $x$  in mg) by per unit mass of the adsorbent ( $m$  in g) i.e.  $x/m$  with fluoride at equilibrium ( $C_e$ ) concentration. The constants  $K$  and  $n$  represent the adsorption capacity and intensity of the adsorption, respectively. The data obtained in this study showed good fits to the Freundlich adsorption isotherm. Values of  $K$  and  $n$  were calculated from the intercept and slope of the plot  $\ln(x/m)$  and  $\ln C_e$  (Fig. 11). The coefficients of the two isotherms as calculated from the plots have been shown in Table 4.

The value of the adsorption parameters give an indication that Al(OH)<sub>3</sub> is one of the best adsorbent materials for fluoride removal from water as it directly reacts and complexes with F<sup>-</sup> ions. The fluoride adsorption of AH coated RHA is equally good and shows a similar trend to that of pure Al(OH)<sub>3</sub>. The weight of Al(OH)<sub>3</sub> on RHA surface is 0.42 g/g of RHA, thereby indicating that the adsorption capacity of the normalized coated RHA is comparable to Al(OH)<sub>3</sub>.

### 3.8. Adsorption kinetics

Adsorption kinetics is one of the most important characteristics which represents the adsorption efficiency. The adsorption rate of fluoride on the coated surface, as a function of the initial fluoride concentration, is shown in Fig. 12. The fluoride adsorption was initially rapid, up to 10 min, after which it was found to reach a constant value. The time required to reach equilibrium was 30 min. The kinetics of fluoride adsorption onto the magnetic adsorbents fit well with the pseudo-second-order kinetic model ( $r^2 = 0.9990-1.0000$ ).

The pseudo-second-order isotherm is given by

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (2)$$

where  $k_2$  is the rate constant of adsorption (in mg/g min),  $q_t$  is the amount of fluoride adsorbed by adsorbent at any time (mg/g),  $q_e$  is equilibrium adsorption capacity (mg/g) and the initial sorption

Table 4  
Adsorption isotherm constants for different adsorbents.

S. no.	Adsorbents	Freundlich isotherm constants	
		$K$	$n$
1	Al(OH) <sub>3</sub>	29	1.47
2	AH coated RHA	23	1.69

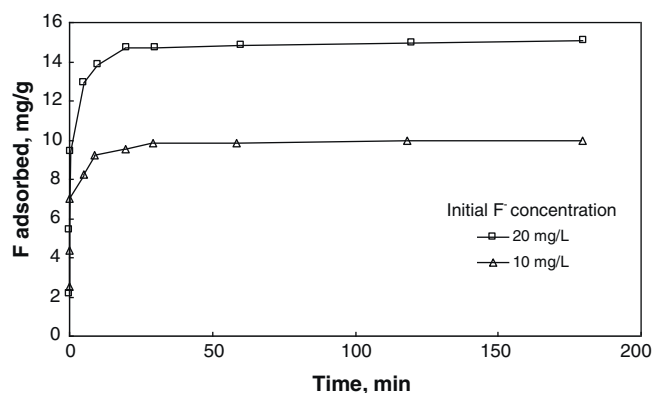


Fig. 12. Effect of contact time on fluoride adsorption rate for different initial F<sup>-</sup> concentrations.

**Table 5**  
Kinetic parameter of pseudo-second-order for fluoride adsorption onto the AH coated RHA.

S. no.	Parameters	Initial F <sup>-</sup> concentrations	
		10 mg/L	20 mg/L
1	$k_2$	0.0784	0.0521
2	$q_e$	9.982	15.083
3	$h_0$	7.874	11.846
4	$r^2$	0.9997	0.9995

rate,  $h_0$  (mg/g min) can be defined as:

$$h_0 = k_2 q_e^2 \quad (t \rightarrow 0) \quad (3)$$

Both  $k_2$  and  $h_0$  could be determined experimentally by plotting of  $t/q_t$  against  $t$ . The constant  $k_2$ , the initial sorption rate  $h_0$  and equilibrium adsorption capacity ( $q_e$ ) obtained from the slope and intercept of plots are presented in Table 5. The results showed decrease in  $k_2$  values and increase in  $h_0$  and  $q_e$  values with higher initial fluoride concentrations. The equilibrium adsorption capacity ( $q_e$ ) evaluated from the pseudo-second-order plot was found to increase from 9.98 to 15.08 mg/g as the fluoride concentration increased from 10.0 to 20.0 mg/L, which suggested that the AH coated RHA adsorbent would be a good adsorbent for scavenging fluoride from the contaminated water.

#### 4. Conclusions

The following conclusions were drawn from the present study.

AH coated RHA has shown the good adsorption capacity for fluoride removal; for example the adsorption studies indicate 15.08 mg/g of adsorption capacity while column studies shows 9.5 mg/g capacity.

The pH of a reaction mixture (AH coated RHA) has a very significant affect on the removal of fluoride from tap water. The maximum removal of the fluoride by AH coated RHA was observed when the pH of a reaction mixture was kept at  $5.0 \pm 0.5$ .

The adsorption capacity of coated RHA is independent of fluoride concentrations of spiked tap water.

The fluoride removal of coated RHA is linearly proportional to the amount of coated RHA used; hence the coated RHA can be easily scaled up to a filtration unit/device for practical use. The fluoride adsorption capacity of coated RHA used in the filter was found to be 9 mg/g. A filter made of 750 g coated RHA has treated 1250 L of 5 mg/L of fluoride spiked tap water to below the WHO limit of 1.5 mg/L of fluoride in treated water. The flow rate of 5 L/h was maintained through the experiment.

The adsorption data followed the Freundlich isotherms confirming multilayer adsorption. The AH coated RHA shows very rapid fluoride adsorption initially for 10 min. Good fit was observed to show that the fluoride adsorption on AH coated RHA followed pseudo second order kinetics. This suggested that the AH coated RHA adsorbent would be a good adsorbent for removal of fluoride from water.

The AH coated RHA can be used as a low cost, effective fluoride removal adsorbent.

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