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Ultrasonication-Assisted Defluoridation: An Overview

Maruwada Srinivasan[1]; Pabani Patra[2], Ambika Nahak [3], Niharika Nahak [4]

[1]HOD, Dept. of Civil Engineering, Gopal Krishna College Of Engineering and Technology

Jeypore, Odisha, India. Email: gkcet.msr@gmail.com
[2], Asso. Professor Dept. of Civil Engineering, Gopal Krishna College Of Engineering and Technology Jeypore, Odisha, India.
[3] Asso. Professor, Dept. of Civil Engineering, Gopal Krishna College Of Engineering and Technology Jeypore, Odisha, India.
[4] Asso. Professor, Dept. of Civil Engineering, Gopal Krishna College Of Engineering and Technology Jeypore, Odisha, India.

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Abstract - Batch adsorption experiments were performed to evaluate the removal of fluoride from water using aluminium hydroxide (AHG), aluminium hydroxide monoacetate (AHGMA), and aluminium hydroxide diacetate (AHGDA) as adsorbents. The extent of fluoride removal was influenced by pH, contact time, and the amount of adsorbent used. The studies were conducted at an initial fluoride concentration of 3 ppm, with the solution maintained at pH 6.6, and subjected to 5 minutes of ultrasonication, using adsorbent doses between 0.01 and 0.1 g/L. The use of an ultrasonic bath significantly shortened the treatment duration compared with conventional mechanical stirring.

Maximum fluoride uptake occurred within the pH range of 5.5–6.5. The adsorption data followed the Freundlich isotherm model, with linear relationships observed between log (x/m) and log Ce, accompanied by positive intercepts. The corresponding Freundlich constants (K and n) indicated favourable adsorption behaviour. Fluoride adsorption was initially fast and nearly proportional, before gradually slowing as equilibrium conditions were approached. The maximum adsorption capacities achieved were 17 mg/g for AHG, 27 mg/g for AHGMA, and 25 mg/g for AHGDA, confirming that the acetate-modified adsorbents exhibited enhanced performance.

Key Words: Adsorbents, aluminium hydroxide, fluoride removal, ultrasonication, defluoridation

1.INTRODUCTION

Fluorosis is recognized as a global public-health concern, with nearly twenty-five countries reporting fluoride-related health issues. In Asia, the most severe cases occur in India and China, the two most populous nations. Within India, fluoride contamination is widespread, particularly in the states of Andhra Pradesh, Bihar, Gujarat, Madhya Pradesh, Punjab, Rajasthan, Tamil Nadu, and Uttar Pradesh [1–6].

Rajasthan, the largest state in India, covers about 3.42 lakh km², representing 10.41% of the country's land area and 5.5% of its population, yet it holds only 1% of the national water resources. Owing to its harsh climatic conditions, limited groundwater availability, and unique geological formations, the state faces serious challenges related to both water quantity and quality. All 33 districts of Rajasthan have been identified as fluoride-affected, with the most severely impacted regions being Nagaur, Jaipur, Sikar, Jodhpur, Barmer, Ajmer, Sirohi, Jhunjhunu, Churu, Bikaner, and Ganganagar [1,6].

Several aluminium hydroxide–based coated adsorbents have been investigated for fluoride removal, such as aluminium- and zirconium-based oxides [11], Al–Ce hybrid materials [12], Al^{3+}-modified adsorbents [13], untreated hydrated alumina (UHA) and thermally treated hydrated alumina (THA) [14], as well as alum-impregnated alumina [15]. Although these materials show promising affinity toward fluoride, none of them have delivered completely satisfactory or universally applicable performance, indicating that further improvement is still required in this area.

Adsorption continues to be one of the most efficient and economical techniques for fluoride removal; however, most conventional

2. **2. Materials and Methods**

2.1 Adsorbents

The adsorbents—aluminium hydroxide, aluminium hydroxide monoacetate, and aluminium hydroxide diacetate—were procured from ASES Chemicals, Jodhpur, and used without any further purification.

A 100 mg/L fluoride stock solution was prepared by dissolving 221 mg of anhydrous NaF (GR-Merck) in 1 L of double-distilled water. Working solutions of 3 mg/L fluoride were prepared by appropriate dilution and used throughout the experiments.

The SPADNS reagent was prepared by dissolving 958 mg of sodium 2-(para-sulfophenylazo)-1,8-dihydroxy-3,6-naphthalene disulfonate (SPADNS) in distilled water and making the final volume up to 500 mL.

The zirconyl acid reagent was prepared by dissolving 133 mg of zirconyl chloride octahydrate in 25 mL of distilled water, followed by the addition of 350 mL concentrated HCl. The mixture was then diluted to 500 mL with distilled water.

A reference solution for establishing the colorimetric baseline was prepared by mixing 10 mL SPADNS reagent with 90 mL distilled water, containing 7 mL concentrated HCl.

2.2 Batch Adsorption Study

The adsorption experiments were carried out in an ultrasonic bath (ELMA) for contact times ranging from 1 to 30 minutes. After sonication, the samples were centrifuged and the fluoride concentration remaining in the supernatant was measured using the SPADNS method [16] with a HACH DR5000 UV–Visible spectrophotometer. These experiments were performed to establish the optimum pH, adsorbent dose, and contact time for maximum fluoride removal.

The pH of the test solutions was monitored using a digital pH meter (Model 152-R Ri) and adjusted as required by adding 0.1 N HCl or 0.1 N NaOH solutions.

3.1 Effect of Adsorbent Dose

A 100 mL fluoride solution containing 3 ppm F^- was treated with varying amounts of adsorbent (0.01–0.1 g) using an ultrasonic bath. The findings, summarised in Figure 1 and Table 1, show that the efficiency of fluoride removal increased with higher adsorbent dosages. This behaviour is attributed to the greater surface area and larger number of active adsorption sites available at higher doses.

At lower adsorbent quantities, the percentage removal of fluoride increased almost proportionally, indicating effective utilisation of available sites. However, beyond a certain dosage, the increase in fluoride removal became insignificant. This plateau effect is typical of adsorption processes where, after surface sites become saturated, additional adsorbent does not significantly enhance uptake.

The comparative performance of the adsorbents followed the order:

AHGMA > AHGDA > AHG

At an initial fluoride concentration of 3 ppm and an adsorbent dose of 1 g/L, the percentage removal of fluoride was:

- AHGMA: 90.7%

- AHGDA: 83.4%

- AHG: 56.8%

These results clearly indicate that aluminium hydroxide modified with acetate groups, particularly AHGMA, exhibits superior defluoridation capability under ultrasonic conditions.

Table:1 Effect of Adsorbent Dose on Defluoridation by AHG and Derivatives

S. No.	**Adsorbent (g)**	**% Removal (AHG)**	**Kd (AHG)**	**% Removal (AHGMA)**	**Kd (AHGMA)**	**% Removal (AHGDA)**	**Kd (AHGDA)**
1	0.01	31.00	1841	75.07	7887	61.21	5156
2	0.02	32.00		78.00		65.52	
3	0.05	39.7		83.0		71.6	
4	0.06	44.1		85.4		75.1	

5	0.07	48.0		87.2		77.9	
6	0.08	51.3		88.6		80.1	
7	0.09	54.2		89.8		81.9	
8	0.10	56.8		90.7		83.4	

3.2 Effect of pH

The influence of pH on the removal of fluoride was studied at pH of 2.00, 3.00, 4.00, 5.00, 6.00 8.00, 9.00 and 10.00 adsorbent dose of 0.05 g and 3 ppm F- concentration the % fluoride removal and pH after 5 min. of stirring in ultrasonic bath was noted. The results included in Table 2. Figure 2 shows the effect of pH on the removal of fluoride by Aluminium hydroxide, aluminium hydroxide mono acetate and aluminium hydroxide di acetate. As the pH of the test fluoride solution increases the % removal of fluoride slightly increases, reaches on maximum around pH 5 and then decreases in all the three cases. It is however observed that the adsorption of fluoride on the aluminium hydroxide and its derivatives take place in the entire pH range 2 to 10. The % fluoride removal at pH 6 was found 40.56, 83.65 and 71.00 with AHG, AHGMA and AHGDA respectively. It was also observed that the pH of the solution increases after

Chemical Reactions Involved in Defluoridation

During defluoridation, fluoride ions (F^-) replace hydroxide ions (OH^-) present on the adsorbent surface. This releases OH^- into the solution, increasing the pH.

1. Reaction for Aluminium Hydroxide Monoacetate (AHGMA)

$Al(OH)_2CH_3COO^- + 2F^- \rightarrow AlF_2CH_3COO^- + 2OH^-$

2. Reaction for Aluminium Hydroxide Diacetate (AHGDA)

$Al(OH)(CH_3COO^-)_2 + F^- \rightarrow AlF(CH_3COO^-)_2 + OH^-$

3. Reaction for Aluminium Hydroxide Species

$[Al(OH)(OH_2)_5]^{2+} + F^- \rightarrow [AlF(OH_2)_5]^{2+} + OH^-$

Charts

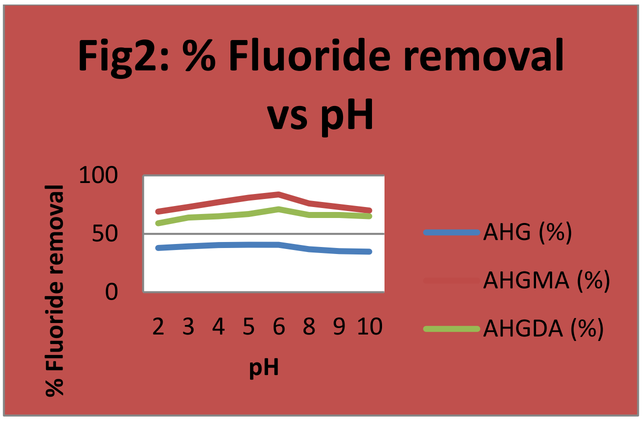


Fig2: % Fluoride removal vs pH

Table 2: Effect of pH on Defluoridation by AHG, AHGMA, and AHGDA

S. No.	Initial pH	Final pH (AHG)	% Removal (AHG)	Final pH (AHGMA)	% Removal (AHGMA)	Final pH (AHGDA)	% Removal (AHGDA)
1	2	6.15	38.00	6.09	69.00	6.20	59.00
2	3	6.47	39.34	6.17	73.00	6.41	64.00
3	4	6.80	40.45	6.49	77.00	6.52	65.00
4	5	7.00	40.50	6.50	81.00	6.50	67.00
5	6	7.00	40.56	6.80	83.65	6.67	71.00
6	8	9.05	36.78	8.91	76.00	8.18	66.00
7	9	9.45	35.00	9.93	73.00	9.29	66.00
8	10	10.23	34.67	10.70	70.00	10.20	65.00

3.3 Effect of contact time

The effect of time on the adsorption of fluoride on Al(OH)3 and its derivatives was investigated at pH 6.60, 0.02 g adsorbent dose and 3 ppm F- initial concentration. Figure 3 and Table 3 shows the percent removal of fluoride by adsorbents after different contact times. As the contact time As the contact time increases, the percentage of fluoride removal also increases rapidly. After this initial rapid increase, the removal rate gradually levels off, indicating that the system has reached equilibrium. Because no significant improvement in fluoride removal was observed after five minutes, an equilibrium contact time of five minutes was selected and used for all subsequent experiments.

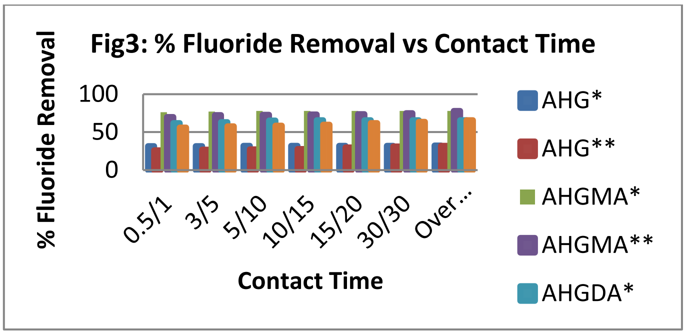


Fig 3: Effect of contact time on % fluoride removal by AHG and derivatives

Table 3: Effect of Contact Time on Defluoridation by AHG, AHGMA, and AHGDA

Conditions: Initial fluoride concentration = 3 ppm, pH = 6.60, Adsorbent dose = 0.02 g, Volume = 100 mL.
mL.

Contact Time (min)	**% Removal AHG***	**% Removal AHG****	**% Removal AHGMA***	**% Removal AHGMA****	**% Removal AHGDA***	**% Removal AHGDA****
0.5 / 1	31.42	26	76.35	70.02	62.08	55.87
3 / 5	31.78	26.98	76.92	72.33	63.00	57.65
5 / 10	32.00	27.54	78.00	73.00	65.52	58.78
10 / 15	32.00	28.00	78.00	73.39	65.55	59.65
15 / 20	32.00	30.09	78.00	73.87	65.54	61.74
30 / 30	32.00	31.32	78.00	74.98	65.55	63.58
Overnight	32.31	31.97	78.00	77.96	65.56	65.55

3.4 Distribution Coefficients

The uptake of fluoride from its aqueous solutions by AHG, AHGMA, and AHGDA was estimated in terms of the distribution coefficient (Kd). The adsorbents (0.01–0.1 g) were stirred in an ultrasonic bath with 100 mL of a 3 ppm fluoride solution at pH 6.60 until complete equilibrium was attained. The adsorbent was then removed by filtration through glass wool, and the remaining fluoride concentration in the filtrate was determined spectrophotometrically by measuring the optical density (OD) at 570 nm using linear calibration curves relating OD to concentration. The Kd values were calculated using the formula provided in reference [17].

Distribution Coefficient (Kd) Formula

Distribution coefficient, $Kd = (100 - x) / x \times (V / m)$
Where:

- V is the volume of the solution in mL
- m is the weight of the adsorbent in grams
- x is the percentage of fluoride remaining in the solution

The average Kd values for the adsorbents were calculated using this formula.
Where V is the volume of the solution in millilitres (mL), m is the weight of the adsorbent in grams (g), and x is the percentage of fluoride concentration remaining in the solution. Using these values, the average Kd (distribution coefficient) was calculated for AHG, AHGMA, and AHGDA.

Adsorption Isotherm

In order to determine the adsorption capacity of aluminium hydroxide and its derivatives, adsorption isotherm (A.I.) studies were conducted (Tables 4, 5, and 6). The experimental data were analyzed using the Freundlich, Langmuir, and BET isotherm equations to understand the nature of adsorption. The adsorption isotherms for fluoride ions in water on AHG, AHGMA, and AHGDA at equilibrium are shown in Figures 4, 6, and 8.

All the adsorption isotherms were found to be regular, positive, and convex toward the concentration axis. The isotherm curves rise proportionately during the initial stages and gradually tend to become parallel to the concentration axis at higher concentrations. The plots of Ce/(x/m) against Ce, based on the Langmuir equation, were not linear, indicating the unsuitability of the Langmuir model for the experimental fluoride concentrations studied.

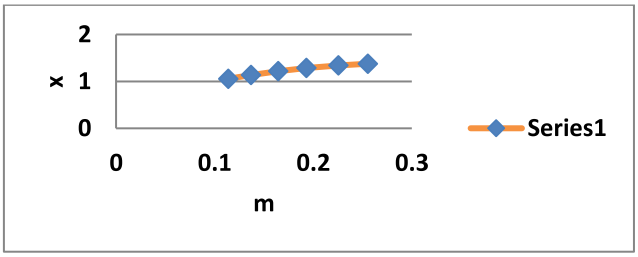
However, the plots of log Ce versus log (x/m), according to the Freundlich equation, were found to be linear (Figures 5, 7, and 9), giving a positive intercept on the ordinate at low fluoride concentrations, which are typical of drinking water. The Freundlich equation is expressed as:

$$\log (x/m) = \log K + (1/n) \log Ce$$

Where:

- Ce is the equilibrium concentration.
- (x/m) is the amount of fluoride adsorbed per gram of the adsorbent at equilibrium.
- K and n are empirical constants representing adsorption capacity and adsorption intensity, respectively.

These values were calculated from the slope and intercept of the linear Freundlich plots using a computerized LGR program and reported in Tables 4–6. The maximum adsorption capacity was observed for AHGMA, which correlates with its higher Kd value. The adsorption intensity (n) was found in the range of 0.44 to 1.00, indicating satisfactory adsorption behavior.



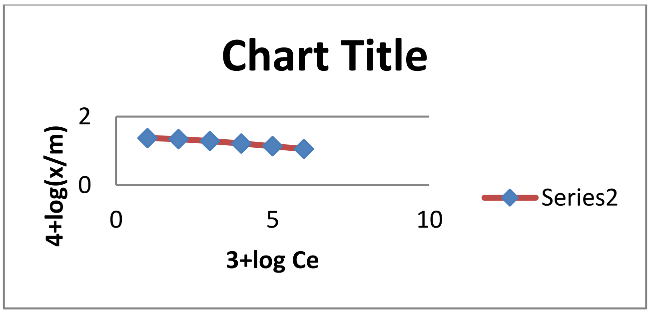


Fig 5: Freundlich isotherm showing adsorption of fluoride on AHG

Table-4 Freundlich Isotherm – Defluoridation with AHG

S. No.	m (g)	% [F-]r	10^3 Ce (g/dm^3)	x × 10^{-4} g	(x/m) × 10^{-4}	3 + log Ce	4 + log (x/m)	K	n
1	0.05	39.7	1.80	1.191	23.8	0.2553	1.3766	6.668	0.4413
2	0.06	44.1	1.68	1.323	22.0	0.2253	1.3424		
3	0.07	48.0	1.56	1.440	20.6	0.1931	1.2858		
4	0.08	51.3	1.46	1.539	19.3	0.1644	1.2159		
5	0.09	54.2	1.37	1.626	18.1	0.1367	1.1362		
6	0.10	56.8	1.30	1.704	17.0	0.1139	1.0565		

Table-5 Freundlich Isotherm – Defluoridation with AHGMA

S. No.	m (g)	% [F-]r	10^3 Ce	x ×	(x/m)	4 + log	4 + log	K	n
			(g/dm^3)	10^{-4} g	× 10^{-4}	Ce	(x/m)		
1	0.05	83.0	0.51	2.490	49.80	0.7076	1.6972	9.996	1.015
2	0.06	85.4	0.44	2.562	42.67	0.6435	1.6300		
3	0.07	87.2	0.38	2.616	37.37	0.5798	1.5725		
4	0.08	88.6	0.34	2.658	33.23	0.5315	1.5215		
5	0.09	89.8	0.30	2.694	29.90	0.4771	1.4757		
6	0.10	90.7	0.28	2.721	27.20	0.4472	1.4346		

Table-6 Freundlich Isotherm – Defluoridation with AHGDA

S. No.	m (g)	% [F-]r	10^3 Ce (g/dm^3)	x × 10^{-4} g	(x/m) × 10^{-4}	4 + log Ce	4 + log (x/m)	K	n
1	0.05	71.6	0.85	2.148	42.96	0.9294	1.6331	8.414	0.991
2	0.06	75.1	0.75	2.253	37.55	0.8751	1.5745		
3	0.07	77.9	0.66	2.337	33.39	0.8195	1.5237		
4	0.08	80.1	0.60	2.403	30.00	0.7782	1.4771		
5	0.09	81.9	0.54	2.457	27.30	0.7324	1.4362		
6	0.10	83.4	0.50	2.502	25.00	0.6990	1.3979		

4. Mechanism of Adsorption

The anchoring of fluoride ions from water onto AHG is complex because several aluminium hydroxide species coexist in aqueous systems. AHG, obtained by precipitation from $AlCl_3$ solution using NH_4OH, is represented as $Al(OH)_{2.52}Cl_{0.48}$ and likely exists as a polymer composed of ten fused six-membered rings. X-ray measurements indicate that Al^{3+} ions in AHG are coordinated octahedrally by oxygen atoms, with the arrangement resembling that found in liquid water.

Further polymerisation can produce larger polymers; however, increasing positive charge slows this process due to ionic repulsion. In acidic conditions (around pH 2), Al^{3+} is coordinated by six water molecules. As pH increases, the strong positive charge repels protons from the coordinated water molecules, forming a monomeric complex ion $[Al(OH)(OH_2)_5]^{2+}$. At around pH 5, this complex ion and the hydrated ion $[Al(OH_2)_6]^{3+}$ are present in equal amounts.

The equilibrium between these species is represented as:

$$[Al(OH_2)_6]^{3+} \rightleftharpoons [Al(OH)(OH_2)_5]^{2+}$$

These aluminium species play an important role in the adsorption and ion-exchange behavior responsible for fluoride removal.

Mechanism of Adsorption (Extended Section)

Two molecules of the monomeric aluminium complex ions may unite to form a dimer, represented as $[Al_2(OH)_2(OH_2)_8]^{4+}$. Further deprotonation and polymerisation of these monomers and dimers lead to the formation of a ring structure consisting of six octahedrally coordinated aluminium ions, having the formula $[Al_6(OH)_{12}(OH_2)_{12}]^{6+}$. Coalescence of such rings into layers results in the formation of gibbsite.

Thus, a variety of aluminium species such as $[Al(OH_2)_6]^{3+}$, $[Al(OH)(OH_2)_5]^{2+}$, $[Al_2(OH)_2(OH_2)_8]^{4+}$, $[Al_6(OH)_{12}(OH_2)_{12}]^{6+}$, and others coexist in the aqueous system.

Fluoride ions may attach to these aluminium species through three primary mechanisms:

1) Electrostatic attraction:

$$[Al(OH_2)_6]^{3+} + 3F^- \rightarrow [AlF_3(OH_2)_6]^0$$

2) Exchange of OH^- by F^-:

$$[Al(OH)(OH_2)_5]^{2+} + F^- \rightarrow [AlF(OH_2)_5]^{2+} + OH^-$$

3) Replacement of OH^- with F^- in acidic medium:

$$[Al(OH)_2]OH^- + F^- \rightarrow [Al(OH)_2]F^- + OH^-$$

All three types of reactions may occur depending on the aluminium species present. Reaction type 1 does not alter pH, whereas reactions 2 and 3 release OH^- ions, increasing the pH of the solution. This behavior agrees with the experimental observations presented in Table 2.

AHG, AHGMA, and AHGDA are insoluble in water. When 2 g of each adsorbent was stirred in 100 mL of deionised water for 10 minutes, the measured pH values increased to 7.04, 5.67, and 6.09, respectively. Similarly, after contact with fluoride-containing water in an ultrasonic bath for 5 minutes, the final pH values increased compared to the initial pH, confirming the displacement of OH^- by F^- ions through anion exchange.

At low pH values, AHG and its acetate derivatives act mainly as anionic ion exchangers, while at higher pH they predominantly behave as cation exchangers. The decrease in fluoride removal at higher pH levels is likely due to reduced ionic charge and steric hindrance.
All three adsorbents demonstrated effective fluoride removal across the pH range 2–10, with maximum removal of 83% observed for AHGMA at pH 6. Both acetate derivatives showed better adsorption performance compared with AHG, consistent with their higher Kd values. Since Langmuir plots did not fit linearly, monolayer adsorption was not indicated. However, the Freundlich isotherm showed good linearity, suggesting a combined mechanism of ion exchange and ionic interaction. The adsorbents exhibited satisfactory adsorption capacity and intensity, and spot tests confirmed no detectable aluminium residue in treated water.

5. Conclusion

Aluminium hydroxide, aluminium hydroxide monoacetate, and aluminium hydroxide diacetate have shown promising results for the removal of fluoride from drinking water. The adsorption capacity of aluminium-based adsorbents is strongly dependent on the dose, and higher fluoride removal is achieved under a contact time of five minutes.

This method of defluoridation is both fast and economical, making it suitable for practical application in treating drinking water. It also serves as an effective alternative to alum, which is water-soluble and may lead to undesirable taste and harmful residual aluminium concentration in treated water.

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