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Khichar M
Department of Chemistry,
J.N.V. University, Jodhpur 342
005, Rajasthan, India.

Kumbhat S
Department of Chemistry,
J.N.V. University, Jodhpur 342
005, Rajasthan, India.

Prakash A
Department of Chemistry,
J.N.V. University, Jodhpur 342
005, Rajasthan, India.

Correspondence
Khichar M
Department of Chemistry,
J.N.V. University, Jodhpur 342
005, Rajasthan, India.

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Ultrasonication assisted studies of defluoridation from drinking water using aluminium hydroxide and its acetate derivatives.

Khichar M, Kumbhat S and Prakash A

Abstract

The batch adsorption studies were conducted to remove the fluoride from aqueous solutions using aluminium hydroxide (AHG) Aluminium hydroxide mono acetate (AHGMA) and Aluminium hydroxide di acetate (AHGDA) as adsorbents. Removal of fluoride was observed to be dependent on contact time, pH and adsorbent dose. The removal of fluoride was investigated at $[F^-] = 3\text{ppm}$, pH 6.6 and contact time 5 minutes on ultra-sonic bath, using adsorbent dose 0.01 to 0.1g per litre. The ultrasonic bath assisted defluoridation takes much lesser time as compared to conventional stirring. The % fluoride removal was found maximum in the pH range 5.5-6.5. The experimental data fitted well in the Freundlich adsorption isotherm, the curves between $\log(x/m)$ against $\log C_e$ were found linear with a positive intercept on the ordinate. The value of adsorption capacity K and the intensity of adsorption n, have been reported. The uptake of fluoride was found rapid and proportionate in initial stages, decreases gradually while approaching equilibrium. The uptake of fluoride from its aqueous solution was found to be 17, 27 and 25 mg/g for AHG, AHGMA and AHGDA respectively.

Keywords: Adsorbents, Aluminium hydroxide, Defluoridation, Defluoridating agent, Fluoride

1. Introduction

The problem of fluorosis is worldwide and almost 25 nations of the world are under its dreadful fate. In Asia, India and China, the most populous countries are worst affected. In India problem is most pronounced in Andhra Pradesh, Bihar, Gujarat, Madhya Pradesh, Punjab, Rajasthan, Tamil Nadu, and Uttar Pradesh^[1-6].

Rajasthan, the largest state in the country, has an area of 3,42,239 lakh Sq kms, 10.41 % of the country's area and 5.5% of nation's population, however it has low water resources i.e. 1% of the country's resources. The state has extreme climatic and geographical conditions and suffers with the problems of quantity as well as quality of water. All the 33 districts of Rajasthan have been declared as fluorosis prone areas. The worst are- Nagaur, Jaipur, Sikar, Jodhpur, Barmer, Ajmer, Sirohi, Jhunjhunu, Churu, Bikaner and Ganganagar^[1,6].

Concerned with the magnitude of health problems due to excessive concentration of fluoride in drinking water several methods of defluoridation of drinking water has been developed. The ion-exchange, adsorption and precipitation are the usual means of defluoridation. However, precipitation and adsorption methods are most preferred. The adsorption method involves the contact of the fluoride containing water with a suitable adsorbent.

A number of $Al(OH)_3$ based adsorbents have been tried for defluoridation. These include $Al(OH)_3$ flocs^[7], Aluminum hydroxide coated rice husk ash^[8], Aluminium hydroxide impregnated limestone^[9], Amorphous $Al(OH)_3$ ^[10]. Recently some aluminium alloy and aluminium hydroxide coated adsorbent eg. Aluminium and zirconium oxide^[11], Al-Ce hybrid adsorbent^[12], Al^{3+} ^[13], Untreated hydrated alumina (UHA) and thermally treated hydrated alumina (THA)^[14], Alumina impregnated with alum^[15], has been tried for removing fluoride from drinking water. None of these have been found fully satisfactory; hence work is still going on in this direction.

Adsorption methods have proved to be cost effective as well as efficient for fluoride removal, however all these processes are time consuming, and to improve ultrasonicator assisted adsorption of fluoride from drinking water using aluminium hydroxide and its acetate derivatives is being reported in this communication.

A comparative study has been conducted using aluminium hydroxide (AHG), aluminium hydroxide mono acetate (AHGMA) and aluminium hydroxide di acetate (AHGDA) and effect of contact time, pH, dose of adsorbent and initial [F⁻] on the adsorption is reported.

2. Material and methods

2.1 Adsorbents: Aluminium hydroxide, Aluminium hydroxide mono acetate and Aluminium hydroxide di acetate were purchased from ASES chemicals Jodhpur and used as such.

The stock solution of fluoride 100 mg/L was prepared by dissolving 221 mg of anhydrous NaF (GR-Merck) in 1 L of double distilled water and test solution of 3 mg/L was prepared by dilution and was used throughout the study.

SPADNS reagent was prepared by dissolving 958 mg sodium-2(Parasulfophenylazo)-1,8-di 32hydroxyl-3,6-naphthalene-di sulfonate (SPADNS) in distilled water and diluted to 500 ml.

Zirconyl acid reagent was prepared by dissolving 133 mg zirconyl chloride octahydrate in 25 ml distilled water, 350 ml conc. HCl was subsequently added and the volume was made up to 500 ml with distilled water.

Reference solution for setting reference point was prepared by adding 10 ml SPADNS solution to 90 ml distilled water, containing 7 ml conc. HCl.

2.2 Batch Adsorption Study: The batch equilibrium studies were conducted by agitating 100 ml of water containing 3 mg per litre F⁻ (3ppm) and 0.01 to 0.10 g adsorbent in skew cap jars at different pH in ultra sonic bath (Trans sonic T 310 ELMA) for different periods ranging from 1 to 30 minute.

The solution was then centrifuged and residual fluoride concentration in the supernatant liquid was determined by SPADNS method^[16] using DR5000 UV visible spectrophotometer HACH. The study was conducted to determine the optimum conditions, for pH, adsorbent dose and contact time on test solutions. The pH (Digital pH meter model 152-R Ri) of the solution was adjusted by adding 0.1 N HCl or 0.1 N NaOH solutions.

3. Result and discussion

3.1 Effect of adsorbent dose

The 100 ml of fluoride solution (3 ppm) was shaken with different amounts of the adsorbent (0.01 to 0.1 g) in ultra sonic bath. Removal of fluoride from water increases with the increase in the dose of adsorbents, the experimental results are presented in Figure 1 and Table 1. It follows from the figure that fluoride uptake increases as the dose of Aluminium hydroxide and its derivatives increase. The increased removal of fluoride is expected due to higher availability of adsorbent surface. Initially, the % removal of fluoride increases proportionately with the amount of adsorbent, however beyond certain dose, no significant increase in the % removal of fluoride was observed. The removal of fluoride by aluminium hydroxide, Aluminium hydroxide mono acetate and Aluminium hydroxide di acetate was found in the following order. AHGMA > AHGDA > AHG

The % removal of fluoride from drinking water by AHGMA, AHGDA and AHG, at [F⁻]_i = 3 ppm and adsorbent dose 1g per litter was found 90.7, 83.4 and 56.8 respectively.

Table 1: Effect of adsorbents dose on defluoridation by AHG and its derivatives

Initial absorbance = 0.75 at λ =570 nm Temperature= 25^oC
 Initial concentration of fluoride= 3 ppm Initial pH=6.60
 Contact time = 5 min (in ultrasonic bath) Volume=100 ml

S. No.	Adsorbent (g)	AHG		AHGMA		AHGDA	
		%fluoride removal	Average K _d	%fluoride removal	Average K _d	%fluoride removal	Average K _d
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	

An average of three runs.

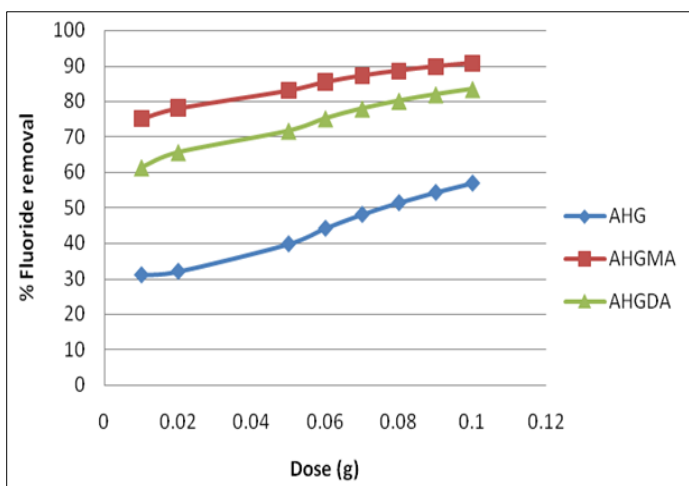
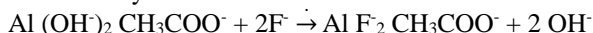


Fig 1: Effect of adsorbent dose on % fluoride removal by AHG and its derivatives

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 defluoridation, in all the three cases. This can be attributed to the release of OH⁻ ion due to the exchange of OH⁻ ion the adsorbent by F⁻ ions.



$Al(OH)^-(CH_3COO^-)_2 + F^- \rightarrow AlF^-(CH_3COO^-)_2 + OH^-$
 $[Al(OH)(OH_2)_5]^{+2} + F^- \rightarrow [AlF(OH_2)_5]^{+2} + OH^-$
 The pH of 2% suspension of AHG, AHGMA and AHGDA has been reported as 7, 4.9 and 6.5 respectively [20, 21]

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

Initial absorbance = 0.75 at λ = 570 nm Temperature = 25^o C
 Initial concentration of fluoride = 3 ppm Adsorbent = 0.05 g
 Contact time = 5 min (in ultrasonic bath) Volume = 100 ml

S. No.	pH**	AHG		AHGMA		AHGDA	
		pH*	%Fremoved	pH*	%Fremoved	pH*	%Fremoved
1	2	6.15	38.00	6.09	69.00	6.2	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	10.2	65.00

An average of three runs. ** pH before adding adsorbent * pH after adding adsorbent

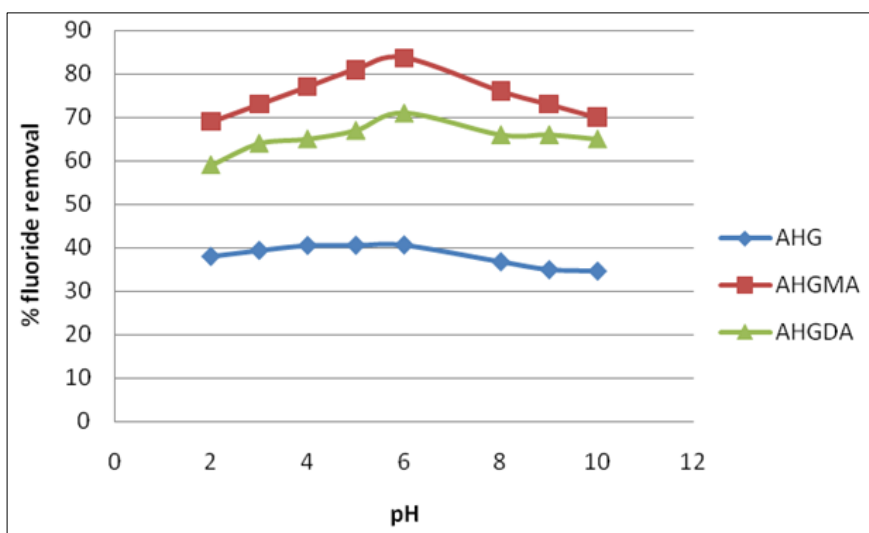


Fig 2: Effect of pH on % fluoride removal by AHG and derivatives

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

increases, % removal increases rather rapidly, it then gradually approaches to a constant value denoting attainment of equilibrium. As there was no significant increase in % fluoride removal was found after five minute, an equilibrium time of five minute was chosen and this was employed in all the subsequent experiments.

Table 3: Effect of contact time on the defluoridation by AHG, AHGMA and AHGDA

Initial absorbance= 0.75 at λ = 570 nm Temperature= 25^o C
 Initial concentration of fluoride= 3 ppm Initial pH=6.60
 Adsorbent = 0.02 g Volume=100 ml

S. No.	Contact time (minute)		% fluoride removal					
			AHG		AHGMA		AHGDA	
	*	**	*	**	*	**	*	**
1	0.5	1	31.42	26	76.35	70.02	62.08	55.87
2	3.00	5	31.78	26.98	76.92	72.33	63.00	57.65
3	5.00	10	32.00	27.54	78.00	73.00	65.52	58.78
4	10.00	15	32.00	28.00	78.00	73.39	65.55	59.65
5	15.00	20	32.00	30.09	78.00	73.87	65.54	61.74
6	30.00	30	32.00	31.32	78.00	74.98	65.55	63.58
7	Over night		32.31	31.97	78.00	77.96	65.56	65.55

An average of three runs. * steried by ultrasonicator ** steried by megnetic stirrer

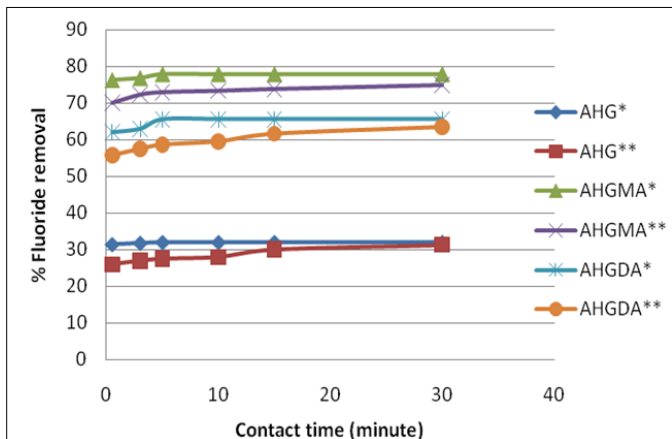


Fig 3: Effect of contact time on % fluoride removal by AHG and derivatives

3.4 Distribution Coefficients

The uptake of fluoride from its aqueous solutions by AHG, AHGMA and AHGDA was estimated in terms of distribution coefficient, K_d . The adsorbents (0.01-0.1 g) were stirred in the ultrasonic bath with 100 ml of 3 ppm fluoride solution at pH 6.60 until complete equilibrium was attained. The adsorbent was removed by filtration through glass wool and the residual concentration of fluoride in the solution was evaluated spectrophotometrically, from the linear optical density (OD) v/s concentration curves by measuring OD at 570 nm. The K_d values were evaluated using formula [17].

$$K_d = \frac{100-x}{x} \cdot \frac{V}{m}$$

Where V is the volume in ml, m is the weight of the adsorbent in grams and the x is the % of fluoride concentration remaining in the solution, the average K_d value for AHG,

AHGMA and AHGDA were obtained as 1841, 7887 and 5156 respectively (Table 1)

Adsorption isotherm

In order to determine the adsorption capacity of aluminium hydroxide and its derivatives, the study of adsorption isotherm (A.I.) were conducted (Table 4, 5 and 6). The experimental data was analyzed in the light of Freundlich, Langmuir and BET equations to predict the nature of adsorption. Adsorption isotherm for fluoride ions in water on AHG, AHGMA and AHGDA when the system is in equilibrium are shown in Fig. 4,6 and 8. All the adsorption isotherm were found regular, positive and convex to the concentration axis. The adsorption isotherm rise proportionately in the initial stages and then try to become parallel to the concentration axis. The plots of $C_e/(x/m)$ against C_e according to Langmuir equation remain no longer linear at experimental fluoride concentration. The plots of $\log C_e$ against $\log (x/m)$ according to Freundlich equation were found linear (Fig 5,7 and 9) yielding an intercept on the ordinate, at low fluoride concentration as are generally available in the drinking water.

$$\log x/m = \log K + 1/n \log C_e$$

Where C_e is the equilibrium concentration, (x/m) is the amount of fluoride concentration adsorbed per gram of the adsorbent at equilibrium. K and n are constants and are the measure of adsorption capacity and the intensity of adsorption, these have been calculated from the intercepts and the slopes of these curves using computerised LGR program and reported in Table 4-6. The adsorption capacity was found maximum for AHGMA which is in accordance with K_d values for AHGMA. The extent of adsorption, denoted by n as found in the range of 0.44 to 1.00 which is quite satisfactory.

Table 4: Freundlich isotherm defluoridation with AHG:

Initial absorbance = 0.75 at $\lambda = 570$ nm Temperature = 25^o C
 Initial [F⁻] = 3 ppm Initial pH = 6.60
 Volume = 100 ml Contact time = 5 min

S. No.	m g	% [F ⁻]r	10 ³ C _e g dm ³	x10 ⁻⁴ g	10 ⁻⁴ (x/m)	3+logC _e	4+log(x/m)	K	n	R ²
1	0.05	39.7	1.80	1.191	23.8	0.2553	1.3766	6.668	0.4413	0.969
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			

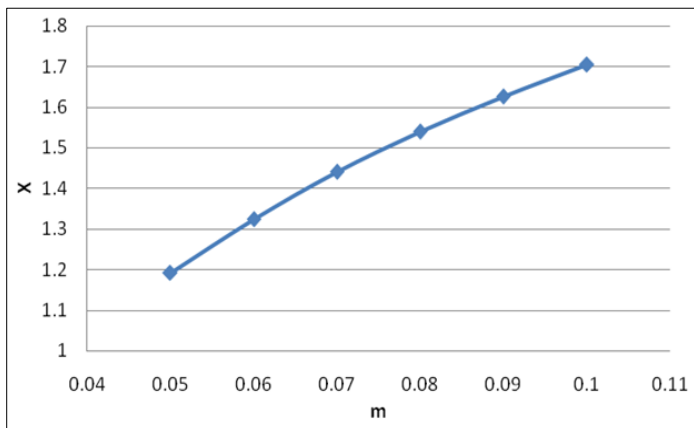


Fig 4: Fluoride adsorption isotherms: plot x against m using AHG

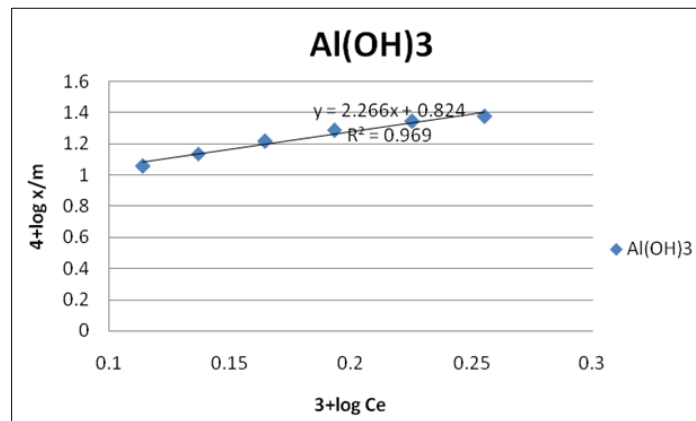


Fig 5: Freundlich isotherm showing adsorption of fluoride on AHG

Table 5: Freundlich isotherm defluoridation with AHGMA:

Initial absorbance= 0.75 at λ =570 nm Temperature= 25⁰ C
 Initial [F⁻] = 3 ppm Initial pH = 6.60
 Volume =100 ml Contact time = 5 min

S. No.	Mg	% [F ⁻]r	10 ³ Ce g dm ³	x10 ⁻⁴ g	10 ⁻⁴ (x/m)	4+logCe	4+log(x/m)	K	n	R ²
1	0.05	83.0	0.51	2.490	49.80	0.7076	1.6972	9.996	1.015	0.998
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			

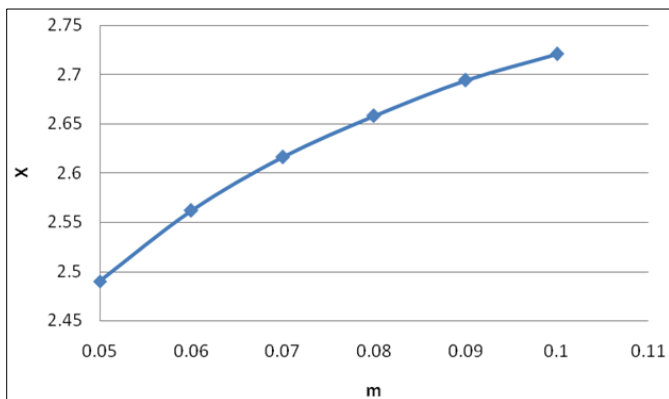


Fig 6: Fluoride adsorption isotherms: plot x against m using AHGMA

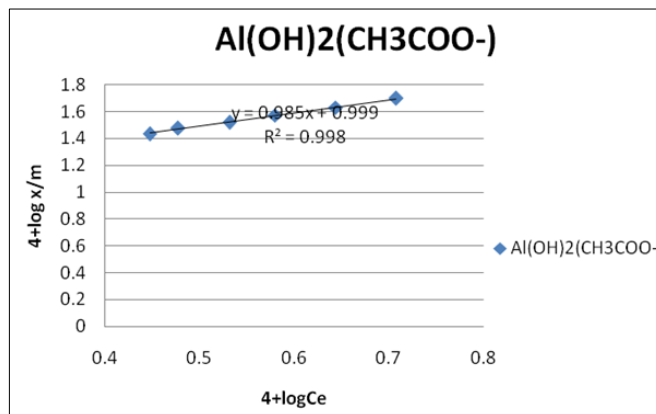


Fig 7: Freundlich isotherm showing adsorption of fluoride on AHGMA

Table 6: Freundlich isotherm defluoridation with AHGDA

Initial absorbance = 0.75 at λ =570 nm Temperature = 25⁰ C
 Initial [F⁻] = 3ppm Initial pH = 6.60
 Volume=100 ml Contact time =5 min

S. No.	mg	% [F ⁻]r	10 ³ Ce g dm ³	x10 ⁻⁴ g	10 ⁻⁴ (x/m)	4+logCe	4+log(x/m)	K	n	R ²
1	0.05	71.6	0.85	2.148	42.96	0.9294	1.6331	8.414	0.991	0.999
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			

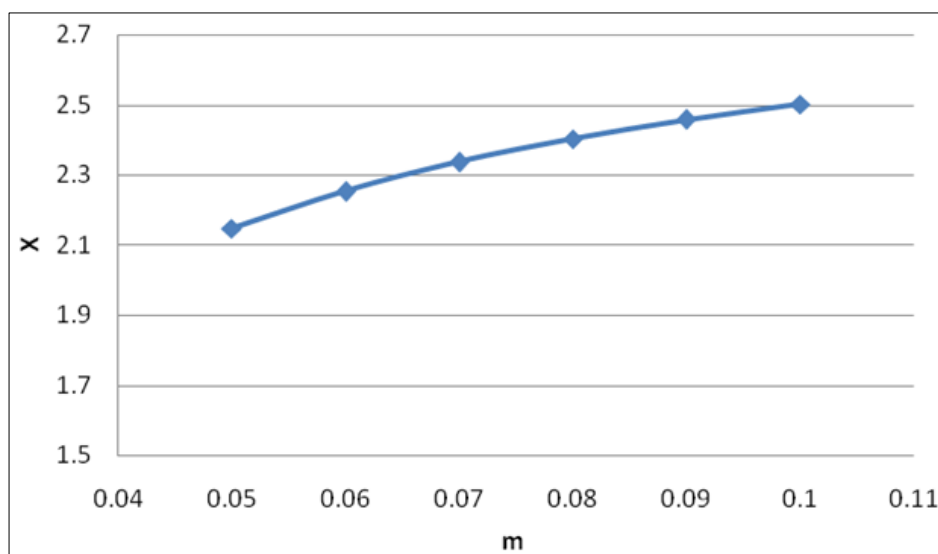


Fig 8: Fluoride adsorption isotherms: plot x against m using AHGDA

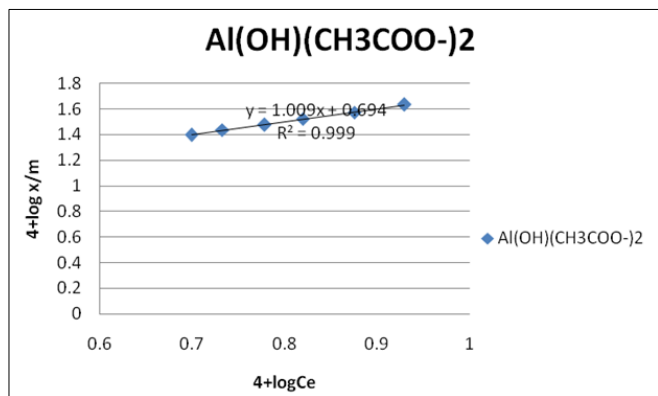


Fig 9: Freundlich isotherm showing adsorption of fluoride on AHGDA

4. Mechanism of adsorption

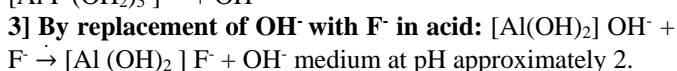
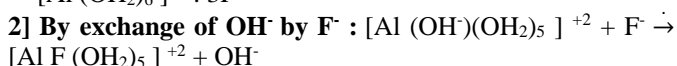
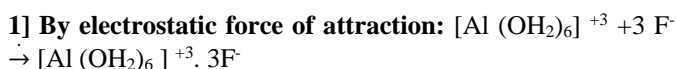
The anchoring of fluoride ion from water on AHG is very complex and difficult to predict, as a number aluminium hydroxide species are known to exist in aqueous system. It has been established that AHG obtained by precipitation from $AlCl_3$ solution by NH_4OH can be represented as $Al(OH)_{2.52}Cl_{0.48}$ and probably exists as polymer of 10 fused six membered rings [18]. It is also reported x – ray measurements, that Al^{3+} ion in AHG is coordinated by octahedral arrangements of oxygen sites and the relationship between the remaining oxygen atoms is essentially same as in liquid water [19].

Further polymerisation may yield higher polymers, however as the positive charge on the polymer increases, the polymerisation is slowed down because of ionic repulsion. Al^{3+} , in acidic solutions i.e. at pH 2, is coordinated by six water molecules, as pH increases the strong positive charge repels the two protons of each water molecule forming a monomeric complex ion $[Al(OH)(OH_2)_5]^{2+}$. At pH 5 this complex ion and hydrated Al^{3+} ion, $[Al(OH_2)_6]^{3+}$ are in equal abundance, with more complex ions at higher pH values and vice versa.



Two molecules of these complex ion unite to form a dimer $[Al_2(OH)_2(OH_2)_8]^{4+}$. Further deprotonation and polymerisation of monomers and dimers lead to the ring structure of six octahedrally coordinated aluminium ions with the formula $[Al_6(OH)_{12}(OH_2)_{12}]^{6+}$. It should be noted that coalescence of these ring into layers result in the formation of Gibbsite. Thus a number species $[Al(OH_2)_6]^{3+}$, $[Al(OH)(OH_2)_5]^{2+}$, $[Al(OH)_2(OH_2)_8]^{4+}$, $[Al_6(OH)_{12}(OH_2)_{12}]^{6+}$, $[Al_{10}(OH)_{22}]^{8+}$, $[Al_{13}O_4(OH)_{24}(OH_2)_{12}]^{7+}$ etc exist in the system [20, 21].

The F^- ion may get attached to these aluminium species by 3 ways-



All the three type of reactions quoted as above can occur with any species present in the solution, no. Of F^- may be different. In case of reaction type 1 there will be no change in pH of the reaction mixture, however in reactions 2 & 3 the liberation of OH^- causes are increase in the pH of the solution. This is in accordance with the experimental results shown in Table 2. AHG and its mono and di acetate derivatives are insoluble in

water [22], 2g of each was stirred in 100 ml deionised water for 10 minutes and the pH was increased, it was found as 7.04, 5.67 and 6.09 respectively. The observed value of pH of reaction solution after contacting with the adsorbents for 5 minutes in ultrasonic bath was found higher than the initial pH of the reaction mixture. This can be taken as a proof of displace of OH^- by F^- ions by way of anionic exchange. AHG and its derivatives in acidic pH range behave as an anionic ion exchanger while at higher pH these behave mostly as a cation exchanger. The decrease in the removal of F^- with the increase in pH may be attributed to the decreases in ionic charge and steric hindrance.

All the three adsorbents, remove the fluoride ions from water in the entire pH range 2 to 10; the removal is found maximum 83% in case of AHGMA at pH 6, considered to be neutral pH. Both the acetate derivatives are found better adsorbent as compared with AHG. (Removal 40% at pH 6), this is also in agreement with K_d values reported in Table 1. As the linear curves are not obtained when the experimental data were fitted in Langmuir adsorption equation, it indicate that there is no monolayer type adsorption, the linear curves obtained according to Freundlich adsorption isotherm suggested a mixed effect of classical ion exchange and ionic interaction type adsorption. All the three adsorbents show fairly good adsorption capacity and intensity of adsorption. The test solutions after contacting with AHG, AHGMA and AHGDA were also tested for residual Al by spot test, and no trace of aluminium was found in the investigated range.

5. Conclusion

Aluminium hydroxide, Aluminium hydroxide mono acetate and Aluminium hydroxide di acetate have given promising results for removal of fluoride from drinking water. It has been observed that the adsorption capacity of aluminium salts is strongly dependant on the dose, and the fluoride removal is greater under condition of five minute contact time. This is the fast and cheap method for defluoridation and can be used for the removal of F^- from drinking water in place of alum which is water soluble and may give rise to distaste and harmful Al residual concentration.

6. Acknowledgement

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