



REMOVAL OF FLUORIDE FROM DRINKING WATER BY QUARTERNARY AMINATED RESINS FROM SAW-DUST

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Safe drinking water is a severe problem in many parts of the various countries including India a fast developing country. Authors have used some low-cost materials and their products as one of the best adsorbents for the removal of fluoride from water mainly used for drinking and other domestic purposes. Results are appreciable to be applied in large scale purposes.

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Introduction

Fluoride has been recognized as an essential component in human diet. Skeletal and dental problems can be prevented by maintaining fluoride concentration of one ppm in dietary intake, however long term consumption of water having high fluoride concentrations lead to bone diseases such as osteofluorosis and systemic fluorosis, which is an endemic problem¹ in many countries, the matter has been reviewed by Susheela.² Cases of endemic fluorosis have been reported from all places of world, particularly China, Japan, Thailand, Persian Gulf, Saudi Arabia, Europe, USA, Canada, Argentina and African Countries² In India cattle and human fluorosis was detected in 1930 and 1937³, respectively, the population of 50 % districts of more than fifteen states are affected by high fluoride concentration in drinking water. Severely affected states are Andhra Pradesh, Uttar Pradesh, Tamil Nadu & Rajasthan. The fluoride level in the ground water used for drinking purposes in Thar and Aravali regions of Rajasthan, has been found as 12-90 ppm and 1.44-28.1 ppm respectably.⁴⁻⁶

Several defluoridation methods based on the adsorption, precipitation & ion exchange has been developed during last four decades, however none of these could solve this problem at a completely acceptable level.⁷ The materials used include lime & related compounds,⁵⁻⁷ trivalent metal oxides, hydroxides & carbonates,^{8,9} activated alumina,¹⁰ activated carbon and ion exchangers¹¹ etc. Attempt has also been made to tackle this problem by Government agencies, NGO's, medical experts, Center of Community Economics and Development Consultant Society, Department of Science and Technology etc.¹² Rajasthan Government had a program to transfer and propagate a domestic defluoridation technology called Nalgonda Technique (NA) in selected villages.¹³ A more recent process of defluoridation is KRASS, which is said to be simpler and effective, however the claims have not been substantiated.¹⁴

Nalgonda Technique involves direct addition of known quantities of lime and alum depending upon the $[F^-]$ in water, unfortunately the technology is not very successful because of the difficulties in controlling the dose of alum and the lack of awareness among people. The process is suitable only for water having $[F^-] < 10$ ppm. The defluoridation by activated alumina (AA) has been studied at length by Bulusu and Nawlakhe.¹⁰ $[F^-]$ less than 1 ppm can be achieved easily by using AA as an adsorbent, however it has certain operational, control and maintenance problems, the important one is the clogging of bed. In the KRASS process, water containing high $[F^-]$ was passed through a PVC column of 64-122 cm in length & 5-6 cm in dia., filled with a low cost material under patent. The column after exhaustion is regenerated with 10% alum solution.

The residual $[Al^{+3}]$ in water treated by NA, AA and KRASS methods was found 2.01-6.46, 0.1-0.3 and 0.1-0.15 ppm respectively. Aluminium is a neurotoxin and its concentration as low as 0.08 ppm in drinking water is reported to have caused Alzheimer's disease,¹⁵ thus generation of residual $[Al^{+3}]$ by these treatments may initiate a secondary toxicity problem, greatest drawback of these processes. In the present communication the efforts have been made to remove $[F^-]$ from water by aluminium free material, quaternary aminised saw dust (SD) derivatives

Experimental Section

Materials

All the reagents and chemicals used in this study are commercially available and are of high purity AR grade.

A 100 m mol L⁻¹ stock solution of $[F^-]$ was prepared by dissolving sodium fluoride in de-ionized water. These solutions were further diluted to suitable concentrations as & when required. The pH of solutions was adjusted by adding dilute HCl or NaOH solution.

AIMIL make MK II model spectrophotometer and Naina make pH meter model 303 with combined glass electrode were used for measuring residual $[F^-]$ & pH measurement respectively.

Table 1. Physical properties of SD derivatives

S.No	Derivatives	Particles		Degree of substitution	Water retain, g g ⁻¹	Salt splitting capacity, meqv g ⁻¹	Weak acid exchange capacity, meqv g ⁻¹
		amount, %	size, mesh				
1	TMAHP- SD	60	>100	0.25	2.52	0.66+0.03	0.25+0.05
		40	60-100				
2	TMAHP- SD	60	>100	0.24	2.64	0.58+0.02	0.25+0.03
		40	60-100				
3	TMAHP- SD	60	40-60	0.21	2.10	0.46+0.03	0.20+0.03
		40	>60				

Stability: 6-8 weeks at pH 3- 10; Swelling in water: slightly.

Table 2. Freundlich constants for the adsorption of fluoride ion on SD derivatives*

Adsorbent	Freundlich constants					
	Average k_d	K	n	SD	R^2	r
TMAHP- SD	2132+50	3.459×10^{-3}	2.52	1.06×10^{-2}	0.99	0.99
TEAHP-SD	1583+70	2.887×10^{-3}	2.60	2.15×10^{-2}	0.99	0.97
DEAE-SD	0782	2.286×10^{-3}	3.10	0.86×10^{-2}	0.98	0.99

([F⁻]=0.02 g dm⁻³, Time of contact =30 min, Adsorbent amount = 0.15 g, Temperature = 30 °C, Volume = 0.1 dm³, pH=8

The adsorbents used in this study are saw dust derivatives, namely quaternary aminised trimethylamino-hydroxypropyl-, triethylamino-hydroxypropyl- and diethylaminoethyl-sawdust referred onward as TMAHP-, TEAHP- & DEAE-SD, respectively. These were prepared as described earlier. The physical properties of SD derivatives viz. degree of substitution, particle size, water regain, salt splitting capacity, exchange capacity, swelling and stability were evaluated by known methods. These are reported in Table 1.

Distribution Coefficients

The uptake of fluoride on the derivatives was estimated in terms of distribution coefficient, K_d . The derivatives (0.02-0.4 g) were stirred with 100 ml of 0.02 g dm⁻³ aqueous solution at pH 7-8, until complete equilibrium was obtained. The adsorbent was then removed by filtration through glass wool and the residual [F⁻] in the solution was computed spectrophotometrically, from the linear optical density (OD) vs concentration curves by measuring OD at the max absorbance region of the complex¹⁸. The K_d values were evaluated using the formula¹⁹:

$$K_d = \frac{(100-x)V}{xm}$$

where

V is the volume of solution in ml,

m is the weight of the adsorbent in grams and

x is the % of [F⁻] remaining in the solution.

Batch Adsorption Study

Adsorption experiments were performed by agitating 0.02- 0.2 g of SD derivatives with 100 ml aq. soln. of fluoride, 0.02 dm⁻³ in skew cap jars. The agitation was continued for 30 min. at ambient temperature (30 + 0.02 °C).

The initial pH of the solution was adjusted by adding requisite amounts of acid or alkali solution. The equilibrated solutions were centrifuged for 10 min at 10,000 RPM in T 24 model (GDR) centrifuge and analyzed for the residual [F⁻].

Results and Discussions

The efficiency of SD derivatives for the removal of F⁻ from water was evaluated by calculating the K_d values for fluoride ion at pH 8. The results (Table 2) show that all the SD derivatives have good affinity for fluoride ion and the order of adsorption for the fluoride ion towards the derivatives is – TMAHP-SD > DEAE-SD > TEAHP-SD

The results also indicate, that the K_d values increase with the decrease in pH of the solution, which may be attributed to the neutralization of surface negative charge of SD derivatives¹⁷

Adsorption Isotherms

Adsorption isotherms (AI) for fluoride ions in water on SD derivatives, when the system is in equilibrium were found regular, positive and convex to the concentration axis followed by a plateau and another rise and formation of plateau. The sharp rise of isotherms in the initial stages of low equilibrium concentration indicates that there are plenty of readily available sites for fluoride ion. Eventually a plateau is reached in all the three cases, this indicates that the saturation of adsorbent surface at this stage. Further rise in the adsorption isotherms and the formation of another plateau probably indicates mono dispersity of adsorption accompanied by the formation of small sized ionic micelles on the surface. A similar behavior has been observed in the adsorption of merocynine over silver halides.^{20,21}

Table 3. Effect of pH on K_d and removal of fluoride (in %) by SD derivatives*

S.No.	pH	Fluoride removal in % and K_d values					
		TMAHP-SD		TEAHP-SD		DEAE-SD	
		% [F ⁻]	K_d	% [F ⁻]	K_d	% [F ⁻]	K_d
1	3	81	2842	76	2111	61	1043
2	4	72	1714	66	1294	55	815
3	5	66	1294	60	1000	49	640
4	8	61	1043	51	694	45	545
5	9	54	783	47	591	41	463

An average of three sets. [F⁻]=0.02 g dm⁻³; Time of contact=30 min; Adsorbent amount=0.15 g; Temperature = 30 °C; Volume = 0.1 dm³

Table 4. Effect of Adsorbent dose on K_d and removal of F⁻ (in %) by SD-derivatives*

Amount of adsorbent	TMAHP-SD		TEAHP-SD		DEAE-SD	
	% [F ⁻]	K_d	% [F ⁻]	K_d	% [F ⁻]	K_d
0.04	33	1203	30	1071	29	996
0.08	41	868	41	851	40	833
0.12	50	833	48	833	43	769
0.16	65	1135	58	845	51	680
0.20	74	1385	65	928	66	949
Average K_d		1126		976		918

An average of three sets. [F⁻] = 0.02 g dm⁻³; Time of contact = 30 min; pH = 8; Temperature =30 °C; Volume = 0.1 dm³; λ_{max} = 570 nm

Table 5. Effect of time on K_d and removal of F⁻ (in %) by SD-derivatives*

Time, min	TMAHP-SD		TEAHP-SD		DEAE-SD	
	% [F ⁻]	K_d	% [F ⁻]	K_d	% [F ⁻]	K_d
30	61.0	1043	51	694	45	545
60	62.5	1110	56	883	48	615
90	65.0	1238	58	920	52	722
120	68.0	1417	60	1000	54	783

An average of three sets. [F⁻] = 0.02 g dm⁻³; pH = 8; Temperature =30 °C; Volume = 0.1 dm³; λ_{max} = 570 nm; Adsorbent amount = 0.15 g

The experimental data was analyzed in the light of Freundlich²², Langmuir²³ and BET²⁴ equations to predict the nature of adsorption. The A I do not strictly follow any one model, however at low concentrations of fluoride ion (1-10 ppm) as are generally available in the drinking waters, the Freundlich model is obeyed. The plots of log C_e against log x/m were found linear yielding an intercept on the ordinate. The Freundlich constants K and $1/n$ were calculated from the intercept and slope of these curves using computerized LRG program and reported in Table 2. The Freundlich constant K is a measure of capacity of the adsorbent while n denotes the intensity of adsorption, a value of n between 1 and 10 is considered to be a favorable adsorption. The adsorption capacity was found maximum for TMAHP-SD. The extent of adsorption, n , was found in the range of 2.52 to 3.1, which is quite satisfactory.

Effect of pH

The effect of pH on the adsorption of F⁻ on to SD derivatives was studied at pH 3, 4, 5, 8 and 9. The % removal of fluoride ion at different pH is given in Table 3. It was observed that the adsorption occurred in the entire range of pH studied, however the uptake of F⁻ increased with the decreasing pH of the solution. The pH of the solution reportedly affect the surface charge of SD derivatives, the

decrease in pH helps in neutralizing the negative charge of SD derivatives and permit the easier movement of fluoride ion in the vicinity of the Vander-Waal's forces, thereby increasing the % removal of fluoride ion at lower pH.

Effect of Adsorbent Dosage

Table 4 shows the amount of fluoride removed as a function of adsorbent dosage at pH 8 and 0.02 g dm⁻³ of initial [F⁻] and at 30 °C. Adsorbent dosage was varied from 0.02 to 0.4 g per 100 ml and equilibrated for 30 min. From the results, it is evident that optimum dosage of adsorbent per 100 ml required for the maximum removal of fluoride is 0.1 g. It is interesting to note that the same dose of other adsorbents exhibit comparatively low fluoride removal capacity.

Effect of Time

The effect of contact time on the adsorption of fluoride on SD derivatives was studied at pH 3. The results (Table 5) show that 85 to 90 % adsorption takes place in 30 min and for the remaining 10 to 15 % at least 90-120 min are required.

Table 6. Effect of temperature on K_d and removal of F^- (in %) by SD-derivatives*

Temperature, °C	K_d		
	TMAHP-SD	TEAHP-SD	DEAE-SD
25	984	661	462
30	1044	694	545
40	1354	1059	771
50	1698	1445	1047
Slope	-2172.4+/-156	-2993.0+/-47	-3170.6+/-28
R	0.994	0.999	0.999
ΔS^* J mol ⁻¹	-136+/-2.80	-117+/-0.84	-115+/-0.51
ΔG^* kJ mol ⁻¹	56.03+/-0.68	56.95+/-0.20	57.84+/-0.12
ΔH , kJ mol ⁻¹	15.55+/-0.87	22.37+/-0.26	23.64+/-0.16

An average of three sets. $[F^-] = 0.02 \text{ g dm}^{-3}$; Time of contact = 30 min; pH = 8; Volume = 0.1 dm^3 ; $\lambda_{\text{max}} = 570 \text{ nm}$; Adsorbent amount = 0.15 g

Table 7. Effect of nature and concentration of surfactants on the removal of fluoride by TMAHP-SD

Fluoride removal in % in the presence of Arkoline surfactants			
Concentration	SPW	N-65	HCS
0.05	60	61	63
0.10	57	60	65
0.15	54	61	68
0.20	50	60	71
0.25	42	60	74
0.30	38	60	71

An average of three sets.; $[F^-] = 0.02 \text{ g dm}^{-3}$; Adsorbent = 0.15 g; pH = 8; Time of contact = 30 min; Volume = 0.1 dm^3 ; Temperature = 30 °C.

Table 8. Effect of added ions on the removal of fluoride (in %) by TMAHP-SD

Concn., g dm ⁻³	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	HCO ₃ ⁻
0.01	60.0	60.0	60.0	58.0
0.02	61.5	61.0	59.0	56.5
0.03	60.5	60.5	60.0	55.0
0.04	60.0	61.5	60.5	54.0
0.05	61.5	61.0	61.5	52.0

An average of three sets; $[F^-] = 0.02 \text{ g dm}^{-3}$; ime of contact=30 min; pH = 8; Volume = 0.1 dm^3 ; Adsorbent = 0.15 g; $\lambda_{\text{max}} = 5$;

Effect of Temperature

The effect of temperature on the % removal of fluoride ion by starch derivatives was investigated at 30, 40 and 50 °C keeping all other parameters constant, these results are summarized in Table 6. The % uptake is highly dependent on $[F^-]$ in solution and increase with the increase in temperature, indicating that the process of adsorption is endothermic in nature.

Effect of Surfactants

The effect of nature and concentration of added surfactants on the adsorption of fluoride ion on the SD derivatives was investigated at room temperature. The

results in Table 7 show that the surfactants have a little effect on the adsorption of fluoride ion on the derivatives. The % removal of fluoride ion increased with the increase in added cationic surfactants concentration and decreased with the increasing [anionic surfactant], nonionic surfactants however have no effect. It appears that cationic surfactants neutralize some negatively charged sites of the adsorbent resulting in the improved migration of F^- on the SD derivative. The decreased adsorption by anionic surfactants may be attributed to the competitive adsorption of fluoride ion and the surfactants.

Effect of Added Co-ions

The effect of added co-ions e.g. Cl^- , SO_4^{2-} , NO_3^- and HCO_3^- on the % removal of fluoride ion was investigated with TMAHP-SD. The results (Table 8) indicate that the addition of co-ions in the range investigated has no appreciable effect, however the increase in $[HCO_3^-]$ slightly decrease the adsorption efficiency. This may be due to the competitive rate of adsorption of fluoride and bicarbonate ions. The observation is in accordance with the studies on activated alumina and magnesia.

The Mechanism of Adsorption

The mechanism of adsorption may be considered as a mixed effect of classical as well as of chromatographic adsorption. The introduction of glycedyl trialkyl ammonium groups in the SD derivatives imparts it a strongly cationic anion exchanger's character.²⁵ At lower pH, these exist in chloride form, the higher exchange capacity of these forms are well documented. Initially all the Cl^- ions of the TMAHP-SD are exchanged by F^- ions with the formation of first plateau, after the saturation point is reached i.e. the capacity of ion exchanger is exhausted the F^- ions are held by hydrogen bonding and weak VanderWaal's forces showing the rise in adsorption isotherm and the formation of another plateau.



where R_1 stands for cross linked cellulose (SD) and R for methyl or ethyl groups.

Saw-Dust is basically a wood cellulose which acquires a negative surface charge by virtue of primary hydroxyls on each D-glucopyranose units. The alkaline treatment of cellulose (SD), during the introduction of quaternary ammonium group, causes degradation of about 2 % with the loosening of the structure and the introduction of some acidic sites which do contribute to negative charge.²⁶ In acidic media the primary hydroxyls on the D-glucopyranose units may get protonated acquiring a partial positive charge which helps the fluoride ions to move in the vicinity of the SD molecule where hydrogen bonding comes into play and the fluoride ion is held by hydrogen bonding, resulting in the increased adsorption after exhausting the anion exchange capacity. It is the reason why the SD derivatives can not be completely regenerated.

Conclusion

The present study demonstrates that the cationic SD derivatives have potential to remove fluoride from drinking water without any other toxic affect. The study has following salient features:

The up take of fluoride ion is rapid in initial stages and decreases gradually while approaching equilibrium.

The major part of total adsorption, nearly 80 % of uptake at equilibrium takes in less than 30 minutes.

The up take of fluoride ion is significantly dependent on the pH of water, increases with the decrease in pH of water.

The up take of fluoride ion by SD derivatives is also influenced by the presence of surfactants. The up take of fluoride ion increases with the increase in [cationic surfactant], and decreases with the increase in [anionic surfactant], nonionic surfactants have no effect.

The material after the use can be burnt, thus pose no waste disposal problem.

References

- ¹Dean, H. T., Arnold, F. A. Jr. and Evolve, E., *Publ. Health Rep.*, **1942**, *57*, 115.
- ²Susheela, A. K., *Proc. Rome Symp.*, **1994**, IAHS Publ. No. 233.
- ³Shortt, H. E., Robert, G. R., Bernard, T. W. and Nayyar, A. S. M., *Indian J. Med. Res.*, **1937**, *25*, 553.
- ⁴Choubisa, S. L., Choubisa, D. K., Joshi, S. C. and Choubisa L., *Fluoride*, **1997**, *30*, 223.
- ⁵Gupta, S. C., Rathor, G. S. and Doshi, C. S., *Indian J. Environ. HLTH*, **1993**, *35*, 97.
- ⁶Choubisa, S. L., Choubisa L. and Choubisa, D. K., *Indian J. Environ. Health*, **2001**, *43*, 177.
- ⁷Sujana, M. G., Thakur, R. S., Das S. N. and Rao, S.B., *Asian J. Chem.*, **1997**, *9*, 561.
- ⁸Tokunaga, S., Haron, M. J., Wasay, S. A., Wong, K. F., Laosangthum, K. and Uchimi, *Int. J. Environ. Stud.*, **1995**, *48*, 17.
- ⁹Bulusu, K. R. and Nawlakhe, W. G., *Indian J. Environ Health* **1988**, *30*, 262.
- ¹⁰Bulusu, K. R. and Nawlakhe, *Indian J. Environ. Health*, **1990**, *32*, 197.
- ¹¹Bhatt, D. B., Bhatt, P. R., Prasad, H. H., Papat, K. M. and Anand, P. S., *Indian J. Chem. Technol.*, **2004**, *11*, 299 and references therein.
- ¹²Nawlakhe, W. G., Kulkarni, D. N., Pathak, B. N. and Bulusu, K. R., *Indian J. Environ. Health*, **1975**, *17*, 26.
- ¹³Kumar, N., *Yojana*, **1999**, *6*, 45.
- ¹⁴Gupta, K. R., Gupta, S. K. and Gupta, A. B., *Water Sci. Techn.* **1999**, *40*, 167.
- ¹⁵Davidson, A. M., Walker, G. S., Oli, H. and Lewins, A. M., *The Lancet*, **1982**, 785.
- ¹⁶Prakash A. and Prasadrao P. T. S. R. K., *Chem Environ. Res.*, **2006**, *15*, 27.
- ¹⁷Prakash, A. and Solanki, S., *Res. Ind.*, **1993**, *38*, 35.
- ¹⁸*Standards methods for the examination of water and waste water*, **1975**, APHA, AWWA, WPCF, Wshington DC 2005.
- ¹⁹Srivastava, S. K., Bhattacharjee, G., Tyagi, R., Pant, N. and Pal, N., *Environ. Technol. Lett.*, **1988**, *9*, 1173.
- ²⁰Gills, C. H. and MacEvan, T. H., *J. Chem. Soc.*, **1960**, 3973.
- ²¹Gills, C. H., Easton, I. A. and Mackay, G., *J. Chem. Soc.*, **1964**, 4495.
- ²²Freundlich, H., *Colloidal and Capillary Chemistry*, **1928**, Methuen, London.
- ²³Langmuir, I., *J. Am. Chem. Soc.*, **1918**, *40*, 1361.
- ²⁴Brunauer, S., Emmet, P. H. and Teller, E., *J. Am. Chem. Soc.*, **1938**, *60*, 309.
- ²⁵*Durolite Ion Exchange Manual 1960*, Western Division of Diamond Alkali Company, Red Wood City, California USA.
- ²⁶Young, R. A. and Liss, L., *Cellul. Chem. Technol.*, **1985**, *24*, 273.

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