HOUSEHOLD DEFLUORIDATION OF DRINKING WATER USING ACTIVATED ALUMINA

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SUMMARY: This paper deals with the development of a simple "Point of Use" domestic defluoridation unit (DDU) using indigenously manufactured activated alumina (AA) and its evaluation for adoption in rural areas in India. Different products of indigenously manufactured AAs were screened for fluoride uptake capacity. Using 3 kg of AA, around 500 L and 1500 L of safe water ($F^- \leq 1.5$ mg/L) could be produced when the raw water fluoride was 11 and 4 mg/L respectively (alkalinity 450 = mg$CaCO_3$/L). Exhausted AA was regenerated with alkali and acid using the simple `Dip procedure'. After 30 cycles of regeneration, the decrease in capacity was only marginal. Effect of raw water constituents on fluoride uptake was studied in the laboratory using simulated as well as natural waters. Results indicated that there was a decrease in treated water volume as raw water alkalinity increased. Presence of 250 mg/L sulphate in raw water decreased the AA fluoride uptake capacity by 15 %. Nearly 400 DDUs have been distributed in tribal areas of Dungarpur district in Rajasthan, India for field evaluation. Reports received till now have been very encouraging.

Key words: Defluoridation; Activated Alumina; Alumina; Domestic Defluoridation Unit Regeneration.

INTRODUCTION

Fluorosis is a chronic menace affecting a large population world-wide. As per the last survey conducted by the Rajiv Gandhi National Drinking Water Mission (RGNDWM) in India, around 25 million people in 8100 villages using mainly ground water sources for culinary purposes, are exposed to health risks related to fluorosis. Taking the health effects into consideration, WHO has set the guidelines of 1.5 mg/L as the maximum permissible limit for fluoride in potable water.[1] Surface waters seldom contain fluoride beyond this level, whereas excess fluoride may be present in ground waters depending on the presence of fluoride rich minerals as well as hydrogeological conditions.

Defluoridation of drinking water has to be practiced, if ground water sources have fluoride levels beyond the recommended limit. Methods practiced for removal of excess fluoride can be divided broadly into two categories, namely precipitation and adsorption. Precipitation methods depend on the addition of chemicals to the raw water, which leads to the formation of fluoride precipitates or adsorption of fluoride onto the formed precipitate.[2-6] Lime and alum are used either individually or in combination. The Nalgonda Technique, as developed in India in 1975, involves the addition of alum and lime.[5] It has been used in domestic as well as at community levels in India.[6] Limitations of these methods are: the daily addition of chemicals; large volume of sludge production; and not effective with water sources having high total dissolved solids (TDS) and hardness.[7] In adsorption method, fluoride of raw water is retained on the adsorbent due to physical, chemical or ion exchange interactions. Although wide variety of adsorbents have been used for defluoridation,[8-16] activated alumina (AA) technology has been the method of choice in developed countries.[12-13] AA, Alcoa F-1 is used in most of these studies and many defluoridation

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plants based on this technology have been installed.[17-18] Laboratory studies on the fluoride uptake using indigenously manufactured AA, grade G-80 was reported by Sharma[19] and by Bulusu and Nawlakhe.[20]

The present study was undertaken to screen various grades of indigenously manufactured AA, development of a `point of use' defluoridation unit for domestic use and its evaluation for adoption in rural areas in India.

MATERIALS AND METHODS

Six grades of AA used for this study are as follows: G-87 and AD-101 supplied by Indian Petrochemicals Ltd (IPCL), Thane, India, pulverized and screened to an effective grain size of 0.3-0.85 mm. OA-25 (1) and OA-25 (2) supplied by M/S Oxide India Ltd., Durgapur, India. Particle size of the supplied material was 0.3-0.6 mm. AA-P (0.4-0.6 mm) supplied by Pavan Industries, Hyderabad, India. AA-B supplied by Indian Alumina Industry Hyderabad was spherical in shape with an average diameter of 1 mm. AA was washed with tap water to remove fine dust and then air dried before using for the defluoridation study.

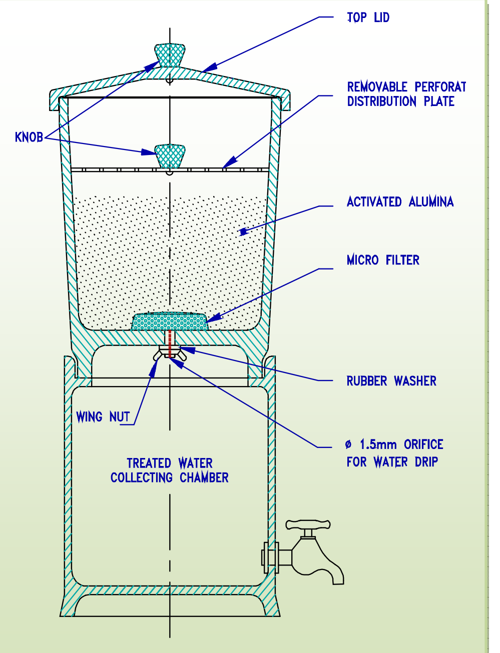

FIGURE 1. Domestic Defluoridation Unit.

Domestic defluoridation unit (DDU). The unit consisted of basically two chambers made of the material of choice such as stainless steel (SS), copolymer plastic etc. Upper chamber was fitted with a microfilter as shown in Figure 1. This had an orifice at the bottom to give a flow rate of about 12 L/h. This chamber was charged with 3 kg of AA and the depth was 17 cm. Perforated plate made of SS was placed on the top of AA bed to facilitate uniform distribution of raw water containing fluoride onto the bed. Upper chamber was covered with the lid. Lower chamber was provided with a tap to withdraw the treated water. If desired, lower chamber can be replaced with an earthen pot in rural areas which not only lowers the initial cost but also keeps water cold in summer months.

Use of the filter is very simple. High fluoride bearing water is filled in the upper chamber. Water percolates through AA bed, where fluoride is adsorbed onto the adsorbent. Treated water, collected in the lower chamber, can be withdrawn as and when needed.

Screening of AA products. This study was conducted by taking 3 kg of different grades of AA in domestic defluoridation unit (DDU). The filter was operated similar to its expected use in the field. Raw water was filled in the upper chamber intermittently (three to four times a day) and the fluoride concentration in treated water was periodically determined. AA was taken as exhausted when the F^- concentration of the treated water exceeded 1.5 mg/L. Simulated raw water was prepared using IIT Kanpur tap water spiked with 10 mg/L fluoride. Tap water characteristics are presented in Table 1.

TABLE 1. Tap water characteristics.

Parameter	Unit	Value
pH	-	7.8
Alkalinity	mg $CaCO_3$/L	400
Total dissolved solids	mg/L	636
Sulphate	mg/L	85
Hardness	mg $CaCO_3$/L	160
Fluoride	mg/L	0.8

Regeneration of AA. The exhausted AA was regenerated using NaOH and H_2SO_4 for successive reuse for defluoridation. AA was transferred into nylon mesh bag which was then dipped in 8 L of 0.25 N NaOH (10 g/L) for eight hours (preferably overnight). Occasional lifting and stirring facilitates better contact between the regenerant and AA. After draining NaOH from nylon bag, AA was washed with raw water and then transferred to a bucket containing 8 L of 0.4 N H_2SO_4 for 4-6 hours. As in the case of alkali, lifting the bag and dipping again facilitates good contact of the regenerant with AA. Subsequent wash with raw water till the pH raises to 6-7 makes the AA ready for the next defluoridation cycle.

Raw water characteristics vs. removal capacity. This study was conducted in the laboratory using simulated as well as natural waters. Batch sorption tests were conducted for studying the effect of pH. Fluoride spiked distilled water (F^- = 20 mg/L) and pH adjusted to the desired value using either 0.1 N HCl or 0.1 N NaOH after adding 500 mg AA per 250 mL. The contents were agitated in a rotary shaker. After 4 hours of contact time, the sorbent was separated and fluoride concentration was estimated in the supernatant.

Effect of alkalinity, sulphate, hardness and initial fluoride concentration was evaluated using simulated as well as natural waters in DDU. Simulated water used was IIT Kanpur tap water spiked with 10 mg F^- per litre and the desired quantity of other constituents. DDU was operated in similar way as described earlier. Volume of safe water produced was determined in each case.

Field testing of the DDU. Under a pilot scale fluorosis control project, in Dungarpur district in Rajasthan, 1945 users in 388 households in four villages are using Domestic Defluoridation Units (DDUs) since December, 1996. The distribution of DDUs was preceded by intensive awareness generation programme among community members about the ill health effects of high fluoride water and preventive measures, capacity building and baseline data collection including prevalence of dental and skeletal fluorosis and water quality of all drinking water sources. The project is being implemented by NGOs in close cooperation with district administration and active community participation.

The raw water characteristics of ground water in the four villages are as follows: Fluoride 2.5 -6.0 mg/L, Alkalinity 120 - 480 mg/L, TDS 390 - 1287 mg/L and pH 7.0-7.8. The performance of DDUs is being monitored on a monthly basis.

TABLE 2. Comparative performance of different indigenously manufactured Activated Alumina.Fel! Bokmärket är inte definierat.

Grade	Grain size (mm)	Volume of water treated for different cycles, L									
		1	2	3	4	5	6	7	8	9	10
G-87 IPCl, Thane	0.30-0.85	500	475	550	475	450	490	460	400	400	525
AD-101 IPCL, Thane	0.30-0.85	850	725	700	640	460*	600	550	500	450	300
AA-B	1.0	500	330	350	475	410	450	450	400	290*	450
OA-25(1)	0.30-0.60	650	475	350	250	Operation discontinued					
OA-25(2)	0.30-0.60	725	600	450	300	Operation discontinued					
AA-P Operation	0.40-0.60	800	400	250*	600	450	350	350	300	300	250

*Operated on continuous flow mode using a pump.

Fluoride Analysis. Fluoride in water samples was estimated using SPANDS reagent[21] as well as orion portable ion meter and fluoride specific electrode following the procedure given in the manufacturer's manual. Alizarin visual method[21] was modified for its use in rural areas. Ten mL water sample was taken in a marked flat bottom 15 mL glass bottle. Ten to fifteen drops of commercially available fluoride reagent (supplied by Century PP Industries, Jodhpur, India) was added. Persistence of pink colour even after one hour, indicates that fluoride is within permissible levels. On the other hand, yellowish tinge indicates high fluoride. This is a qualitative test mainly aimed for use in rural areas.

RESULTS

Screening AA products. Results of the screening study are presented in Table 2. Exhausted AA was regenerated and reused for ten defluoridation cycles to assess the regeneration and reuse efficiency which determines the field application potential of different grades of AA. Among the six grades used in the present study, OA - 25 (1) and OA-25 (2) exhibited a significant loss in treated water volume after each successive cycle. G-87 produced an average of 450-500 L of safe water per cycle and exhibited minimum loss in fluoride uptake capacity. Although treated water volume was higher in the first cycle with AD 101 as compared to G-87, there was a decrease during subsequent defluoridation cycles. Decrease of 15-20 % in treated water volume with AA-B as compared to G-87 can be attributed to its larger particle size of 1 mm. AA-P yielded 800 L of treated water in the first cycle, which was reduced to 400 L in second cycle itself. These results indicate, among the screened grades of indigenously available AA grades, G-87 and AD-101 both supplied by IPCL and AA-B supplied by AI, Hyderabad are better suited for field application. All further work was carried out with G-87.

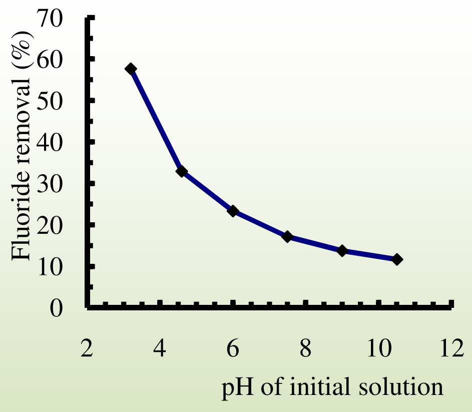

FIGURE 2. Fluoride removal vs. initial pH. Initial F^- = 20 mg/L. AA dosage = 2.0 g/L..

Water constituents vs. defluoridation capacity. The fluoride uptake study in the pH range of 3-9 showed a decrease in the binding capacity of AA from pH 5 to 9 with no optimum pH, cf. Figure 2. When pH was raised from pH 5 to 8, fluoride uptake decreased by 12%.

Alkalinity increase from 400 to 600 and 800 mg/L decreased the treated water volume from 500 L to 430 L and 350 L respectively when simulated fluoride spiked water of 10 mg F/L was used as raw water. Results of sulphate and fluoride spiked simulated water showed that the presence of 250 mg/L sulphate in raw water reduces the fluoride uptake capacity by 15 %. Hardness up to 800 mg/L did not significantly affect the performance of DDU. Increase in fluoride concentration decreased the treated volume output, although, fluoride uptake capacity per kg AA increased (Table 3).

TABLE 5. Effect of Initial Fluoride Concentration on the Performance of DDU

Initial Fluoride Concentration,	mg/L	3.8	6.8	10.8
Vol. of Treated Water,	L	1550	870	500
Fluoride Uptake Capacity	mg/g AA	1.55	1.74	1.83

Natural waters having different concentrations of fluoride, alkalinity, sulphate and total dissolved solids were tested to determine the effect of these constituents on fluoride uptake capacity of AA. Characteristics of these waters and treated water volume are given in Table 4.

Results indicate, among characteristics of raw water considered in the present study, defluoridation cycle is significantly affected by the raw water alkalinity.

TABLE 4. Performance of DDU Treating Natural Waters from Rajasthan and Uttan Pradesh

Site No	Place of sample collection	Raw water parameters					Vol.of Treated Water (L)
		F^- conc (mg/L)	alkalinity (mg/L $CaCO_3$)	TDS (mg/L)	SO_4^{2-} (mg/L)	pH	
1	Belsi, Unnao, UP	3.3	580	780	38	8.37	1300
2	Nainpura, Jaipur, Rajasthan	3.7	1225	5880	1300	7.47	470
3	Prahladpura, Jaipur, Rajasthan	4.4	1320	3080	168	7.17	540
4	Padampura,Jaipur, Dungarpur	5.0	1100	1960	85	8.34	580
5	Dungapura, Jaipur, Rajasthan	5.0	634	2100	-	7.50	590
6	Padampura, Jaipur, Rajasthan	5.1	1100	2210	250	7.50	660
7	Dungarpur, Rajasthan	6.0	350	1050	-	7.91	820
8	Makkar, Unnao, UP	6.5	500	990	150	7.60	810
9	Jaipur, Rajasthan	7.0	475	1200	24	8.09	460
10	Maharajpura, Jaipur	8.3	775	3080	730	7.29	330
11	Sivadaspura, Jaipur	9.7	1025	2310	16	7.36	300
12	Sivadaspura, Jaipur	9.8	900	1610	37	8.46	310
13	Padampura, Jaipur	17.0	990	1368	28	7.89	185

- Not Determined

Field Evaluation. The key findings of the field performance monitoring of 388 DDUs till June 1997 are as follows:

1. Households are using DDU regularly and expressed satisfaction;
2. No major operational problems were reported excepting leakage from micro-filter joint due to improper tightening of wing nut;

3. In all cases, fluoride level in treated water was within the permissible limit of 1.5 mg/L;
4. It is feasible to carry out AA regeneration at the village level;
5. Households were using 25-30 litres of water per day. Many households complained of inadequate capacity (9 Litres) of upper and lower containers;
6. Out of 179 respondents in Rayana and Kankri villages, 178 reported increased appetite, 116 reported decrease in gas formation, 158 reported relief in joint pain, 14 reported decrease in thirst for water and 28 felt less tired. It is noteworthy that all households reported symptomatic relief; and
7. The per-capita cost is 4-6 U.S.$ and cost per regeneration is 0.50 US$ per DDU. The frequency of regeneration is once in 1.5 to 3 months depending on raw water characteristics.

DISCUSSION

Fluoride uptake capacity, acid resistively and attrition loss of AA are probably three important parameters which are to be considered for field application of this process. Fluoride uptake capacity after successive regeneration reflects the efficiency of regeneration as well as loss of efficiency due to acid treatment as it is one of the regenerants employed. Further, repeated reuse of AA without much decrease in fluoride uptake capacity also indicates that attrition loss is not significant.

Alcoa F-1 (Alcoa Company, USA) has been extensively used for defluoridation of drinking water in western countries.[12,16,17] Defluoridation plant at Barlett, Texas, USA, which used Alcoa F-1, was constructed in 1952 and continued to operate essentially with the original medium for 25 years.[17] Maier *et al.*[12] reported that the plant showed an exchange capacity of 1272 mg F^-/kg of AA, when the raw water contained 8 mg F/L. A high exchange capacity of 3680 mg/kg of AA was observed for the same material at defluoridation plant in Arizona, USA.[18] In this plant, raw water pH was decreased to 5.5 prior to defluoridation. Exhausted AA was regenerated by successive treatments of alkali and acid. Our results have shown that G-87 exhibits an average capacity of 1833 mg /kg of AA at raw water pH 8.2-8.4 when fluoride concentration was 10 mg/L. There was no loss up to 5 cycles whereas loss of 15 % was observed after 35 cycles (data not shown). This reflects the regeneration efficiency as well as minimum loss due to acid treatment and attrition after prolonged use. Bulusu and Nawlakhe[22] reported a decrease of 83 % in fluoride uptake capacity after 20 defluoridation cycles, which remained more or less constant even after 40 cycles. 0.1 N HCl was used as regenerant by these investigators. Clifford[16] has reported that essentially complete removal of fluoride from exhausted AA is possible by successive treatment of alkali and acid. Our results are similar to that of Clifford.[16] It is well documented in literature that pH, alkalinity and initial fluoride concentration of water significantly affect fluoride uptake capacity.[13,23] Figure 2 shows that G-87 does not exhibit discrete optimum pH. This is in contrast to the reported behaviour of Alcoa F-1,[15] which exhibits maximum uptake at pH 5.0. The decrease as pH is raised from 5 to 8 is around 12% with G-87, where as it is 40% with Alcoa F1. Application of defluoridation technology with Alcoa F1 generally involves prior acidification to pH 5 to achieve maximum fluoride uptake followed by the neutralization of treated water.[18] However, Hao and Huang[15] have shown that the soluble alumino fluoro complexes are formed at pH<6 resulting in the presence of aluminium ions in the treated water. Hence they suggest that it may be preferable to carry out defluoridation at a pH>6. Barbier and Mazounie[23] reported that acidification to pH 5.0 is not economically feasible if the raw water alkalinity is high due to the resultant buffering characteristics. However, raw water pH could be decreased to 7 to minimise hydroxyl ion competition. Fluoride uptake capacity of 2.24 mg/g AA was observed by these investigators when the raw water fluoride concentration was 11.5 mg/L and alkalinity of 395 mg/L.

A tap attachable defluoridation home unit was developed by Svedberg[24] using commercially available AA which was pre-treated by the manufacturer for the specific application. An exchange capacity of 1000 mg F/L was observed for raw water with fluoride and alkalinity concentration ranging from 7-10 mg/L and 80-160 mg/L respectively at pH 8.2. Our results show that even at a pH 8.2-8.4 and an alkalinity of 400 mg/L fluoride exchange capacity of 1833 mg/kg AA was observed. Results with simulated as well as natural waters showed that increase in alkalinity decreases the fluoride uptake capacity of G-87. Similar behaviour was reported for other grades of AA. Bicarbonate ions like hydroxyl ions probably compete for fluoride binding sites of AA. However it should be mentioned that there was no significant decrease in the bicarbonate concentration after defluoridation.

Clifford[16] has reported that sulphate affected fluoride uptake capacity beyond 250 mg/L. Our results are also similar to this observation. Treated water volume was drastically reduced with natural water having high bicarbonate and sulphate levels.

From the results of this study it is clear that DDU is simple to use and its user acceptability is excellent. While it is too early to arrive at a conclusion on its long term sustainability in rural areas besieged with adverse indicators such as low income generation, illiteracy and a lack of awareness about the water quality and its impact on human health, the initial results are encouraging. The next twelve months will confirm if users contribute towards regeneration of AA and regeneration is carried out efficiently by a village entrepreneur with out external support. However, it is clear that awareness generation among users, local capacity building and involvement of NGOs and private sector in service delivery are essential components for ensuring sustainability of domestic defluoridation.

Furthermore it can be concluded that indigenously manufactured AA is well suited for fluoride removal from drinking water in domestic defluoridation units.

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