



DEVELOPMENT OF NEW LOW COST DEFLUORIDATION TECHNOLOGY (KRASS)

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ABSTRACT

Systemic fluorosis is an endemic problem in several developing countries. In India 15 states are endemic for fluorosis, of which 5 have indicated hyperendemicity for fluorosis in all districts. WHO standards permit only 1 mg/l as a safe limit for human consumption. People in several districts of Rajasthan are forced to consume water with fluoride concentrations of up to 44 mg/l which has resulted in permanent deformities, joint pains, general debility and misery. About 60% of fluoride intake is through water. Considerable work on fluoride removal from water has been done all over the world. However a safe, efficient, free from residual aluminium in treated water, and cost effective defluoridation technique/process is not available and needs to be developed in order to prevent the occurrence of fluorosis. This paper describes the development of a defluoridation process which differs from the known processes in its simplicity, cost effectiveness and results in traces of residual aluminium in treated water. The parameters like fluoride concentration, temperature, pH, alkalinity, humidity and total dissolved solids of input water do not affect this process. © 1999 IAWQ Published by Elsevier Science Ltd. All rights reserved

KEYWORDS

Alum recharging; defluoridation filter; fluorosis; residual aluminium.

INTRODUCTION

Long term consumption of high fluoride water can cause fluorosis. Systemic fluorosis is an endemic problem in several developing countries (India, Pakistan, Africa, Far East countries etc.) and has been reported sporadically in other parts (Argentina, Japan, Canada etc.) of the world. In India 15 states are endemic for fluorosis (Susheela, 1991). Out of these 15 states, 5 states have indicated hyper-endemicity for fluorosis in all districts. Rajasthan is one state where all the 32 districts have been identified as fluorosis prone areas. As per the survey carried out by the Public Health Engineering Department, Rajasthan in the years 1991-93, for status of water supply in villages/habitations, nearly 16560 (about 20% of the total) villages/habitations were found to be affected by excess fluoride (more than 1.5 mg/l), out of which 5461 villages/habitations had fluoride higher than 3 mg/l. The WHO standards permit only 1 mg/l fluoride in drinking water as a safe limit for human consumption (WHO, 1970, 1984). As per the manual on Water Supply and Treatment (CPHEEO, 1991) the permissible limit of fluoride in drinking water is 1.0-1.5 mg/l and the U.S. Public Health Service Drinking Water Standards allow a fluoride concentration in drinking water from 0.8 to 1.7 mg/l (USPHS, 1962).

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Permissible limits of fluoride in drinking water are dependent on the environmental temperature of the area concerned. The fluoride temperature relationship is based on the premise that children drink more water in warm climates, and therefore the fluoride content in the water supply should be reduced to prevent excessive total fluoride consumption (Choi and Chen, 1979).

Fluoride also has beneficial effects on human beings. Fluoride up to 0.6 mg/l in drinking water is required to prevent dental caries.

People in several districts of Rajasthan, India are consuming water with fluoride concentrations of up to 44 mg/l. This has resulted in permanent deformities, joint pains, general debility and misery. Fluorosis not only affects older persons but there is ample evidence that even newborn babies and children of younger age have also been its victims. It not only affects the body of a person but also renders them socially and culturally crippled. There is a need to develop a well thought out strategy to attack this problem which requires urgent attention from both medical as well as social workers.

Commonly used defluoridation techniques and their drawbacks are given below

Nalgonda process (NA)

This process involves direct addition of lime in water to maintain the pH of water and addition of a known quantity of alum in water directly depending on water fluoride content (Nawlakhe *et al.*, 1975). The quantity of lime and alum depends upon quality and fluoride content of water, therefore it is difficult to control the alum dose as it is different for each source of water. It is a cumbersome technique and hence is not suitable for use by illiterate persons, who need it most. Further, the process can be used only for water having a fluoride content of less than 10 mg/l. There is a high free residual aluminium content available in output water, when treated with alum in this process and in addition to this, when this treated water is boiled in aluminium utensils (a common practice in Indian kitchens), it further aggravates the free aluminium concentration in treated water. It is reported that the residual aluminium ranges from 2.01 mg/l to 6.86 mg/l in this process which far exceeds the maximum limit of 0.2 mg/l as prescribed in IS 10500 (Selvapathy and Arjunan, 1995). Also the taste of the treated water is generally not acceptable. It is relevant to note that aluminium is a neurotoxin and a concentration as low as 0.08ppm of aluminium in drinking water is reported to have caused Alzheimer's disease (Davidson *et al.*, 1982; Martyn *et al.*, 1989).

Activated Alumina (AA)

It is an expensive process. Reactivation of filter material is cumbersome (done by treatment of bed by acid and alkali) and it can be done only with the help of trained persons, who are generally not available in most of our villages (Bulusu and Nawlakhe, 1988, 1990; Vencobachar and Iyengar, 1996). This process also results in moderately high residual aluminium in output water ranging from 0.1 ppm to 0.3 ppm

Other processes

Processes like electro-dialysis, reverse osmosis etc. require special equipment, a lot of manpower, especially trained persons to operate, need constant maintenance and are very expensive (Killedar and Bhargava, 1988; Solsona, 1985).

Keeping in view drawbacks of the above defluoridation methods it was felt that a safe, efficient and cost effective defluoridation technique needs to be developed in order to prevent the occurrence of fluorosis. The process should be suitable for any fluoride concentration, pH, TDS, alkalinity and temperature of input water; should have residual aluminium in treated water well below the permissible limit; and it could be handled by our illiterate population without the help of any trained person once the process has been demonstrated to them.

The present paper describes a study which led to the development of a direct flow-through type of column for defluoridation, which requires a simple procedure for recharging once it is exhausted. The defluoridation studies were conducted in columns using a support material (under patent) in a downflow mode and the

process was named as the KRASS process (Gupta, 1997). Effects of recharging solution quantity, initial fluoride concentration and pH on the process efficiency were studied. An attempt was made to develop a domestic filter suitable for a rural family. Aluminium concentration in the treated water was also measured and compared with aluminium in treated water by NA and AA methods. Changes in hardness, alkalinity and total dissolved solids after treatment were also observed. A detailed cost analysis for these processes was also carried out.

MATERIALS AND METHODS

The defluoridation experiments were carried out in 5 cm and 6 cm diameter PVC columns of length 64 cm and 122 cm respectively run in continuous downflow mode. A low cost support material (under patent) was used to fill the columns. The columns after exhaustion were regenerated with 10% alum solution. Effect of parameters like influent F, pH and quantity of recharging solution were studied on fluoride removal capacity. A domestic water filter of 22 cm diameter was operated subsequently and its performance data were used for detailed cost analysis. A column of 5 cm diameter and 34 cm length with Activated Alumina as filling material was also operated to measure aluminium concentration in treated water. Comparisons were made with NA and AA techniques for fluoride removal efficiency, residual aluminium and costs.

Tap water was used for the preparation of high fluoride influent water. Sodium fluoride NaF of reagent grade was used to increase the influent fluoride to a range of 3.1 to 24.1 mg/l which is commonly found in Rajasthan.

Alum of commercial grade was used for preparation of 10% strength recharging solution. A sieve analysis of the support material was made to determine grain size distribution using IS Sieves of 42.5 micron, 300 micron, 150 micron and 75 micron pore sizes.

Column operation

High fluoride water was run into the columns above the surface of the material and a constant water level was maintained. Samples of treated water were collected for analysis and the volume and the collection time were recorded. The operation of the initial cycle was terminated when the residual fluoride in the composite effluent water reached 1.5 mg/l to prevent over-exhaustion of support material. The column was now charged with 10% alum solution and the run was continued until the residual fluoride in my sample of effluent or composite sample reached more than 2.0 mg/l. Each column was recharged 6-7 times before rejecting the support material. The flow rate was maintained at 0.6-0.7 l/h in the column by out-flow control.

Analytical procedure

Fluoride ion concentration was measured using the Ion Selective Electrode Method through the ORION Ion meter Model 94-09. The pH of water was measured through 'Digital pH Meter APX 17Y' control dynamics. Conductivity of water was measured through conductivity meter Type MC-1 (Mark IV), Electronic Switchgear (London) Ltd. in μmhos . The TDS was taken as 2/3 of the conductivity in ppm. The total alkalinity of water was determined by titration with 0.02 NH_2SO_4 to methyl orange end point and expressed in CaCO_3 scale. The total hardness of water was determined by titration with standard EDTA solution. Erichrome Black T was used as indicator. For all the above parameters procedures given in 'Standard Methods' (APHA, 1989) were followed. Aluminium in the water samples of treated water was measured with the help of spectrophotometer 'Spectronic 21 D, Milton Ray' by Aluminone method given in 'Examination of Waters and Water Supplies' (Taylor, 1958).

RESULTS AND DISCUSSION

Grain size of support material

It was observed that more than 50% of the support material was retained on the 75 micron IS sieve. Cumulatively 75% of the support material was finer than the 300 micron IS sieve The D_{10} size as found

from the frequency distribution curve was 0.08 mm and the uniformity coefficient was 2. The uniformity coefficient of the sand used in slow sand filters is 3 to 5 and D_{10} size is 0.25 to 0.35 mm. Though the effective size of this material was less than that of a slow sand filter, due to a lower uniformity coefficient the flow rate through it, was comparable to slow sand filtration.

Optimization of recharging solution

Table 1 shows the results of observed fluoride removal capacity of alum with quantity of recharging solution. It is clear from the table that fluoride removal capacity of recharged support material increased with a decrease in the quantity of recharging solution. Since the capacity continuously increased with a decrease in alum quantity it is possible that a lesser quantity or a lower concentration of alum solution may give still better results. Three concentrations of alum regenerant viz. 2.5, 5.0 and 10.0 percent were investigated for regeneration of Defluoron 2. The defluorating capacity was maximum with 5.0 percent concentration of alum solution and decreased appreciably with 10.0 percent because of the high acidity in the latter (Thergaonkar *et al.*, 1969). Similar trials in the present system may help in optimising the quantity of alum recharging solution.

Table 1. Observed fluoride removal capacity of alum with quantity of recharging solution

Recharging solution (ml/kg)	Maximum fluoride capacity (mg/kg)
250	4313
367	3005
570	1903
700	1044.0
1000	761.0

Fluoride removal efficiency with changes in chemical parameters

Figure 1 represents the performance data of a typical column run with influent fluoride concentration of 6.06 mg/l and pH of 7.83. Table 2 shows the results of fluoride removal capacity with increase in initial fluoride concentration and decrease in pH. It is clear that fluoride removal capacity of recharged support material increased with increase in initial fluoride concentration and decrease in pH of influent water to a certain extent.

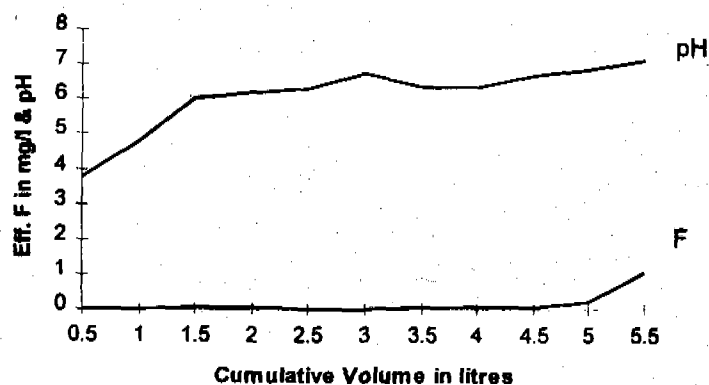


Figure 1. Cumulative volume V/S effluent F and pH influent F = 6.06 mg/l, pH = 7.83.

Table 3 shows the results of fluoride removal capacity with increase in both initial fluoride concentration and pH. It is clear that fluoride removal capacity of recharged material also increased slightly with increase in initial fluoride concentration and pH to a certain extent.

Table 2. Fluoride removal capacity with increase in initial fluoride concentration and decrease in pH

Initial fluoride concentration (mg/l)	pH	Capacity (mg/kg)
5.59	9.054	884
5.72	8.699	970
6.32	8.142	1056
8.62	7.57	1337
11.5	7.50	1433
11.6	7.00	1430

Table 3. Fluoride removal capacity with increase in both initial fluoride concentration and pH

Initial fluoride concentration (mg/l)	pH	Capacity (mg/kg)
9.17	4.89	865
11.6	7.00	1430.00
11.5	7.5	1433.00
11.73	7.72	1831.00
12.14	7.797	1903.00
13	8.15	1441.75

Maximum fluoride removal capacity was observed for an initial fluoride concentration range of 11.5 to 12.5 mg/l and pH range 7.0 to 8.0 of influent water. The pH of the effluent was initially near about 4 but rose steadily towards the raw water pH with the progress of the run.

At the beginning of the operation, the pH was 4-5 and as the runs progressed it gradually reached a value of 6.9 to 7.1 and fluoride concentration in the effluent was less than 2.0 mg/l. In a study on Defluoron-2 process, at the beginning of the operation the pH was 4.73.1 and as the runs progressed it gradually increased to a value of 6.042. Beyond a pH value of 6.5, there was a steep fall in the fluoride removal capacity and the operation was stopped (Thergaonkar *et al.*, 1969).

The alkalinity in treated water was between 5 to 17% of influent alkalinity at the beginning of the operation. At a fluoride concentration of 1 to 1.75 mg/l in the effluent the alkalinity varied from 39 to 80% of the influent alkalinity. In Defluoron-2 process the alkalinity was between 3 to 7% of influent alkalinity at the beginning of the operation and at a fluoride concentration of about 1 mg/l in the effluent the alkalinity varied from 16 to 23% of influent alkalinity (Thergaonkar *et al.*, 1969).

The hardness of the treated water was between 8 to 73% of influent hardness in this process. In Defluoron-2 process hardness was only 8% of influent hardness (Thergaonkar *et al.*, 1969).

Total dissolved solids were initially more but after treatment of about one litre of water these decreased in the range 50 to 85% of influent TDS.

Presence of aluminium in drinking water has been a major cause of concern as aluminium is a neuro-toxin and at 0.08 mg/l has been reported to result in Alzheimer's disease. The present WHO limit is 0.2 mg/l. Aluminium in treated water was high at the beginning of the operation but as the runs progressed it decreased to traces for the rest of the run. In this column the recharging solution was used more than the optimized value. After rejection of initial treated water having a pH less than 5, the composite effluent will have only traces of aluminium. By using the optimized value of recharging solution the aluminium in the effluent may be further reduced.

In the Nalgonda technique the dose of alum and lime increases with increase in influent fluoride concentration and alkalinity. With increase in alum dose the fluoride concentration in the treated water decreases while the residual aluminium increases. Aluminium content of the water increases after pH adjustment using lime. This may be due to mobilization of aluminium into solution from the precipitated aluminium compounds by the alkali addition. Aluminium was found in the range of 2.01 to 6.86 mg/l after

pH adjustment in the supernatant water when alum dose was 4-20 mg/l to reduce an initial fluoride concentration of 1.8 to 8.0 mg/l (Selvapathy and Adunan, 1995).

Aluminium was found in a range of 0.1 to 0.3 mg/l in the treated water obtained through an Activated Alumina column. Whereas in treated water through the KRASS technique, after rejecting the initial 10 % of the treated water in a cycle it was reduced to traces. Aluminium is now regarded as a neurotoxin and is far from innocuous. WHO (1984) has recommended a guide line limit of 0.2 mg/l in drinking water.

The experiments on a 22 cm diameter steel filter showed that the maximum fluoride removal capacity of recharged support material was achieved at an influent water fluoride concentration of 11.28 mg/l and pH 7.47. This capacity reduced up to 50% with the reduction in influent fluoride concentration to 6.23 mg/l. The fluoride removal capacity of recharged support material was further increased by decreasing slightly the quantity of recharging solution, i.e. from 267 to 250 ml per kg of support material. pH of the initial effluent water was about 5 then it increased slowly to the initial pH value of the influent. By rejecting initial effluent water, the pH of usable treated water will be more than 6 and fluoride concentration within 1.50 mg/l.

Raw water of initial fluoride concentration 6.23 to 11.3 mg/l and pH 5.12 to 8.37 could be treated through a domestic filter using the KRASS technique by recharging with 10% alum solution for various fluoride concentrations, whereas in NA technique the dose of alum and lime depends upon raw water fluoride concentration (Nawlakhe *et al.*, 1975). The dose of lime and alum increases as fluoride concentration and alkalinity in raw water increases. Thus dosing of alum can easily be regulated in the KRASS process. With increase of alum dose the residual aluminium also increases in treated water and aluminium was found up to 6.86 mg/l (Selvapathy and Munan, 1995).

The AA method requires cumbersome regeneration by acid/alkali and aluminium concentration in a column run of activated alumina in our laboratory was also found in an objectionable range of 0.1 to 0.3 mg/l. In the KRASS technique the aluminium concentration was observed only in traces. The regeneration of filter was also simple.

Therefore by using the KRASS technique excess fluoride could be removed without major limitations of other processes and this new process proved to be very easy to operate at domestic level.

Cost analysis

The calculated cost of treatment per litre treated water through KRASS, AA and NA techniques was found to be 2.5, 4.3 and 2.3 paise respectively. The KRASS process was found cost effective and with a further optimization of the process the cost may be brought down further.

CONCLUSIONS

The excess fluoride removal from drinking water was possible using low cost support material in the KRASS technique, with 10% alum solution used for recharging. The fluoride removal capacity of recharged support material increased on decreasing the quantity of recharging solutions per unit of bed material.

Maximum fluoride removal capacity observed was 4g fluoride per kg of alum used for recharging the column. The fluoride removal capacity of recharged support material increased on increasing influent fluoride concentration and pH. The optimum ranges being 11-12 mg/l for influent fluoride concentration and 7-8 for pH. Fluorides from water could be removed for an influent pH range 4.29-9.054. More than 65 litres of treated water could be obtained through a domestic filter of KRASS technique in one recharge which is sufficient for a rural family of 6-7 members, for one day. Operation of the domestic filter was very easy and it can be handled by any adult in the house. Aluminium in traces only was found in treated water through this process whereas up to 7 mg/l aluminium concentration has been reported in the NA technique. Aluminium up to 0.3 mg/l was found in treated water through the AA process. The KRASS process was found cost effective. Cost of treated water was equivalent to that of the NA technique but less than that through the AA method.

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