Defluoridation

Introduction

Literally Defluoridation means removal of fluoride from water using suitable techniques. It is defined as the downward adjustment of level of fluoride in drinking water to the optimal level. Fluoride is known for both beneficial and harmful effect on health. In low level between 1-1.5 mg/l it improves the enamel. Fluoride concentration in the range of 1.5-4 mg/l results in dental fluorosis, whereas at high concentrations 4-10 mg/l causes skeletal fluorosis.

Depending upon the amount of fluoride ingested illness varying degree of skeletal, dental and non-skeletal fluorosis. Due to leaching of fluoride bearing rocks fluoride content in ground water have been found varying from 0.1 to 12.0 ppm. The Bureau of Indian Standard (BIS), this range is 0.6 from 1.2 ppm. Fluoride concentration from 0.6 to 1.5 ppm in drinking water has been set by the World Health Organisation (WHO). The Indian Standards Organization (ISO) suggests that the maximum permissible limit can be extended up to 1.5 ppm. The main source of ingestion of fluoride in our body is through drinking water. Obviously potable water must be subjected to defluoridation to avoid adverse impact of fluoride on health of common people.

2 Fluoride Removal Methods

2.1 **Bone Charcoal Method**

Bone charcoal has the ability to improve the colour, taste and odour of water. Most importantly, it can remove fluoride from water. The major components of bone charcoal are calcium phosphate 57-80 %, calcium carbonate 6-10 %, activated carbon 7-10 %. The fluoride removal process is mainly by the replacement of the hydroxide groups of hydroxyapatite by fluoride.

$Ca_{10}\ (PO_4)_6(OH)_2 + 2F^- \rightarrow Ca_{10}\ (PO_4)6F_2 + 2OH^-$

Advantages

—High fluoride sorption capacity,
—local availability and
—cheapness of animal's bones

no chemicals are added during the defluoridation process.
—However, there is limited acceptability of animal's bones as filter materials for drinking water due to religious beliefs.

2.2 **Contact Precipitation:**

Addition of calcium and phosphate compounds and then bringing the water in contact with saturated bone charcoal medium. Dissolution of calcium chloride

$CaCl_2.2H_2O(s) \rightarrow Ca^+ + 2Cl^- + 2H_2O$

Precipitation of calcium fluoride

$Ca^+ + 2F^- \rightarrow CaF(s)$.

Precipitation of calcium fluorapatite

$10Ca^+ + 6PO^- + 2F^- \rightarrow Ca(PO)6F(s)$

Fluoride is removed from the water by the addition of phosphate and calcium compounds in contact with a saturated bone charcoal medium.

As compared to bone charcoal method, fluoride uptake capacity and life of the filter using contact precipitation is significantly higher. However, the chemical processes of fluoride removal by contact precipitation are not yet fully understood, the calcium phosphate pellets cannot be regenerated and the process is time consuming.

2.3 The Nalgonda Technique

This method used at both community and household levels was originally developed by the NEERI, Nagpur in India. Lime and aluminium sulphate are added in calculated quantities in the process. Lime aids in forming dense flocks for rapid settling of insoluble fluoride salts. The choice of either $Al_2(SO_4)_3$ or $AlCl_3$ depends on SO_2- and Cl- conc. of raw water. As rule of thumb, the dose of lime is 1/20th of that of dose of aluminium salt.

Coagulation / flocculation and sedimentation removes the fluoride. The addition of lime helps to form dense flocs which settle rapidly and help to remove the fluoride. Also, a pH of around 6-7 is achieved at which aluminium is completely removed.

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For disinfection bleaching powder is added to the raw water. The reactions involved in this process are:

$6Ca(OH)_2 + 12H^+ \rightarrow 6Ca^+ + 18H_2O$

$Al_2(SO_4)_3 .18H_2O \rightarrow 2Al^{3+} + 3SO^{2-} + 18H_2O$

$2Al^{2+} + 6H_2O \rightarrow 2Al(OH)_3 + 6H^+$

$F^- + 2Al(OH)_3 \rightarrow$

Al-F complex+undefined product

Advantages: The chemicals used in the process are cheap and locally available, and the treatment is well accepted by locals.

Problems: Work-intensive method due to the need of daily mixing of alum and lime.

The fluoride elimination rate is

Also, there is a risk of contamination of the treated water by aluminium in case of overdosing of aluminium sulphate.

2.4 Activated Alumina (AA)

AA surface is amphoteric in nature and can exist as AlOH+, AlOH and AlO-. Fluoride binding to AA is due to exchange of surface hydroxyl groups, which can be represented by the following reaction.

$AlOH_2 + F^- \rightarrow AlF + H_2O$

$AlOH + F^- \rightarrow AlF + OH^-$.

Activated alumina is a good adsorbent due to its small size, and large surface area.

The fluoride removal ability of AA depends on the grade of AA,
particle size and
the pH,
alkalinity and fluoride concentration in water.
The AA technique requires minimum contact time with fluoride contaminated water for defluoridation.

Advantages:
—The exhausted AA can be easily regenerated.
—AA is available indigenously and quite cheap.
—AA is easy also to relatively handle.
— Defluoridation filters with AA can be fabricated easily and the filter requires no electricity and no maintenance.
Problems:
—Adsorption efficiency of the AA gets lowered with increasing number of regeneration cycles.
—The activated alumina is needed to be replaced very frequently which make the technique expansive.
—Regeneration generates fluoride rich solution, causing disposal problem.

2.5 Clay

Clay is finely powdered rock composed of hydrous aluminium silicate and other minerals and impurities. Clay powder and fired clay are both capable of adsorption of fluoride from water. If clay is locally available then fluoride removal using clay is very low cost. However, the fluoride adsorption capacity of clay is low, and the fluoride removal is time consuming.

Different sources of clay have been used for defluoridation: brick pieces, Kaolinite clay, raw **bentonite,** natural red soil and locally available material like laterite, sand and gravel for fluoride removal from water have been used also.

Principle mechanism for the fluoride removal is the exchange of hydroxyl ions by fluoride ions in the clay structure. The adsorption capacity of clay has been enhanced by coating the clay samples with aluminium and iron oxides.

2.6 Reverse Osmosis

In Reverse Osmosis (RO) water is forced under pressure through a semi-permeable membrane, thereby removing dissolved solutes from solution. This process can remove 85-95 % of fluoride from water. The RO is the best technique for removing both fluoride and arsenic.

Problems:

It has high water wastage of 20-40 %, high energy consumption and high capital costs.

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For cleaning of the RO membrane, chemical handling facilities and a skilled operator is needed.

2.7 Electro Dialysis (ED)

In Electro-Dialysis (ED) an applied D. C. current, instead of pressure is used to separate ionic contaminants from water. Thus, ED membranes are not technically considered as filters as water does not physically pass through the membrane in the ED process. Also, particulate matter is not removed. The ED process can remove 85-95 % fluoride from water. The ED method relies heavily on our present technical familiarity with the membrane-based separation systems. However, it is very costly, there is significant water loss in form of brine discharge, high energy consumption and high capital costs. There may be a requirement of pre-filtration and post-pH / alkalinity adjustment.

2.8 Bio-adsorbents

Bio-adsorbents prepared from dry fruits collected from plants *Enterolobium saman* (ESC), *Acasia arabic* (AAC), *Prosopis juliflora* (PLC) have been used by Maheshwari *et al.* for defluoridation purposes.

A number of bio-adsorbents have been used by different workers:

—Tea ash ,
— Na_2CO_3 modified bagasse and chitosan,
—Rare earth modified chitosan
—The rice husk and seed extract of *Moringa oleifera* (drum stick), modified by $MnCl_2$ and $MnSO_4$ and
—*Phyllanthus albicato.*

2.9 Ion Exchange

In the ion exchange process, water is allowed to flow down through a column packed with an ion exchange resin. When the resin becomes saturated, the filter material has to be regenerated with a mild acid/alkali solution.

$$Matrix\text{-}NR + Cl^- + F^- \rightarrow Matrix\text{-}NR_3 + F^- + Cl^-$$

To avoid recontamination of nearby ground water the effluent from backwashing rich in accumulated fluoride, must be disposed of properly.

The ion exchange method is simple to operate, does not require any electricity and also makes hard water soft. However, it is initial capital cost is high.

2.10 MgO, CaO, $CaCl_2$ and $NaHSO_4$ Technique (IISc Method)

Principle of the Method is as follows:

$$MgO + H_2O \rightarrow Mg(OH)_2$$

F^- in water gets trapped into the $Mg(OH)_2$ precipitate as settles down. Water becomes alkaline between pH 10.1 to 10.3 on addition of MgO. $NaHSO_4$ is used to reduce the pH of MgO treated Water to Within Potable Water limits (6.5 to 8.5)

$$HSO^- + OH^- \rightarrow SO^{2-} + H_2O \quad 2$$

$$HCO^- + OH^- \rightarrow CO_2 + H_2O$$

additional $NaHSO_4$ is consumed

$$CO^{2-} + HSO^- \rightarrow HCO^- + SO^{2-}$$

$Ca(OH)_2$ is added to convert soluble bicarbonates to insoluble $CaCO_3$ as

$$HCO^- + Ca + OH^- \rightarrow CaCO_3 + H_2O$$

$CaCl_2$ is added to increase conc. of Ca^{2+} in water. A new method of defluoridation using MgO, CaO, CaCl2, and NaHSO4 has been developed. The defluoridation filter consistent of two chambers, in the top chamber calculated doses of MgO, CaO and an aqueous solution of $CaCl_2$ are added to fluoride contaminated ground water and stirred well either using a mechanical or a handheld stirrer. The solution is left undisturbed for 16 hours for the flocs to settle down. The clear supernatant water is transferred to the bottom container using a flexible tube fitted at the bottom of the top container. The pH adjustment is done using $NaHSO_4$ in the bottom container. Using a tap, the potable water can be drawn off from the bottom container.

Conclusion:

The fluoride removal methods are of two types. Reverse osmosis, Electro dialysis, ion

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exchange are membrane techniques. Adsorption methods such as, Activated alumina and Nalgonda technique, Bone charcoal, Bio-Adsorbents, MgO, CaO, CaCl2, and HCl (IISC Method). Not all the methods are suitable for all circumstance and hence proper justification required for appropriate method to implement. Certain method like MgO, CaO, CaCl2, and HCl (IISC Method) have been very effective fluoride removal also cost effect and simple to adopt this technology at village level.

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