

Comparative Study of Defluoridation Technologies in India



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Abstract : Present study was undertaken to analyze and select most appropriate method for removal of fluorides in rural areas. Five methods were analyzed in details with mechanism and limitations. The methods are: Activated Alumina, Red Mud, Montmorillonite, Nalagonda Technique and Magnesia. The Study reveals that magnesia is the most appropriate fluoride treatment device for rural areas.

Key words : Montmorillonite, TDS, Nalagonda, Micropores, Regeneration.

Introduction

Fluoride in minute quantity is an essential component for normal mineralization of bones and formation of dental enamel (Jackson *et al.*, 1973). However, its excessive intake may result in slow, progressive crippling scourge known as fluorosis. The worst affected areas in India are Rajasthan, A.P., Orissa, Gujrat, Madhya Pradesh & Chattisgarh (Susheela 2001; Sharma *et al.*, 2008). The W.H.O recommended values for fluoride in drinking water is 0.1 to 0.5 ppm. There is minor aberration from this standard as U.S. standard recommends that the fluoride content in water should be between 0.6 and 0.9 ppm. The Bureau of Indian Standard which is main regulating agency for drinking water specifications in India specify that the maximum desirable limit of fluoride in drinking water is 0.5 ppm but in absence of alternatives, the maximum permissible limit is 1.5 ppm. The fluoride problem in India is primarily of hydrogeochemical origin. It has been observed that low calcium and high bicarbonate alkalinity favour high fluoride content in groundwater (Bulusu and Pathak, 1980; Meenakshi and Maheshwari, 2006). Though drinking water is the major contributor (75–90% of daily intake), other sources of fluoride poisoning are food,

industrial exposure, drugs, cosmetics, etc (Meenakshi and Maheshwari, 2006).

Health Impacts of Fluoride

Fluorine being a highly electronegative element has extraordinary tendency to get attracted by positively charged ions like calcium. Hence the effect of fluoride on mineralized tissues like bone and teeth leading to developmental alternations is of clinical significance as they have highest amount of calcium. Due to excessive fluoride intake, enamel loses its lustre. Normally, the degree of dental fluorosis depends on the amount of fluoride exposure up to the age of 8–10, as fluoride stains only the developing teeth while they are being formed in the jawbones and are still under the gums (Choubisa and Sompura, 1974). The effect of dental fluorosis may not be apparent if the teeth are already fully grown prior to the fluoride over exposure. Therefore, the fact that an adult shows no signs of dental fluorosis does not necessarily mean that his or her fluoride intake is within the safety limit. Skeletal fluorosis affects children as well as adults. It does not easily manifest until the disease attains an advanced stage. Fluoride mainly gets deposited in the joints of neck, knee, pelvic and shoulder bones and makes it difficult to move or walk. The symptoms of skeletal

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fluorosis are similar to spondylitis or arthritis (Dinesh, 1998). Vertebrae may fuse together and eventually the victim may be crippled. It may even lead to a rare bone cancer, osteosarcoma and finally spine, major joints, muscles and nervous system get damaged. Besides skeletal and dental fluorosis, excessive consumption of fluoride may lead to muscle fibre degeneration, low haemoglobin levels, deformities in RBCs, excessive thirst, headache, skin rashes, nervousness, neurological manifestations (it affects brain tissue similar to the pathological changes found in humans with Alzheimer's disease), depression, gastrointestinal problems, urinary tract malfunctioning, nausea, abdominal pain, tingling sensation in fingers and toes, reduced immunity, repeated abortions or still births, male sterility, etc. It is also responsible for alterations in the functional mechanisms of liver, kidney, digestive system, respiratory system, excretory system, central nervous system and reproductive system, destruction of about 60 enzymes (Sharma *et al.*, 2004).

Materials and Methods

Major defluoridation devices have been referred with advantages and limitations. It includes Activated Alumina, Red mud, Nalagonda technique, Magnesia & Montmorillonite.

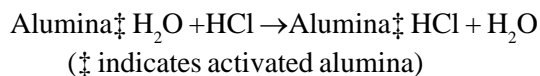
Results and Discussion

1. Activated Alumina

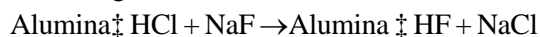
Activated Alumina is an aluminium oxide that is highly porous and exhibits high surface area. The crystal structure of alumina contains cation lattice discontinuities giving rise to localized areas of positive charge. This makes alumina attract various anionic species. Alumina has a high preference for fluoride compared to other anionic species, and hence is an attractive adsorbent. It also does not shrink, swell, soften nor disintegrate when immersed in water. The activated alumina was proposed for the first time for defluoridation of water for domestic use in the 1930s. Since

then, the activated alumina has become a popular defluoridation method. The maximum absorption capacity of activated alumina for fluoride is found to be 3.6 mg F/g of alumina.

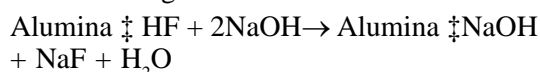
In practice, alumina is first treated with HCl to make it acidic.



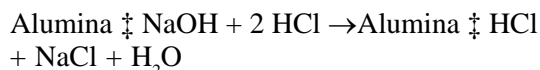
This acidic form of alumina when contacted with fluoride ions displaces the chloride ions and gets attached with the alumina.



To regenerate the adsorbent a dilute solution of sodium hydroxide is mixed with the adsorbent to get a basic alumina.



Further treatment with acid regenerates the acidic alumina.



It has been found that maximum adsorption takes place at certain pH range, the most effective pH range is 5.0 to 7.0. At pH > 7, silicate and hydroxide become stronger competitor of the fluoride ions for exchange sites on activated alumina and at pH less than 5, activated alumina gets dissolved in acidic environment leading to loss of adsorbing media.

Limitations

- The process is pH specific and works effectively only in certain pH range.
- If Activated Alumina is fitted on hand-pump and remains non-operational due to any reason for 2-3 days or longer, the alumina bed becomes hot bed for microorganism.
- This treatment is not effective if TDS exceeds 1500 mg/L.
- It requires time to time regeneration as after some time Activated alumina is exhausted.

- The regeneration steps result in an aqueous solution containing fluoride. On the other hand, if the spent alumina is discarded, the cost of the defluoridation increases. Apart from that, spent alumina may leach out fluoride ions when it comes in contact with alkali.

2. Red mud

Red Mud is a very fine material (particle size of which is generally below 75μ) and high specific surface area (around $10\text{ m}^2/\text{gm}$) which is produced during the Bayer process for alumina production (Hind *et al.*, 1999). It is the insoluble product after bauxite digestion with sodium hydroxide at elevated temperature and pressure. It is mainly composed of iron oxides and have a variety of elements and mineralogical phases. The variation in chemical composition between different RMs worldwide is high (Table 1).

Table 1. Constituents and their percentage weight in Red Mud

S.N.	Constituents	% weight
1	Fe_2O_3	30 to 60
2	Al_2O_3	10 to 20
3	SiO_2	3 to 50
4	Na_2O	2 to 10
5	CaO	2 to 8
6	TiO_2	trace to 25

Source: The International Aluminium Institute, modified for TiO_2 content

The removal of fluoride from aqueous solution by using the original and activated red mud forms has been studied by many researchers (Lopez *et al.*, 1998). The fluoride adsorption capacity of activated form has been found to be higher than that of the original form. The adsorption is highly dependant on pH. Research have revealed that the maximum adsorption of fluoride is at pH 5.5. For pH greater than 5.5 fluoride removal decreases

sharply. It was found that the sufficient time for adsorption equilibrium of fluoride ions is 2 h. The possibility of removal of fluoride ion by using red mud is explained on the basis of the chemical nature and specific interaction with metal oxide surfaces (Yunus *et al.*, 2002).

Limitations

- The process is highly dependent on pH and works best only in a narrow pH range.
- High concentration of total dissolved salts (TDS) can result in fouling of the alumina bed.
- Presence of sulfate, phosphate or carbonate results in ionic competition.
- The process has low adsorption capacity, poor integrity and needs pretreatment.
- The regeneration is required after every 4–5 months and effectiveness of adsorbent for fluoride removal reduces after each regeneration.

3. Nalgonda Technique

The Nalagonda technique was developed by the National Environment Engineering Research Institute (NEERI), Nagpur, after extensive testing of many materials and processes (Nawlakhe *et al.*, 1975). The Nalgonda technique involves addition of alum (aluminium sulphate, lime (calcium oxide) and bleaching powder followed by rapid mixing, flocculation, sedimentation, filtration and disinfection. Induced by a subsequent gentle stirring, “cotton wool”-like flocs develop (aluminium hydroxides) which is removed by simple settling (Eli *et al.*, 1996). In the guidelines for household defluoridation published by NEERI in 1987, alum is to be added as a 10 per cent solution to a 40 litre bucket equipped with a tap. This is a modification of the previously described method, where alum would be added as tablets.

The dose of aluminum salt increases with increase in the fluoride and alkalinity levels of

the raw water. The dose of lime is empirically 1/20th of the dose of aluminum salt. Lime facilitates forming dense floc for rapid settling. Bleaching powder is added to the raw water at the rate of 3 mg/l for disinfection. Nalgonda technique is effective even when the fluoride concentration is above 20 mg/L. It is possible to lower the concentration of fluoride below 1mg/L in the treated water and adequate alkalinity is essential to reduce the fluoride level to 1mg/L or below.

Limitations

- It has been found that some of the fluoride, which has been captured in the flocs, is released slowly back to the water.
- The process removes only a smaller portion of fluoride form of precipitant and converts a greater portion of ionic fluoride into soluble aluminium fluoride complex ion.
- Due to use of aluminium sulfate as coagulant, the sulfate ion concentration increases tremendously and in few cases, it crosses maximum permissible limit of 400 mg/l, which causes cathartic effect on human beings.
- The residual aluminium in excess of 0.2 mg/l in treated water causes dangerous dementia disease.
- Discarding the sludge from the Nalgonda process is a serious environmental health problem. The sludge is toxic as it contains the removed fluoride in a concentrated form Sludge disposal is a problem.
- Regular analysis of feed and treated water is required to calculate the correct dose of chemicals to be added, because water matrix keeps on changing with time and season as evident from our earlier studies conducted in laboratory.

4. Montmorillonite:

Montmorillonite is a very soft phyllosilicate mineral (special type of clay) that forms in microscopic crystals, forming a clay. It is named after Montmorillon in France. Montmorillonite, a member of the smectite family, is a 2:1 clay, meaning that it has 2 tetrahedral sheets sandwiching a central octahedral sheet. The particles are plate-shaped with an average diameter of approximately 1 micrometre. It is the main constituent of the volcanic ash weathering product, bentonite. Chemically, it is hydrated sodium calcium aluminium magnesium silicate hydroxide $(\text{Na,Ca})_{0.33}(\text{Al,Mg})_2(\text{Si}_4\text{O}_{10})(\text{OH})_2 \cdot n\text{H}_2\text{O}$. Potassium, iron, and other cations are common substitutes, the exact ratio of cations varies with source. It often occurs intermixed with chlorite, muscovite, illite, cookeite and kaolinite.

The removal of fluoride from aqueous solution by using montmorillonite has been studied by batch equilibration technique (Ali Tor, 2006). Using this technique, influence of various parameters like contact time, pH, initial fluoride concentration and adsorbent dosage has also been studied. It has been found that : the sufficient time for adsorption equilibrium of fluoride ions is 180 min and, the maximum removal of fluoride ion was obtained at pH 6 (Agrawal *et al.*, 2002; Karthikeyan *et al.*, 2005). The mechanism for fluoride removal was explained by considering the interaction between the metal oxides at the surface of montmorillonite and fluoride ions. The adsorbed fluoride could be easily desorbed by washing the adsorbent with a solution pH of 12.

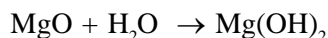
Limitations

It has been observed that significant concentration of Al^{3+} , Fe^{3+} and silica are released from acidified montmorillonite lattice (pH ~ 2; 1:10 w/v) which will eventually be coming into treated water.

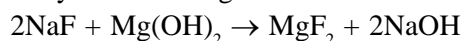
5. Magnesium Oxide

The application of Magnesium oxide for

defluoridation is not a new one. (Venkateswarlu and Rao, 1953, 1954). However, it has been modified of late and the efficiency has been increased (Sudhakar and Mamatha, 2004). The mechanism of removal of fluoride ions from water by magnesium oxide is as follows : Addition of magnesium oxide to fluoride-bearing water results in the hydration of magnesium oxide to magnesium hydroxide as:



The magnesium hydroxide formed in above reaction combines with fluoride ions to form practically insoluble magnesium fluoride as:



Precipitation of fluoride ions as insoluble magnesium fluoride lowers the fluoride ion concentration in water. It has been found that for a given mass of magnesium oxide, the amount of fluoride retained increases with concentration of fluoride ions in the spiked water samples. Further, at a given solution concentration, the amount of fluoride retained by magnesium oxide decreases with Magnesium oxide in conjunction with calcium oxide (lime) is commonly used for chemical stabilization of soils. The cementitious nature of magnesium oxide in conjunction with calcium oxide provides an environmentally safe route for re-use of fluoride-bearing magnesium oxide sludge in soil-based building materials, such as stabilized soil blocks, tiles, etc. The possible re-use of fluoride-bearing magnesium oxide sludge in environmentally safe modes and the non-toxic nature of magnesium oxide prompted the development of IISc method of de-fluoridation of water using magnesium oxide for domestic purposes. Though the earlier works succeeded in establishing the fluoride-removing ability of magnesium oxide, vital issues necessary for successful field implementation of the method were not addressed. For example, the dosages of magnesium oxide required for treating water containing different fluoride and dissolved salts concentrations were not specified, the issue of

lowering the pH of magnesium oxide-treated water within potable water limits was not comprehensively addressed, the optimum conditions for mixing the magnesium oxide–water suspension were not defined. Failure to address the above issues has impeded the commercial success of the magnesium oxide treatment method for fluoride removal from water.

Conclusion

- The fluoride treatment system to be installed depends upon many factors to be considered. These factors can be broadly divided into Social and Scientific. Prime social factors are cost involved, location (whether urban or rural), population and scientific understanding. Scientific factors are TDS, Volume of water to be treated, flow rate & concentration of fluoride ion in water sample. It has been evident from the comparative study that all defluoridation devices have some merits as well as certain limitations. Even, Reverse Osmosis technique can't be applied for removing fluoride content when fluoride ions concentration is less than 3.0 mg/L because taking 95 % efficiency of RO, the remainant fluoride in treated water will be 0.15 mg/L which is lower than the prescribed limit. This treated water which has low fluoride content might lead to dental carries. Reverse Osmosis is applicable only when the fluoride ion concentration is extremely high.

- Comparing all defluoridation devices, the most feasible option for fluoride removal for rural regions seems to be magnesia. It is selective for fluoride removal as it binds well with fluoride ions. Unlike Activated Alumina, it doesn't leach any harmful chemicals (like alumina) in treated water. Unlike montmorillonite, it is relatively easily available and easily synthesizable. It is cost effective as well. Apart from adopting cost effective defluoridation devices, capacity development of community needs to be addressed for initiating and managing defluoridation devices.

Secondly, looking for alternate sources of ground water with less fluoride is effective. Thirdly, fluoride contamination can also be addressed by promoting foods that are rich in calcium and available locally. These are the alternative measures that can be adopted in project areas where fluoride is the major contaminant in drinking water.

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