International Journal of Applied Dental Sciences 2018; 4(3): 167-171

ISSN Print: 2394-7489
ISSN Online: 2394-7497
IJADS 2018; 4(3): 167-171

www.oraljournal.com
Received: 29-05-2018
Accepted: 30-06-2018

Dr. Sreekanth Bose
Post Graduate Student, Department of Public Health Dentistry Government Dental College and Research Institute, Bangalore, Karnataka, India

Dr. Yashoda R
Associate Professor, Department of Public Health Dentistry Government Dental College and Research Institute, Bangalore, Karnataka, India

Dr. Manjunath P Puranik
Professor and Head, Department of public health dentistry Government Dental College and Research Institute, Bangalore, Karnataka, India

Correspondence
Dr. Sreekanth Bose
Post Graduate Student, Department of Public Health Dentistry Government Dental College and Research Institute, Bangalore, Karnataka, India

A review on defluoridation in India

Dr. Sreekanth Bose, Dr. Yashoda R and Dr. Manjunath P Puranik

Abstract
Fluoride is often described as a double-edged sword as inadequate ingestion is associated with dental caries, whereas excessive intake leads to dental, skeletal and soft tissue fluorosis which has no cure. Fluoride in water derives mainly from the dissolution of natural minerals in the rocks and soils with which water interacts. The problem of excessive fluoride in drinking water has engulfed many parts of the world, and millions of people rely on groundwater with concentrations above the World Health Organization (WHO) guideline value of 1.5 mg/L. In India, endemic fluorosis is thought to affect 65 million people. Rajiv Gandhi National Drinking Water Mission was set up to control fluorosis with a plan to overcome the problem. Nalgonda technique, Prasanti technology using activated alumina, UNICEF in India using household based defluoridation, KRASS defluoridation process, Delfuoridation based on ion exchange mechanisms, Fluoride removal by IISc method at Kolar, Karnataka are examples of defluoridation methods used in various field programs in India. The main techniques of defluoridation that have been investigated with varying degrees of success include adsorption, precipitation/coagulation, ion exchange and membrane processes. Many chemical, indigenous and herbal materials are used along with this. Precipitation is the well-established method and most widely used method, particularly at community level. Adsorption can be done with locally available adsorbent materials with high efficiency and cost effectiveness. Ion Exchange removes fluoride up to 90-95% and retains the taste and color of water intact.

Keywords: Fluorosis, defluoridation, India, field programs

Introduction
Fluoride is often described as a double-edged sword as inadequate ingestion is associated with dental caries, whereas excessive intake leads to dental, skeletal and soft tissue fluorosis which has no cure. While fluoride is present in air, water, and food, the most common way it enters the food chain is via drinking water. Fluorides in drinking water may be beneficial or detrimental depending on their concentration and total amount ingested. Fluoride is beneficial especially to young children for calcification of dental enamel below eight years of age when present within permissible limits. An excess of fluoride in drinking water causes dental fluorosis and skeletal fluorosis. The World Health Organisation has recommended a guideline value of 1.5 mg/L as the concentration above which dental fluorosis is likely. This overview throws some light on harms of excessive fluoride in water, defluoridation- history and techniques used and defluoridation in India [1].

Fluoride in Water
Though groundwater contributes only 0.6% of the total water resources on earth, it is the major and preferred source of drinking water. Fluoride in water derives mainly from the dissolution of natural minerals in the rocks and soils with which water interacts. High fluoride concentrations are also a feature of arid climatic conditions. Here, groundwater flow is slow and reaction times between water and rocks are therefore enhanced. Fluoride buildup is less pronounced in the humid tropics because of high rainfall inputs and their diluting effect on groundwater chemical composition. Besides natural sources, fluoride ions can also be found in effluents from the semiconductor, metal processing, fertilizers, and glass manufacturing industries. However, it is also important to consider climatic conditions and quantity of water intake and dietary fluoride content. Water consumption in hot humid regions is generally higher than in temperate regions and therefore the fluoride concentration limit for likely fluorosis should be lower [2].

Fluoride and diseases

At concentrations above 1.5 mg/L (79 µmole/L) however, fluoride is dangerous to human health, leading to dental and skeletal fluorosis, a disease that can cause mottling of the teeth, calcification of ligaments, crippling bone deformities, and many other physiological disorders that can, ultimately, lead to death [1]. over 10mg/l) to develop, skeletal fluorosis is more severe than its dental counterpart, characterized by deformation of the bone structure can be detected early on radiologically. It is now well established that fluoride in drinking water can cause 'non-ulcer dyspeptic' complaints in human subjects. The main complaints are nausea, loss of appetite, pain in the stomach, gas formation and bloated feeling, constipation followed by intermittent diarrhea and headache [3]. Fluoride has also been linked to cancer[4], decreased cognitive ability, lower Intelligence Quotient (IQ), and developmental issues in children [5].

Fluorosis has significant economic impacts in the developing world. In addition to fluorosis removing people from the workforce, water supply programs have thrown away significant finances while providing costly boreholes that become useless upon the discovery of the toxic levels of fluoride that they contain [6].

Global scenario

The problem of excessive fluoride in drinking water has engulfed many parts of the world, and today many millions of people rely on groundwater with concentrations above the World Health Organization (WHO) guideline value. There are more than 20 developed and developing nations in which fluorosis is endemic [7].

Indian scenario

In India fluorosis was first detected in teeth of cattle at Nellore district of Andhra Pradesh in 1937. Since then, considerable work has been done in different parts of India to explore the fluoride-laden water sources and their impacts. Fluorosis is an endemic disease prevalent in 20 states of Indian Republic. The problem of excessive fluoride is more severe, particularly in arid parts of the country.

- 70-100% districts are affected in Andhra Pradesh, Gujarat and Rajasthan.
- 40-70% districts are affected in Bihar, National Capital Territory of Delhi, Haryana, Jharkhand, Karnataka, Maharashtra, Madhya Pradesh, Odisha, Tamil Nadu and Uttar Pradesh
- 10-40% districts are affected in Assam, Jammu & Kashmir, Kerala, Chattisgarh and West Bengal [30].
- In India, endemic fluorosis is thought to affect 65 million people [8].

Remedies

Worldwide, a major challenge is to develop effective and inexpensive techniques for the remediation of fluoride in groundwater. Most important types of control measures used are:

1. Provision of a new or alternative source of water containing lower levels of fluoride
2. Blending the existing water supply with another containing lower levels of fluoride
3. Provision of bottled water
4. Treating the water at the "point-of-use" such as in a small treatment device attached to household drinking water outlet
5. Treatment of water at its source [9].

History of Defluoridation

Though an ancient problem [10], fluorosis was not identified until recent history and there were little attempts to defluoridate water before the 20th century. As many parts of the world where fluorosis is common are relatively isolated, many cultures in fluorotic regions never considered dental fluorosis to be an abnormality until increased communication and travel resulted in changes in perception. Additionally, skeletal fluorosis can often take an extended time to develop visible symptoms, so it is not necessarily obvious for people to link fluorosis to a problem in water quality [11]. The earliest diagnoses of dental fluorosis come from 1888 in Mexico and 1891 in Italy. Still, the link between drinking water and fluorosis wasn't established until the 1920s in Colorado, by Dr. Fedrick S. McKay [12].

It was in the 1930s that several nations first began to more seriously investigate the negative effects of fluoride and how to remove it from drinking water supplies. An aluminum and sand filter that removes fluorine from water has been devised by Dr. S. P. Kramer in 1933. In the year 1945 M. Kenneth received a French patent in water defluoridation technique. A successfully functioning activated alumina community defluoridation plant was commissioned in Bartlet, Texas, the USA in the year 1952 [12].

By mid-1980's, it was evident that excess fluoride was present in groundwater in many parts of the country. In 1987, Rajiv Gandhi National Drinking Water Mission estimated that about 25 million people in 8700 villages were drinking water with excess fluoride. A Sub-Mission to control fluorosis was set up with a plan to overcome the problem. Testing of all of the water sources for fluoride and technology interventions were initiated in many states. The technology option considered was mainly "Nalgonda" technique [13].

Defluoridation techniques

While various defluoridation techniques have been explored, each has limitations. Existing techniques are often too costly to implement easily (because the geographic areas prone to fluorosis are among some of the poorest regions on the planet), ineffective, or even dangerous (So far as some of the remediation process itself has added other contaminants to the water). Many defluoridation techniques have been examined since the 1930s when the danger of excess fluoride in drinking water was first identified [14]. More than 70 years since the problem was recognized, however, the attempts to develop a method of defluoridation that can be sustained under differing social, financial, environmental and technical constraints have not been successful. The main techniques that have been, and continue to be, investigated with varying degrees of success include the following [15]:

1. Adsorption
2. Precipitation/coagulation
3. Ion exchange
4. Membrane processes

Adsorption

This technique functions on the adsorption of fluoride ions onto the surface of an active agent. In the adsorption method, raw water is passed through a bed containing defluoridating material. The material retains fluoride either by physical, chemical or ion exchange mechanisms. The adsorbent gets saturated after a period of operation and requires regeneration [16]

A. Activated Alumina

Activated alumina (Al_2O_3), which has been in use for defluoridation since 1934, is prepared by low-temperature dehydration (300-600 °C) of aluminum hydroxides. The ligand exchange reaction at the surface of activated alumina is responsible for fluoride removal. Alumina (aluminum oxide, Al_2O_2) is practically insoluble in water. The solubility depends upon previous heat treatment. There are different grades of activated alumina, indigenously available at a very nominal cost. The suitability of the grade for defluoridation depends upon the porosity and surface area of the alumina [17]

B. Bone char

The fluoride-scavenging potential of bone was first identified and reported by Smith and Smith in 1937. It was reported that degreased, caustic and acid treated bone material could effectively reduce fluoride concentration from 3.5 to less than 0.2 mg/L. The suggested removal mechanism was of ion exchange in which the carbonate radical of the apatite ($Ca_9(PO_4)_6 \cdot CaCO_3$) comprising bone was replaced by fluoride to form an insoluble fluorapatite [18], as:

$Ca_9(PO_4)_6 \cdot CaCO_3 + 2F^- \rightarrow Ca_9(PO4)_6 \cdot CaF_2 + CO$ [19]

But the high cost of bone became an inhibiting factor for its wider use. However, soon it was recognized that bone char, produced by carbonizing bone at temperatures of 1100–1600 ^{0}C, had superior scavenging potential to the unprocessed bone. Thereafter, bone char replaced bone as a defluoridating agent [18]

C. Calcined Clay and mud pots

Various researchers have assessed the fluoride binding effect of simple pottery. It has been reported that fluoride binding capacity in clayware of 80 mg-F/kg and studies have concluded that fluoride uptake in clayware is slow and of limited capacity [20] The major advantages of mud pots are they are economic and readily acceptable for the rural communities [18].

D. Natural Adsorbents

A relatively less known approach of potential utility, particularly in third world rural communities, that has attracted the attention of researchers in recent years is plant-based (natural) defluoridation techniques. The plants can be grown locally as needed and the costs for production and transportation can be relatively low. The use of plants for defluoridation might also achieve widespread acceptance and application by local communities more easily. Researchers at M. S. Swaminathan Research Foundation (MSSRF) had shown drumstick seeds to have remarkable defluoridation efficiency, which was higher than that of activated alumina. Many natural adsorbents from various trees and animal sources like coconut shell, tamarind seeds, bone charcoal, tulsi leaves have been tried as defluoridation agents [21].

Ion Exchange

Ion exchange is an exchange of ions between two electrolytes or between an electrolyte solution and a complex. In most cases, the term is used to denote the processes of purification, separation, and decontamination of aqueous and other ion-containing solutions with solid polymeric or mineral 'ion exchangers'.

Typical ion exchangers are ion exchange resins (functionalized porous or gel polymer), zeolites, montmorillonite, and clay and soil humus. Ion exchangers are either cation exchangers that exchange positively charged ions (cations) or anion exchangers that exchange negatively charged ions (anions). There are also amphoteric exchangers that are able to exchange both cations and anions simultaneously. However, the simultaneous exchange of cations and anions can be more efficiently performed in mixed beds that contain a mixture of anion and cation exchange resins or passing the treated solution through several different ion exchange materials. The different ion exchange materials studied include bone, bone char, anion, and cation exchange resins such as carbon, defluoron-1, defluoron-2 etc [22]

Precipitation

In this method, chemicals added to raw water cause precipitation of the fluoride salt as insoluble fluorapatite, which is separated from the water. Commonly used materials in precipitation technique are Aluminium salts (e.g. Alum), lime, Poly Aluminium Chloride, Poly Aluminium Hydroxy sulfate and Brushite [22].

Membrane process

It is a water purification technology that uses a semi-permeable membrane to remove ions, molecules, and larger particles from drinking water. In reverse osmosis, an applied pressure is used to overcome osmotic pressure. The result is that the solute is retained on the pressurized side of the membrane and the pure solvent is allowed to pass to the other side. To be "selective", this membrane should not allow large molecules or ions through the pores (holes) but should allow smaller components of the solution (such as solvent molecules) to pass freely. Reverse osmosis can remove many types of dissolved and suspended species from water including bacteria, and is used in both industrial processes and the production of potable water.

The fluoride removal by reverse osmosis method has not been widely reported. Literature published by the various reverse osmosis manufacturers indicate that a wide fluoride removal range of 40 to 90%. Although reverse osmosis is not normally used on low total dissolved solid water and has not been specially used for fluoride removal, the process should be an effective method. In spite of its high operating costs, this process may be practical for treating small community water supplies and should be considered as a good alternative [23].

Methods implemented in India

Nalgonda Technique

The first community defluoridation plant for removal of fluoride from drinking water was constructed in the district of Nalgonda in Andhra Pradesh, in the town of Kadri. The technology was developed by National Environmental Engineering Research Institute (NEERI), Nagpur in 1961. Nalgonda Technique involves the addition of Aluminium salts, lime, and bleaching powder followed by rapid mixing, flocculation, sedimentation, filtration, and disinfection. Aluminium salt may be added as aluminum sulfate (alum) or aluminum chloride or combination of these two. It is responsible for removal of fluoride from water [24].

Prasanti Technology using Activated Alumina

The Prasanti technology for fluoride removal using activated alumina presently being used for water defluoridation in Indian villages, originated as a result of research and development activities carried out at the Bioscience Department at Satya Sai University for Higher Learning at Prasanti Nilayam at Puttaparthi (Anantapur District) in Andhra Pradesh [25].

UNICEF in India using Household based defluoridation
UNICEF supported the research for the development of technology along with water, environment. Sanitation section (WESS) by the Department of Chemistry, IIT Kanpur. Pilot projects were taken up in Andhra Pradesh and Rajasthan in 1996-2002. Handpump attached Defluoridation Units and Domestic Defluoridation Units have been developed in India by using indigenously manufactured activated alumina. The advantages of this approach domestic defluoridation units are: a lower cost for treatment as only a limited volume of water is required (for cooking and drinking) to be treated and the lower requirement of treated water correspondingly lowers the need of chemicals and generates lower volume of sludge [24].

KRASS Defluoridation Process
Fluoride contaminated water is passed through a bed of specially designed filter media to get defluoridated water. The process has been verified by Council of Scientific & Industrial Research (CSIR) and Public Health Engineering Department (PHED) of Rajasthan [26].

Delfuoridation based on ion exchange Mechanisms
Defluoridation units using carbion and defluoron-1 in 8:1 proportion was installed at Gangapur (Rajasthan). Filter alum of 2, 3, 5, 6 and 10% were used to regenerate the mixed medium. The fluoride content of raw water was 4.8 mg/ liter. Most of defluoron-1 were washed out in the first few cycles. Cost of treatment: Rs.0.3 / m^3 of water with 4.3 mg/liter fluoride [24].

Fluoride Removal by IISc method at Kolar, Karnataka.
The device has two units, each of 20 liters capacity. The upper unit has a mixing cum sedimentation unit. It is equipped with manually operated, geared mechanical stirring device for mixing of Magnesium oxide and water. The lower unit collects treated water. Fifteen liters of water is poured into the upper unit. $Ca(OH)_2$ + MgO are added and manually stirred for five minutes. The suspension is allowed to stand for 16 hours. Fluoride bearing sludge settles at the bottom. The clear water is decanted into lower collection unit through flexible connecting pipe fitted with a fine filter to trap any escaping sludge. Water soluble sodium bisulfate is dissolved in the lower chamber and the water is ready for use. Sludge is stored in a concrete-lined pit until further use. The cost of treating 1 liter of fluoride water with 2-5 ppm by IISc method is 7 paise/ liter and the cost of Domestic Defluoridation Unit is around Rs.2000/unit [24].

Conclusion
Precipitation is the well-established method and most widely used method, particularly at community level. But the technique has only moderate efficiency and the high chemical dose is required. Excessive use of aluminum salts produces sludge and adverse health effects through aluminum solubility.
Adsorption can be done with locally available adsorbent materials with high efficiency and cost-effectiveness. Herbal and indigenous products which are cost-effective and locally available are promising materials used in this technique. These materials are suitable for Indian conditions. But the process is dependent on pH and presence of sulfate, phosphate, and bicarbonate results in ionic competition. Disposal of fluoride-laden sludge is a disadvantage.
Ion Exchange removes fluoride up to 90-95% and retains the taste and color of water intact. Sulfates, phosphates, and bicarbonates create ionic competition in this method also. Relatively higher cost is a disadvantage and treated water sometimes has a low pH and high levels of chloride.
Membrane processes is a highly effective technique and no chemicals are required. It works at wide pH range and interference by other ions is negligible. But it requires relative higher cost and skilled labor. This process is not suitable for water with high salinity.

References

1. Fawell JK, Bailey K, Chilton J. Fluoride in drinking-water. World Health Organization, 2006.
2. Ayoob S, Gupta AK. Fluoride in drinking water: a review on the status and stress effects. Critical Reviews in Environmental Science and Technology. 2006; 36(6):433-87.
3. Susheela AK. Fluorosis: Early detection and management. Touch. 2001; 3:2-6
4. Yiamouyiannis JA. Fluoridation and cancer. The biology and epidemiology of bone and oral cancer related to fluoridation. Fluoride. 1993; 26(2):83-96.
5. Li XS, Zhi JL, Gao RO. Effect of fluoride exposure on intelligence in children. Fluoride. 1994; 28(4):189-192.
6. Gumbo FJ, Mkongo G. Water defluoridation for rural fluoride affected communities in Tanzania. In first International Workshop on Fluorosis Prevention and Defluoridation of Water, Int. Soc. Fluoride Res 1995; 18: 109-114.
7. Johnston R, Heijnen H. Safe Water Technology for Arsenic Removal, Report; World Health Organization (WHO): Geneva, Switzerland, 2002
8. Arlappa N, Aatif Qureshi I SR. Fluorosis in India : an overview. Int J Res Dev Heal. 2013; 1:97-102.
9. Cummins BT. Controlling fluoride levels: a literature review. Geneva, swizerland, world Health Organization, 1985.
10. Judith Littleton. Paleopathology of Skeletal Fluorosis, American Journal of Physical Anthropology. 1999; 109:465-483
11. Jerry R, Taricska LKW, Yung-Tse Hung, Kathleen Hung Li. Fluoridation and Defluoridation. Advanced Physicochemical Treatment Processes. New York, Springer-Verlag, 2006.
12. Rajchagool S, Rajchagool C. Solving the fluorosis problem in a developing country. InDahi, E. and Nielsen, JM (eds). Proceedings of the 2nd international workshop on fluorosis and defluoridation of water, Addis Ababa, Ethiopia, 1997,
13. Daw RK. Experiences with domestic defluoridation in India. In Proceedings of the 30th WEDC International Conference on People-Centred Approaches to Water and Environmental Sanitation, Vientiane, Lao PDR 2004; 25: 467-473.
14. Boruff CS. Removal of fluorides from drinking waters. Industrial & Engineering Chemistry. 1934; 26(1):69-71.
15. Krishnan S, Indu R. How can we think ahead on Fluorosis Mitigation? Available at http://www.inrem.in/fluorosis/pdf/t1p3.pdf
16. Khairnar MR, Dodamani AS, Jadhav HC, Naik RG, Deshmukh MA. Mitigation of fluorosis-a review. Journal of clinical and diagnostic research: JCDR, 2015; 9(6):ZE05.
17. Susheela AK. Defluoridation of drinking water: merits of alternative technologies. Bull Nutr Found India. 1992;

13:6-7.
18. Ayoob S, Gupta AK, Bhat VT. A conceptual overview on sustainable technologies for the defluoridation of drinking water. Critical Reviews in Environmental Science and Technology. 2008; 38(6):401-70.
19. Bardsen A, Klock KS, Bjorvatn K. Dental fluorosis among persons exposed to high- and low-fluoride drinking water in western Norway. Commun. Dentistry Oral Epidemiol. 1999; 27:259-267.
20. Bjorvatn K, Bårdsen A. Use of activated clay for defluoridation of water. In1st International Workshop on Fluorosis Prevention and Defluoridation of Water, Ngurdoto, Tanzania 1995, 49-55.
21. Harikumar PS, Jaseela C, Megha T. Defluoridation of water using biosorbents. Natural Science. 2012; 4(4):245.
22. Susheela AK. Defluoridation of drinking water–merits of alternative technologies. A Nutrition Foundation of India paper.
23. Patil SS, Ingole NW. Studies on defluoridation-Acritical review‖. Journal of Engineering research and studies. 2012; 3(1):111-9.
24. Eswar P, Devaraj CG. Water defluoridation: field studies in India. Ind J Dent Adv. 2011; 3:526-33.
25. Rao VK. Defluoridation of drinking water by Prasanthi technique. National Workshop on defluoridation technologies for Fluorosis control, 1997.
26. Agarwal KC, Gupta SK, Gupta AB. Development of new low cost defluoridation technology (KRASS). Water science and technology. 1999; 40(2):167-73.