J. Chil. Chem. Soc., 68, N°2 (2023)

A REVIEW OF FLUORIDE REMOVAL FROM GROUND WATER BY VARIOUS ADSORPTION TECHNIQUES

MARGANDAN KARUNANITHI [1], RACHNA AGRAWAL [2] AND KUSHAL QANUNGO [3]*

[1]*Department of Chemistry, IFET College of Engineering, Villupuram, India.*
[2]*Department of Chemistry, Mody University (Sikar), Rajasthan, India.*
[3]*Dept. of Chemistry, University Institute of Science, Chandigarh University, Gharuan, Dist. Mohali, Punjab, India.*

ABSTRACT

This paper reviews a number of fluoride's negative consequences on human health. Due to the high concentration of fluoride in the ground water, the majority of the arid and semiarid regions of the Indian subcontinent are severely afflicted by the fluorosis problem. The groundwater becomes fluoridated as a result of fluoride leaching from the fluoride-bearing rocks. A thorough analysis of the various methods for removing fluoride, including the Nalgonda process, bone charcoal, contact precipitation, clay column, electro-dialysis, ion-exchange, and by activated alumina, is then provided.

Keywords: Fluoride, Ground water, adsorption.

1. INTRODUCTION

High fluoride levels in drinking water in many parts of the world has become a critical health hazard. High concentration of fluoride occurs naturally in ground water and causes fluorosis[1 2 3]. The World Health Organisation (WHO) has set the guideline for the fluoride from 0.6 to 1.5 ppm in drinking water as suitable for human consumption[4]. According to the Bureau of Indian Standard (BIS), the desirable range of fluoride in drinking water is 0.6 to 1.2 ppm. However, the standard suggests that the maximum permissible limit can be extended up to 1.5 ppm[5].

In ground water, low or high concentration of fluoride depends upon the nature of the rocks and occurrence of fluoride bearing minerals. High level of fluorides are found in these minerals like fluorspar CaF_2, fluorapatite $Ca_5(PO_4)_3F$, cryolite Na_3AlF_6, micas $X_2Y_4–6Z_8O_{20}(OH,F)_4$ where X = K, Ca, Na, Y = Al, Mg, Fe, Z = Si, Al, topaz $Al_2SiO_4(OH, F)_2$, sellaite MgF_2, villiaumite NaF, biotite $K(Mg, Fe)_3AlSi_3O_{10}(OH,F)_2$, muscovite $KAl_2(AlSi_3O_{10})(OH,F)_2$, amphiboles such as hornblende $Ca_2(Mg,Fe,Al)_5(Si,Al)_8O_{22}(OH)_2$ and tremolite $Ca_2Mg_5Si_8O_{22}(OH)_2$[6 7 8].

The problem of high fluoride in ground water is due to leaching of fluoride from the fluoride bearing rocks. It has been observed that low calcium and high alkalinity favours high fluoride content in ground water[9]. Most of the people who are affected by high fluoride concentration in ground water live in the tropical countries[7, 10] where water consumption is more because of the prevailing climate, for example, Syria, Jordon, Egypt, Libya, Algeria, Sudan, Kenya, Afghanistan, Northern Thailand, Indonesia, Ethiopia, Tanzania, South Africa, Korea and India[6 7].

Fluoride is also found above permissible limits in many parts of Japan, Germany, China, Sri Lanka, Pakistan, Iran, Turkey, Southern Algeria, Mexico[11], Italy, Brazil, Malawi, North Jordon, Canada, Norway, Kenya and the United State of America [6 7]. In India[12 13 14], the most fluoride affected states are Andhra Pradesh, Tamil Nadu, Uttar Pradesh, Gujarat, Bihar, Haryana, Maharashtra, Madhya Pradesh, Punjab, Orissa, West Bengal and Rajasthan. Rajasthan is the only state in India where all of its districts (33 in number) are affected by fluorosis. There are large deposits of fluoride containing minerals like fluorspar, fluorapatite and mica in Rajasthan[15 16 17 18].

Fluoride is found in all natural waters at some concentrations. Sea water typically contains about 1 ppm fluoride. In river and lakes, fluoride concentration is less than 0.5 ppm. High fluoride concentrations in water occur in large and extensive geographical belts associated with volcanic rocks, sediments of marine origin in mountainous areas, granitic and gneissic rocks.

In areas where fluoride containing coal is burned or phosphate fertilizer are produced or used, the fluoride concentration in air is high, leading to increased exposure due to breathing. Also due to volcanic activity, fluoride may be released into the atmosphere[7 19].

Other possible sources of the intake of fluoride are from food, beverages, fluoridated dental product like toothpaste etc. Generally, fruits, vegetables and milk have low levels of fluoride concentration. However, high levels of fluoride have been found in barley and rice (about 2 ppm). The fluoride content of food items depends upon the fluoride content of soil, and water used for irrigation. Therefore, the fluoride content of the food items may vary from place to place[20].

Fluoride in water may be beneficial or harmful for human health. This depends upon amount of the fluoride in drinking water, because 60 % of fluoride ingested in body is through the water. A certain amount of fluoride is essential for the development of the enamel of teeth. Fluoride stabilizes the skeletal system by increasing the size of the apatite crystals and reducing their solubility. Approximately 75-90% of the ingested fluoride is absorbed in the intestine. Once absorbed into the blood, fluoride readily distributes throughout the body. Approximately 95% of the fluoride in the body is deposited in the hard tissues and it continues to be deposited in the calcified structure, even after other bone constituents (calcium, phosphorus, magnesium, carbonate and citrate) have reached a steady state. Age is also important factor for fluoride incorporation into the skeletal system and dental enamel [21 22].

Dental fluorosis begins when the fluoride concentration in drinking water is more than 2 ppm. The children whose age is less than eight years are more affected by fluorosis. The symptoms of dental fluorosis begin by the formation of yellow glistening patches on the teeth which may eventually turn brown, and presents itself as horizontal streaks. The brown streaks may turn black and affect the whole tooth which may get pitted, perforated and chipped off at the final stage. Dental fluorosis not only poses cosmetic problems but has also serious aspects too, in terms of matrimonial issues[23].

Drinking water containing more than 3-6 ppm of fluoride for long periods causes skeletal fluorosis. Skeletal fluorosis affects young and old alike. Fluoride can also damage the foetus- if the mother consumes water and food, with a high concentration of fluoride during pregnancy/breast feeding. Infant mortality due to calcification of blood vessels can also occur. Some symptoms of skeletal fluorosis are severe pain in the backbone, joints, hip region, stiffness of the backbone[24], immobile /stiff joints, increased density of bones, besides calcification of ligaments, constriction of vertebral canal and inter-vertebral foramen-pressure on nerves and paralysis[25].

The non-skeletal manifestations of fluorosis include nervousness, depression, tingling sensation in fingers and toes, excessive thirst, tendency to urinate frequently, muscle weakness, stiffness, pain in the muscle and loss of muscle power. Allergic manifestations include very painful, round or oval shaped pinkish, reddish or bluish red spots on the skin. Gastrointestinal symptoms of fluorosis include acute abdominal pain, diarrhoea, constipation, blood in stools, bloated feeling (gas), tenderness in stomach and feeling of nausea[7 8].

There are various methods to remove fluoride from drinking water[26 27 28 29] for example, the Nalgonda technique, bone charcoal technique, contact precipitation technique, activated carbon technique, ion-exchange technique, reverse osmosis technique, fly ash technique, electro-dialysis technique, clay column technique, and the activated alumina technique. These techniques are reviewed briefly in the following section.

1.2 Review of fluoride Removal methods

The various methods of fluoride removal from water are briefly discussed below.

1.2.1 Nalgonda Technique

This method was developed in India by the National Environmental Engineering Research Institute (NEERI) and used at both community and household levels. The process involves addition of aluminium sulphate and lime.

**Corresponding author email: margandan.123@gmail.com*

The fluoride removal is by a process of coagulation/flocculation and sedimentation. The addition of lime ensures an optimal removal of fluoride and pH of around 6-7 which ensures the complete precipitation of aluminium. The addition of lime also helps to form dense flocs which settle rapidly[6 7]. The reactions involved in this process are:

Aluminium dissolution

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

Aluminium precipitation

$2Al^{3+} + 6H_2O \rightarrow 2Al(OH)_3 + 6H^+$

Co-precipitation

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

pH adjustment

$6Ca(OH)_2 + 12H^+ \rightarrow 6Ca^{2+} + 18 H_2O$

The Nalgonda technique method has the following disadvantages: fluoride elimination rate is low (70-80%), there is a risk of contamination of the treated water by aluminium in case of overdosing of aluminium sulphate. This is partly due to the very low permissible limit of aluminium according to WHO (0.2 ppm). This is a work-intensive method, especially at a household level, due to the need of daily mixing of alum and lime[6 7].

The Nalgonda technique has the following advantages: chemicals are cheap and generally locally available, treatment is well accepted by locals and the fluoride removal processes are well understood[6 7]. A few important papers using the Nalgonda technique for fluoride removal are reviewed briefly below. Suneetha et al.[30] have modified the Nalgonda technique by doubling the concentration of alum and lime. This ensured that the fluoride levels in water treated by this method decreases by 75 to 88.2%, as compared to 44.6 to 59% by the dosage recommended in the original Nalgonda technique. The weight of the flocculated precipitate was significantly greater on using the increased dosage, indicating that the salts were being precipitated to a greater extent.

1.2.2 Bone Charcoal Method

Bone charcoal is a blackish, porous, granular material. The major components of bone charcoal are calcium phosphate 57-80%, calcium carbonate 6-10%, activated carbon 7-10%. Bone charcoal has the ability to absorb a wide range of pollutants such as colour, taste and odour components and has an ability to take up fluoride from water. The fluoride removal process is mainly by the replacement of the hydroxide groups of hydroxyapatite by fluoride[6 7].

$Ca_{10}(PO_4)_6(OH)_2 + 2F^- \rightarrow Ca_{10}(PO_4)_6F_2 + 2OH^-$

The bone charcoal method has the following advantages: high sorption capacity, locally available and cheap raw materials (animals bones), fast reaction time (less than 30 min), no addition of chemicals are needed for the treatment process and the filtered water is neutral in taste and colour[6 7].

The bone charcoal method has the following disadvantages: limited acceptability of animals bones as filter materials for drinking water, initial investments and experience are needed to set up bone char production, maintenance and regular monitoring of the filter is necessary, and if the filter is saturated it needs to be regenerated or replaced[6 7].

A few important papers using the bone charcoal method and calcium hydroxyapatite method for fluoride removal are reviewed briefly below.

Larsen and Pearce[31] have studied the defluoridation of drinking water using fluorapatite precipitation technique. Their results suggest that apatite precipitation may be a low technology way to defluoridate drinking water. Pearce and Larsen[32] have studied the fluoride removal from drinking water containing fluoride concentration in the range of 1-5 ppm. Fluoride removal using a two steps, brushite and fluorohydroxyapatite process lowers the fluoride concentration of water (in the range of 3-10 ppm) by over 2 ppm. Repeating the process will further reduce the fluoride concentration by 2 ppm.

1.2.3 Contact Precipitation

Contact Precipitation is a technique in which fluoride is removed from the water by the addition of calcium and phosphate compounds and bringing the water in contact with a saturated bone charcoal medium[6 7]. The method has the following advantages: enhanced fluoride uptake capacity and filter life (as compared to bone charcoal method) locally available materials, local production and low cost[6 7].

The method has the following disadvantages: the calcium phosphate pellets cannot be regenerated, it is time consuming and the chemical processes are not fully understood yet[6 7].

A few important papers using the contact precipitation for fluoride removal are reviewed briefly below.

Dahi[33] has described the defluoridation technique using contact precipitation. In this process, the fluoride contaminated water is mixed with $CaCl_2$, $Ca_3(PO_4)_2$ and placed in contact with bone char. Experiments were conducted using a Jar Test, column setup and filter contact column. The results for a pilot defluoridation plant using this method are also discussed.

Okello et al[34]. have investigated the contact precipitation as a viable water defluoridation technique. The defluoridation capacity of bone charcoal and plan minjigu rock has been determined using column experiments.

1.2.4 Clay

Clay is an earthy sedimentary material composed mainly of fine particles of hydrous aluminium silicate and other minerals and impurities. Clay is fine textured, plastic when moist, retains its shape when dried and sinters hard when fired. These properties are utilized in manufacture of pottery, brick and tile. Both clay powder and fired clay are capable of sorption of fluoride as well as other pollutants from water[6]. The ability of clay to clarify turbid water is well known. This property is believed to known and utilized at domestic level to filter water in ancient Egypt[6 7].

The method has the following advantages: low cost and locally available. The method has the following disadvantages: low fluoride adsorption capacity, time consuming and has hygienic aspects because of the use of clay.

A few important papers using the clay for fluoride removal are reviewed briefly below.

Wang and Reardon[35] have studied the use of soil as a defluoridating material for drinking water. Their study showed that heavily weathered tertiary soil from Xinzhou, China is a F^- specific sorbent. Heat treatment of soil can generate a permeable granular material which is suitable for column use. The soil sorbent can be regenerated using iron oxyhydroxy oxide, and perhaps the FeOH surface groups are most likely responsible for the soil's F - adsorbing ability.

Yadav et al.[36]have used powered brick as a defluoridating agent. The adsorption of fluoride by brick powder was found to be a first order reaction. Surface adsorption as well as intraparticle diffusion contributes to rate determining step. The optimum pH was found to be in the range of 6 to 8 for maximum adsorption of fluoride, which makes it an ideal candidate for drinking water treatment. Brick powder was found to be a selective adsorbent for fluoride and the presence of other ions in ground water did not significantly affect the defluoridation process. A comparison of brick powder and available commercially activated charcoal reveal, that the powdered brick is an economical adsorbent due to its greater surface area and easy availability and its ability to remove fluoride at the natural pH of water.

Zevenbergen et al.[37] have studied the fluoride adsorption on Ando-soil in Kenya. The adsorption follows the Langmuir equation and fluoride adsorption is high at acidic pH values.

Soni and Modi[38] have used red mud for defluoridation purposes. The maximum fluoride removal occurs at pH 5.5 and the equilibration time is 2 hrs. They have reported that fluoride removal decreases sharply above pH 5.5. The removal of fluoride is explained on the basis of its interaction with metaoxides in the red mud.

Tikariha and Sahu[39] have studied the fluoride adsorption characteristics of clay collected from different regions of Ethiopia for fluoride removal. The effects of contact time, amount of adsorbent dose, pH, particle size and heat treatment of clays have been investigated.

Chidambaram et al.[40] have studied the defluoridation ability of natural red soil. According to their study, FeOH, AlOH bonds present in soil play the main role in contributing to the efficiency of fluoride removal.

Sarkar et al.[41] have investigated the use of laterite on fluoride removal. The thermodynamic parameters such as free energy change, enthalpy and entropy of the process have been evaluated. The equilibrium data were fitted to Langmuir or Freundlich isotherm models. The process was found to be thermodynamically favourable, spontaneous and exothermic in nature. Column studies have shown that the defluoridation process is dependent on the feed fluoride concentration, pH, flow rate and column bed height. The Bed Depth Service Time model has been used to predict fluoride removal.

Brick pieces have been used by J. P. Padmasiri [42] for making defluoridation filters. The outer body of the filter was made by PVC pipe or cement bricks. The defluoridation process works in an upward flow method. The fluoride filter operates at 85 % efficiency at the start of the operation and 25 % at the end of the process. The saturation of the brick pieces was reached between 90 and 250 days after which the brick pieces have to be replaced. A number of these filters have been distributed in Sri Lanka.

Yadav et al.[43] have used aluminium oxalate as an adsorbent for preparing traditional soil pots to minimize fluoride content in drinking water samples. Their studies show that the adsorption isotherm of fluoride ions follows the mixed model of Langmuir and Freundlich.

Coetzee et al.[44] have used selected South African clays for fluoride removal from ground water. Bauxite clays were found to have the best overall potential as a fluoride adsorbent. The clays could be chemically activated for adsorption using 1% NaHSO4 solution and dilute HCl.

1.2.5 MgO-Lime Technique

The method treats fluoride-contaminated ground water with fluoride ion concentration ranging from 1.5 to 7ppm. The fluoride ions are removed by magnesium oxide through chemisorptions mechanism. On adding to water samples, magnesium oxide hydrates to brucite [$Mg(OH)_2$] as :

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

During brucite formation, fluoride ions in the contaminated water samples are incorporated into the brucite lattice by isomorphous substitution of hydroxyl ion by fluoride ions. The isomorphous substitution reaction leads to the formation of the Mg(OH)2-y.Fy phase. In addition to magnesium oxide, calcium chloride solution, sodium bisulphate solution and calcium hydroxide (as solids) are added to the raw water. Addition of magnesium oxide increases the pH of water between 10.1 and 10.3. Sodium bisulphate solution reduces the pH of magnesium oxide treated water within the potable water limits (6.5 to 8.5) by the reaction:

$$HSO_4^- + OH^- \rightarrow SO_4^{2-} + H_2O$$

The bicarbonates ion present in the fluoride-bearing water samples convert to carbonate ion in the alkaline pH created by magnesium-oxide addition according to the reaction;

$$HCO_3^- + OH^- \rightarrow CO_3^{2-} + H_2O$$

The carbonate ions formed in the above reaction, in turn consume an additional equivalent of sodium bisulphate as:

$$CO_3^{2-} + HSO_4^- \rightarrow HCO_3^- + SO_4^{2-}$$

Calcium hydroxide (hydrated lime) and calcium chloride solution reduces the interference of bicarbonate ions towards sodium bisulphate consumption by transformation of soluble bicarbonate to insoluble calcium carbonate as:

$$HCO_3^- + Ca^{2+} + OH^- \rightarrow CaCO_3 + H_2O$$

Rao and Mamatha[45] have developed the method of defluoridation using MgO-Lime-$CaCl_2$-$NaHSO_4$. The defluoridation filter consistent of two chambers with the upper chamber fitted with a manual or electric stirrer. In the top chamber fluoride contaminated ground water and calculated doses of MgO, lime and aqueous solution of $CaCl_2$ are added. The solution is left for 16 hr. for the flocs to settle down. A flexible tube fitted at the bottom of the top container is used to transfer the clear supernatant water to the bottom container. The tube also functions as an inlet for adding $NaHSO_4$ for pH adjustment in the bottom container. The potable water can be drawn off from the bottom container using a tap.

In a variation of this method, Mamatha and Rao[46] have used a two stage filter unit with an electric stirrer and layers of cotton cloth to filter out any sludge particles before the pH adjustment step.

The various doses of MgO, lime, $CaCl_2$, $NaHSO_4$, for defluoridation of water containing different bicarbonate concentrations and fluoride levels are also documented[47].

The fluoride containing sludge can be encapsulated in stabilised mud blocks for environmentally safe disposal and conversion into building materials[48].

1.2.6 Reverse Osmosis

Reverse Osmosis (RO) is a membrane technology that uses pressure to force water through a semi-permeable membrane, thereby removing dissolved solutes from solution based on particle size, dielectric characteristics, and hydrophilic/hydrophobic tendencies. The RO can be used as a stand-alone treatment for most water sources. The RO can remove 85-95% of fluoride from water[27].

The RO method has the following advantages: RO is the best technique for removing both fluoride and arsenic; present technological familiarity with membrane separation system, the RO will treat current (F/As) and possible future contaminants of concern and positive public perception.

The RO method has the following disadvantages: high water loss (20-40%), high energy consumption, high capital costs, pre-filtration and post-pH/alkalinity adjust the treatment may be needed, chemical handling facilities and skilled operator is needed for cleaning of the RO membrane.

Few important papers using the reverse osmosis for fluoride removal are reviewed briefly below.

$CaCO_3$ has been used to treat the reject water from the reverse osmosis process by Babu et al.[49]. It was observed that the fluoride concentration in the final effluent was within the safe limits. Byoung et al.[50] have used reverse osmosis for fluoride removal.

1.2.7 Electrodialysis (ED)

Electrodialysis (ED) is a membrane process similar to RO, except that the ED uses an applied d. c. potential (electric current), instead of pressure, to separate ionic contaminants from water. Because water does not physically pass through the membrane in the ED process, particulate matter is not removed. Thus, the ED membranes are not technically considered as filters. This process can remove 85-95 % fluoride from water[27].

The ED method has the following advantages: the present technical familiarity with the membrane separation systems, this method will treat current fluoride and arsenic contaminates and possible future contaminants of concern and a positive public perception[27].

The ED method has the following disadvantages: it is very costly, there is significant water loss, brine discharge, high energy consumption, high capital costs, pre-filtration and post-pH/alkalinity adjustment/ treatment may be needed for the membrane maintenance, chemical handling facilities needed, multiple systems needed to achieve water conservation goals and skilled operators are required.

A few important papers using Electrodialysis for fluoride removal are reviewed briefly below.

Amor et al.[51] have studied the defluoridation using the electrodialysis technique. Their results show that defluoridation and desalination rates increase with operating voltage and temperature.

Adhikary et al.[52] have studied defluoridation of water during the desalination of brackish water by electrodialysis. The optimum operational conditions of the electrodialysis cell have been determined for obtaining water with less than 600 ppm TDS and < 1.5 ppm F^- concentration, from brackish water of 5000 ppm TDS and 15 ppm F^-.

Dialysis has been used by Hichour[53] for defluoridating water. Their studies show that dialysis is an efficient defluoridation process in which permissible limit of fluoride is achieved despite the presence of different cations and anions in the raw water.

Elazhar et al.[54] have compared the performance of electrodialysis and nano-filtration in fluoride removal from Moroccan ground water. Pilot plant studies show that the fluoride reduction and performance of two technologies are comparable.

Tahaikt et al.[55] have used electrodialysis in continuous operation for fluoride removal from Moroccan ground water for fluoride removal. An optimization study of the electrodialysis operation was carried out under various experimental conditions. The water quality parameters as well as power consumption and recovery rate where followed to determine the optimum operating conditions.

Ali et al.[56] have studied the fluoride removal from polluted water using electrodialysis. The efficiency was evaluated by the fluoride removal rate, demineralization rate and power consumption. The defluoridation process was independent of the feed solution.

1.2.8 Ion Exchange

In this method water is allowed to flow down through a column packed with an ion exchange resin. When the adsorbent becomes saturated with fluoride ions, the filter material has to be back washed with a mild acid or alkali solution to clear and regenerate it. The effluent from backwashing is rich in accumulated fluoride and must be therefore disposed off carefully to avoid recontamination of nearby ground water[27].

The ion exchange method has the following advantages: the chemicals used are safe for the operator to handle and operation is simple, the process can be almost totally automated, because resins have the ability to remove all hardness from water.

The treated water must be blended with water that has been by-passed around the softener (or adjustments made) to obtain a hardness level which the operator needs to maintain[27].

The ion exchange method has the following disadvantages: it is costly, low capacity, sorption of other anions from water and the fluoride concentration in raw water must be less than 10 mg/l.

A few important papers using the ion exchange method for fluoride removal are reviewed briefly below.

Oke et al.[57] have studied the defluoridation of drinking water using Al doped Amino-methylene-phosphine-acid resigns called Lewatit Mono Plus TP 260. They have carried out pilot plant studies using this technique and have reported the suitability of this process under weakly acidic conditions (pH = 4).

Castel et al.[58] have studied the selective removal of fluoride by ion-exchanger HP-555 followed by another ion exchanger column (IR-458). This patented process successfully achieved the fluoride removal from a carbonated water containing Cl^- and SO_4^{2-} as major ions. The process has a fluoride removal efficiency of 90-95%.

Kumar et al.[59] have designed a cost effective and dual functional muslin-based anion exchanger that can function both as a defluoridating agent and antimicrobial antifungal agent. The experimental data fitted into pseudo second order kinetics and Langmuir adsorption isotherm. The maximum fluoride uptake was observed at pH 4, temperature 20 0C and with 10 ppm of fluoride concentration in the inlet water.

1.2.9 Bio-adsorbents

Various kinds of bio-adsorbents have been used to remove fluoride and several papers in this context are reviewed in detail. Veeraputhiran and Algomuthu88 60 have used a bio-adsorbent made from Phyllantus Albica to remove fluoride from water. Their studies show that equilibrium is achieved at 75 min. Higher adsorption of fluoride is achieved with smaller particle size and fluoride adsorption increases with increasing dose of adsorbent. The effect of the interference of co-ions on fluoride removal was found to be in the following order $HCO_3^- > SO_4^{2-} >$ Cl. $> NO_3^-$.

Merugu et al.[61] have used a fungal bio-sorbent prepared from Aspergillus Niger for removal of fluoride. Their studies have shown that calcium and alkaline treated biomass were effective in removal of fluoride. The fluoride removal was maximum at pH 8. The fluoride removal decreased with increasing bicarbonate concentration, but was independent of presence of Cl^- and SO_4^{2-}. The kinetics of fluoride removal exhibited a rapid phase of binding for a period of 1 hr and lower phase of binding during the subsequent period.

Maheswari et al.[62] have used bio-adsorbents prepared from dry fruits collected from plants Enterolobium Saman (ESC), Acasia Arabic (AAC), Prosopis Juliflora (PLC) for defluoridation purposes and compared them with granular activated carbon. The optimum dose of adsorbent and contact time for fluoride removal has been determined.

Mondal et al.[63] have used tea ash as a bio-sorbent for fluoride removal. The defluoridation capacity increases with increasing adsorbent dose and contact time, but decreases with initial concentration of fluoride solution. The maximum defluoridation occurs at pH 6. The defluoridation follows a pseudo second order kinetics. The experimental data follows the Langmuir and Freundlich adsorption isotherm.

Mamilwar et al.[64] have used an adsorbent derived from bark of babool tree (Acacia nilotica) as an adsorbent for defluoridation. The maximum defluoridation occurred at pH 8 with an equilibrium time of 8 hrs. The experimental data fitted well with Langmuir and Freundlich adsorption isotherm and pseudo first order kinetic model. Their studies showed that the fluoride adsorption increases with increasing percentage of Mg^{2+}, SO_4^{2-}, Fe^{2+} and remains nearly constant in presence of NO_3^- ions.

Kamble et al.[65] have studied the fluoride removal from drinking water by chitin, chitosan, lanthanum-modified chitosan. They observed that fluoride removal is maximum at pH 6.7 which is the pH of the studied fluoride contaminated ground water. The Langmuir isotherm model was used for fitting the equilibrium adsorption data. It was found that SO_4^{2-}, CO_3^{2-}, HCO_3^- ions greatly affected the adsorption of fluoride. Fluoride uptake was more in distilled water than from fluoride contaminated ground water, indicating the competing effect of other ions in the adsorption process.

Kumar et al.[66] have used thermally prepared carbon from Neem (Azadirachta Indica) and Kiker leaf (Acacia nilotica) for the defluoridation process. Their studies show that fluoride removal is dependent upon pH, contact time, particle size and dose of adsorbent. A first order kinetics and the Freundlich adsorption isotherm were obeyed for the adsorption process.

1.2.10 Aluminium Based Adsorbents

Various kinds of aluminium based adsorbents have been used to remove fluoride and several papers in this context are reviewed in detail.

A mixed alumina magnesia hydroxide adsorbent (PURAL@MG-20) has been used by Patanker et al.[67] for the defluoridation purposes. The maximum fluoride removal efficiency was observed in the range pH 5 to 7. The Langmuir adsorption isotherm best fitted the experimental data. The adsorption process follows the pseudo second order kinetics. Column breakthrough studies were used to test performance of the adsorbent media in continuous mode. Since PURAL @ MG-20 is commercially available, and it has a high fluoride uptake capacity, the authors suggest that this adsorbent can be used for field applications.

A new high capacity alumina hydroxide based adsorbent has been developed and tested for fluoride adsorption from water by Mulugeta et al.[68].When used with a calcite post-column treatment, this material is highly promising at both household and community defluoridation levels.

Thermal treatment of pseudo-boehmite agglomerates have been used to prepare a novel adsorbent for defluoridation purposes by Vazquez and Petriciolet[69]. Taguchi and surface response methodologies were used to synthesize the adsorbent and obtain best fluoride removal rate.

Das et al.[70] have studied the defluoridation of drinking water using activated titanium rich bauxite using batch equilibrium experiments. The adsorption of fluoride with respect to variation of pH, adsorbent dose, initial fluoride concentration, presence of interfering ions and heat treatment were investigated. It was found that heat treatment at moderate temperature (300-400 0C), greatly increased the fluoride removal capacity of titanium rich bauxite. The rate of adsorption of fluoride was high, and equilibrium was attained within 90 min. The fluoride removal was maximum at pH 5.5 to 6.5. The first order rate equation was followed in adsorption kinetics. The adsorption data fitted well in both the Langmuir and Freundlich adsorption isotherms. The presence of common interfering ions like SO_4^{2-}, Cl^-, HCO_3^-, CO_3^{2-} and NO_3^- marginally lowered the fluoride removal capacity of titanium rich bauxite. The adsorbed fluoride can be removed from bauxite by treating with aqueous solution of pH > 11.1. Janardhana et al.[71] have used metal ion impregnated activated charcoal in column studies for fluoride removal. $ZrOCl_2$, CaO, $CaCl_2$, alum and borax were impregnated into coconut shell charcoal. Their studies show that impregnated coconut charcoal showed maximum fluoride uptake and proved to be the most effective defluoridating agent followed by CaO and Alum.

1.2.11 Miscellaneous Techniques

Shivasamy et al.[72] have studied the use of coal based adsorbents like lignite, fine coke and bituminous coal for fluoride removal from water. These coals based adsorbents obeyed the Freundlich and Langmuir adsorption isotherms. The adsorption process follows a first order adsorption rate equation.

Fan et al.[73] have studied fluoride adsorption using hydroxyapatite, fluorspar and quartz, activated using ferric ions. The kinetics of the fluoride adsorption and the adsorption process has been described by the Langmuir and Freundlich isotherm models.

Garmes et al.[74] have combined the adsorption process using adsorbent such as Al_2O_3 and ZrO_2 with Donnan Dialysis procedure to treat fluoride contaminated ground water from phosphate mines in Morocco. In a continuous mode, a dialysis unit was used with anions exchange membrane Neo Septa – ACS (Tokuyama Co.). The cation composition remains unchanged in the process whereas all anions, except Cl^- were partially eliminated and substituted by Cl^- ions.

Haghighat et al.[75] have studied the adsorption of fluoride using AA and compared them with fluoride removal using single-walled and multi-walled carbon nanotubes. Their studies showed that highest removal efficiency was obtained at pH 5 with an initial fluoride concentration of 1 ppm. The highest fluoride removal occurred when 30% by weight of alumina was used in the experiment. The fluoride adsorption ability of carbon nanotubes is high as compared to AA.

Kagne et al.[76] have studied the removal of fluoride from aqueous solutions using bleaching powder. Bleaching powder showed significant fluoride removal in mid of high or low pH regions. The extent of fluoride removal is affected by the presence of SO_4^{2-}, NO_3^- and Cl^-. The Langmuir isotherm was followed in the adsorption process. The fluoride removal by bleaching powder was found to be better in synthetic water than fluoride contaminated ground water.

Zhua et al.[77] have studied fluoride distribution in the electrocoagulation process. It was found that fluoride could be distributed in three parts; firstly the fluoride which remains in water, secondly, absorbed by the flocs generated, and thirdly, removed by the gelatine layer attached to electrode. The overall defluoridation efficiency varies with the fluoride distribution.

Li et al.[78] have studied defluoridation of water using aligned carbon nanotubes (ACNTS). Their studies show that the Freundlich adsorption isotherm provided a better fit of experimental data than the Langmuir adsorption isotherm.

Loucini[79] have studied the electro sorption process effective to remove fluoride from ground water. The various parameters like temperature, volumetric flow, initial fluoride concentration and hardness were optimized for the process.

Srimurali et al.[80] have studied the removal of fluoride using various low cost materials. Their results show that the fluoride removing ability of the materials are in the following order, bentonite < charfine < kaolinite < lignite < nirmali seeds. Their studies showed that the removal of fluoride decrease with increasing pH, decreasing size of adsorbent and increasing adsorbent dose.

1.2.12 Activated Alumina

Activated alumina (AA) is a granular, highly porous material, synthesized from aluminium trihydrate [$Al(OH)_3$]. It has an amphoteric character. It is a good adsorbent due to its small size, and large surface area. The fluoride uptake capacity of AA depends on the specific grade of AA, its particle size and the water chemistry like, pH, alkalinity and fluoride concentration6 7.

1.2.13.1 Advantages of Defluoridation Using Activated Alumina

The main advantages of AA based defluoridation are as follows : it requires minimum contact time with fluoride contaminated water for defluoridation, it can be regenerated easily, percentage of regeneration is considerably high, there is very little attritional loss (to a negligible extent) during the regeneration at the initial stage of operation, it is indigenously available and cheap, its defluoridation capacity at neutral pH is appreciable, although it has greater defluoridation efficiency at pH 5-7, its defluoridation capacity is independent of temperature, AA is easy to handle, filter fabrication with AA is easy and most importantly AA and the filter requires no maintenance and no electricity6 7.

The effect of other ions present in drinking water like Cl^-, SO_4^{2-} and CO_3^{2-}, over defluoridation efficiency of AA is minimum. However, the presence of HCO_3^- ions shows considerable influence on the process of defluoridation.

1.2.13.2 Mechanism of fluoride removed by Activated alumina

AA surface is amphoteric in nature and can exist as $AlOH^{2+}$, AlOH and AlO^-. Fluoride binding to AA is proposed to be due to exchange of surface hydroxyl groups, which can be represented by the following reaction.

$$*AlOH2+ \;+\; F- \;\rightarrow\; AlF \;+\; H2O$$

$$*AlOH \;+\; F- \;\rightarrow\; AlF \;+\; OH-$$

where Al* represents solid AA surface. Since the use of AA technique of defluoridation has been researched on in this thesis, therefore the relevant papers are reviewed in detail below.

George et al.[81] have carried out modelling and simulation studies on residual aluminium in water which has been defluoridated using AA. An Activated Alumina Defluoridation Modelled Simulator (AAD) has been developed to represent the fluoride adsorption on the basis of surface complexation theory incorporating aspects of aluminium solubility. The model has been validated for high fluoride concentration and pH variations. Batch experiments were done using AB-101 grade AA with fluoride concentration ranging from 1 to 10 ppm. The total residual Al in defluoridated water was due to presence of dissolved and precipitated alumino fluoro complexes.

Bulusu and Nawlakhe[82] have studied fluoride removal using AA (ACC, G-80) in batch operations. They found that the initial rate of adsorption of fluoride decreases progressively after the initial 30 min and finally approaches the equilibrium slowly. In the initial adsorption process, the amount of fluoride adsorbed varies nearly linearly with the square root of time. The adsorption of fluoride was more rapid at low fluoride concentrations than at high concentrations. Freundlich and Langmuir isotherms are poorly followed in the adsorption process.

Daw[83] has summarised the experience of UNICEF in tackling the problem of fluorosis in rural areas using domestic defluoridation units containing AA. The UNICEF has supported the research work of the development technology for these filters at IIT Kanpur since 1991. Pilot projects of domestic defluoridation were carried out in Andhra Pradesh and Rajasthan during the period 1996-2002.

Draft standards for AA suitable for use in filters have been also reviewed[84]. The AA should confirm to IS: 9700 (1991) specification. The recommended grain size is from 0.4 to 1.0 mm. Mechanical grinding of AA is not acceptable. The yield of defluoridated water should be greater than 170 lit./kg of AA per cycle. When raw water having alkalinity of 420 mg/lit., pH 7.3 and fluoride concentration of 10.5 ± 5 mg/lit. is passed through 3 kg AA bed with flow rate of 9 to 12 lit. /hrs, under these conditions, the fluoride uptake capacity should not be less than 180 mg/kg AA. The manufactures should specify the FUC after 10 cycles of regeneration. The attrition loss in each regeneration cycle and residual Al in treated water due to leaching should also be specified. The AA should not impart residual Al to treated water.

Iyenger[85] has summarized the defluoridation studies conducted at IIT Kanpur from 1991 to 2005. A hand pump based defluoridation unit was developed using 110 kg of AA grade G-87 (IPCL) with particle size from 0.3 to 0.9 mm. The Public Health Engineering Department (PHED) Rajasthan has also developed two different models of hand pump based defluoridation units in collaboration with the DST Rajasthan using AA grade (AAFS-50) (Alkali Chemicals Ltd., UK). The AA has high efficiency; it is cost effective for one time use and disposal in landfill, instead of "regeneration and reuse". The screening of indigenously manufactured AA grades in defluoridation units were carried out for 15 grades of AA. Domestic Defluoridation Unit (DDU) have been fabricated using GI sheets and AA with a flow rate of 8-10 lit./hr. A regeneration process of AA using 1% NaOH and 0.4 N H2SO4 have been developed. A method of disposal of the spent regenerant by adding $CaCl_2$ to precipitate the fluoride, mixing of acid or alkali regenerants and adding alum and lime to remove fluoride have also been carried out.

Chauhan et al.[86] have studied the Domestic Defluoridation Unit (DDU) using indigenously manufactured AA, particle size from 0.4 to 1.2 mm. The specific safe water yield (SSY) has been determined as a function of AA amount and depth of AA bed. The reuse potential of exhausted AA was determined by regenerating the AA. High FUC of the AA as well as retaining 95% of the FUC in up to 5 regeneration cycles showed the suitability of AA for defluoridation. The specific safe water yield decreases with AA depth in the filter, even though the same amount of AA was used.

Venkobacher et al.[87] have discussed the development of DDU's for use in rural in India. Six grades of AA have been used in the study G-87 and AD-101 by IPCL, particle size (0.3 to 0.85 mm), OA-25 (1), OA-25 (2) from Oxide India Ltd., particle size (0.3 to 0.6 mm), AA-P (Pawan Industries Hyderabad, India), particle size (0.4 to 0.6 mm) and AA-B (Indian Alumina Industries Hyderabad, India)(average particle diameter of 1 mm). The DDU's were fabricated using a micro filter and two chambers made from stainless steel with the flow rate of 12 lit./hr. Three kg of AA was filled in the upper container and the DDU's evaluated and field tested in Dungarpur Dist. of Rajasthan. The exhausted AA was regenerated with acid and alkali. After 30 cycles of regeneration, the decrease in fluoride uptake capacity was marginal. The FUC was significantly affected by pH, alkalinity and sulphate concentrations of the ground water.

Stewart[88] has submitted a term paper on removal of fluoride from water using AA. The author concludes that there is significant gap between researches conducted in laboratory for the removal of fluoride in natural waters; although a number of field studies have been conducted utilizing AA packed columns for removal of fluoride in Africa.

Karthikeyan et al.[89] have studied the fluoride removal from water using AA (LR grade, S.D. Fine Chemical Pvt. Ltd. India). Their results showed that a minimum 20 min contact time is required for defluoridation. The defluoridation capacity was found to be 20.4 mg F-/gm of AA at pH 3, and decreases to 3 mg F- /g of AA at pH 12. It is suggested that a solution of 2% HCl, 2% NaOH, 1% H2SO4 are good regenerants for the exhausted AA.

Vaish et al.[90] have discussed the fluorosis mitigation programme in Dungarpur district of Rajasthan using the Nalgonda technique and AA based filters. They conclude that because of the daily disposal problem of sludge, this technique is less preferable. They further suggest that a number of NGO's should come forward to implement the fluorosis mitigation problem.

Lenyva-Ramos et al.[91] have studied the kinetics of fluoride removal using AA prepared from pseudo-boehmite. The AA was mainly composed of γ-Al2O3 as determined by XRD spectra. The fluoride adsorption was found to be maximum at pH 4 and adsorption capacity decreases when pH was between 4 to 11. This behaviour has been attributed to the electrostatic interaction between fluoride ions in solution and the surface charge on the AA below pH 4.3. Aluminium dissolution also causing a decrease in fluoride adsorption capacity of AA. The Langmuir and Freundlich isotherm models were studied for the process of fluoride adsorption.

Wu et al.[92] have studied the process of defluoridation of water using AA. Their study indicates that the maximum removal of fluoride from water occur at pH 5. At this pH, the rate of adsorption of fluoride from water is a function of the ratio of the initial fluoride concentration to the AA dose. When this ratio is less than 10-2 mg F-/mg of alumina added, the adsorption rate constant decreases with increasing ratio of fluoride to alumina. At fluoride to alumina ratio above 10-2, there is no significant change in the adsorption rate constant. The Langmuir isotherm can be used to model the fluoride adsorption on AA. From the Langmuir model, the total adsorption of capacity of AA from fluoride was found to be 12 mg/g. This grade of AA, according to the authors, has a low cost and has relatively high acid resistance to minimize loss during regeneration.

CONCLUSION

An attempt has been made to provide a succinct overview of the various adsorbents used to remove fluoride from water that has been polluted with fluoride. The two main categories of fluoride removal procedures are membrane and adsorption approaches. Ion exchange, electrodialysis, and reverse osmosis have all been covered under membrane techniques. Activated alumina, the Nalgonda process, bone charcoal, bio-adsorbents, MgO, CaO, CaCl2, and HCl are examples of adsorption techniques (IISC Method). The amount of fluoride in ground water has been reported to range from 0.1 to 12.0 ppm as a result of the leaching of fluoride-bearing rocks.Similar to this, several regions of the world and India, including Rajasthan, A.P., Punjab, Haryana, Tamil Nadu, Karnataka, Madhya Pradesh, and Gujarat, have observed fluoride-containing water.

It is well recognised that fluoride can have both positive and negative effects on health. Bone and teeth are severely affected by fluoride in drinking water. It enhances the enamel when present in low concentrations of 1–1.5 mg/l. Dental fluorosis is caused by fluoride concentrations between 1.5 and 4 mg/l, whereas skeletal fluorosis is brought on by high amounts of 4 to 10 mg/l. A severe health issue is fluorosis disease, which is brought on by an excessive consumption of fluoride through food, water, and air. Fluoride from water consumption accumulates in bones until age 60 or beyond. Fluorosis in the skeletal, dental, and non-skeletal systems can vary in severity depending on the amount of fluoride consumed.

There are several defluoridation procedures available to remove fluoride, but not all of them are appropriate in all situations, thus appropriate methods must be justified before being used. A few techniques, like as the removal of fluoride using activated alumina, have proven to be exceedingly efficient, cost-effective, and simple to implement at the village level.

ACKNOWLEDGEMENT

As a part of a Department of Science and Technology, New Delhi, Government of India Water Technology Initiative Project, focusing on low cost defluoridation fil-ters for rural use, MgO, CaO and CaCl2 based filters have been adapted and tested, both in the laboratory and in the field for the last three years.

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