POTENTIALLY LOW-COST DRINKING WATER DEFLUORIDATION METHODS - A REVIEW

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ABSTRACT

Excessive fluoride in drinking water causes dental and skeletal health problems commonly known as fluorosi s. Both high fluoride concentration and fluorisis are prevalent in many parts of the Ethiopian rift valley. The recommended limit of fluoride by the World Health Organization (WHO) ranges from 0.5 - 1.5 ppm, whereas water with fluorid concentrations as high as 9 mg/l are used in some part of the Ethiopian Rift Valley. A number of studies have been conducted to identify the fluoride concentrations in different areas and their effect on the population. However only limited research have been carried out to develop appropriate defluoridation techniques affordable for developing countries like Ethiopia.

In this review, an extensive list of materials that are proposed for the treatment of fluoride has been compiled and evaluated to provide a summary of available information on a wide range of potentially low-cost methods. Techniques that can utilize locally available materials and simple technologies have been given more emphasis. Future research directions for further improvements of the proposed methods and the development of new defluoridation techniques based on locally available materials has been suggested.

INTRODUCTION

Excessive levels of fluoride in drinking water supplies are common problems in the Rift Valley of Ethiopia and many parts of the world. The maximum amount of fluoride in drinking water is regulated at 1.5 mg/l [1]. The 1984 WHO guidelines suggest the permissible fluoride level to be 1.0 mg/l in warm climate and 1.2 mg/l in cooler areas. It should be known; however, that the WHO guidelines are not universal as many countries have established their own guidelines regarding fluoride content of drinking water. For countries in the tropical region, the recommended fluoride concentration is even lower (about 0.8 mg/l) because of the relatively higher water consumption. These guidelines stem from a concern over public health safety because dental and skeletal fluorosis has been linked to high concentration of fluoride in drinking water. Prevalence of dental and skeletal fluorosis has been reported in several parts of the world including Ethiopia, where fluoride concentration in drinking water exceeded the guideline level [2, 3, 4].

People in several regions of the Rift Valley of Ethiopia are consuming water with up to 33 mg/l of fluoride [2, 5]. For a community, being supplied with water containing excessive fluoride i.e., consistently and significantly in excess of 1.5 mg/ over long period of time, there are two possible control options. The first approach is to seek an alternative water source either for direct consumption or for mixing with contaminated water; the use of bottled water is an extreme example of this approach and the second one is to reduce fluoride content or eliminate fluoride by treatment of contaminated water. In areas where alternative sources are not available and the provision of bottled water is not economical, as in the case of most tropical regions of developing countries, the second option is probably the most reasonable approach.

The methods by which excess fluoride can be removed from drinking water include chemical precipitation, adsorption, ion exchange and membrane separation. The membrane separation method is relatively expensive and requires sophisticated technology. Almost all of the currently available potentially low cost methods are based on chemical precipitation, adsorption methods and ion exchange using bone char. The purpose of this paper is to review potentially low-cost defluoridation methods, which could be used to alleviate the fluorosis problem either at household or small community levels. Emphasis is given to techniques that can utilize locally available materials and are simple for design, production, operation and maintenance. Future research directions for further improvements of the proposed methods and the development of new defluoridation techniques based on locally available materials has been suggested.

POTENTIALLY LOW-COST METHODS

As a matter of fact, most of the countries where fluorosis problems are observed are developing countries. Only few developed countries are affected by excess fluoride in drinking water. The challenge for the developing countries is enormous because the most efficient defluoridation methods are very expensive and require sophisticated technology, which are lacking in these countries. However, some researches are being undertaken in some developing countries, like India, Bangladesh, Kenya, Tanzania and Ethiopia to develop, low cost drinking water defluoridation techniques appropriate for developing countries. The term "potentially low cost" in this paper takes into account the availability of the materials used in the methods, the simplicity of the technique for manufacturing, operation and maintenance in addition to the cost of the equipment and the chemicals used since all these affect the cost of the defluoridated drinking water. The following section discusses the different low cost defluoridation options.

Chemical Precipitation

Aluminum Sulfate

Alum treatment to remove fluoride is similar to that for turbidity removal except that the required dose is larger. Some study showed that about 350-mg/l of alum is needed to reduce the fluoride concentration from 3.6 mg/l to 1.0 mg/l (135 mg/mg F). Another study in a full-scale plant showed that 500mg/l alum was needed to reduce the fluoride concentration from 3.8 to 1.0 mg/l at raw water alkalinity of 200 mg/l as $CaCO_3$ and pH 6.9. This value increased to 700 when the raw water alkalinity increased to 380 mg/l as $CaCO_3$. The amount of alum dose generally increases with alkalinity/or pH and fluoride concentration (Nema et al., 1989).

The mechanism of removal is not clear, but is generally believed that Alum dissociates and then hydrolyzes in water to form the hydrated aluminium species, $Al(H_2O)_6^{3+}$. This species finally tends to be $Al(OH)_3.(H_2O)_3$. The mononuclear-complex can be coagulated by hydroxyl through bridging into polynuclear-complex. The complex is of linear structure, and may adsorb fluoro-complex and fluorion through Van Derwall gravitation, hydrogen-bonding, physical and chemical adsorption to form flocs and finally settles. It has been suggested that aluminium ion is not responsible for the precipitation of fluoride and that aluminium hydroxide itself is also not responsible for the insolubility of fluoride salt. The hydroxylated aluminium complex formed in the precipitation of alum combines with, precipitates, or removes the fluoride ion along with the flocculated material by adsorption because the fluoride ions can possibly be adsorbed into the diffuse layer of the flocculant.

Problems associated with alum treatment may include the existence of residual aluminium species at larger alum dosage, the decrease in pH and the requirement of large amount of chemical. The variation with raw water quality may mean that the process is suitable for certain water quality range. Further more, the fluoride removal may directly depend upon the efficiency of coagulation-flocculation, which in turn is related to pH. Addition of certain types of coagulant aids may also facilitate the fluoride adsorption and flocculation processes within acceptable pH range. Detailed investigation will be required in the context of Ethiopian water quality situation.

Aluminum Sulfate and Lime

This method, commonly known as Nalgonda Technique, has been very successfully used for domestic as well as for community water supplies in India, which was first proposed in 1975. The process comprises the addition of lime, alum and bleaching powder in sequence followed by flocculation and sedimentation. It is reported to be simple and can be designed for community water supplies of any size. Addition of lime ensures adequate alkalinity for effective hydrolysis of alum, so that residual aluminium does not remain in the treated water. Addition of lime following alum and formation of alum hydroxide flocs also results in an increase in the size of the flocs thereby accelerating the settling process.

For domestic treatment, any container of 20-60 liter capacity is suitable and the required dose depends mainly on the alkalinity and initial fluoride content of the water. Mixing time of 11 minutes and settling time from 1-2 hours were reported to be sufficient (Technical Digest, National Environmental Engineering Research Institute of India (NEERI), 1978). The lime required was 1/20th of alum. Laboratory treatability studies should be carried out to arrive at optimum alum dose to bring down fluoride level to permissible limits (1 mg/l) for different water quality conditions.

Major problems associated with the use of the Nalgonda Technique include the large amount of chemicals required when the initial fluoride concentration is high, large amount of sludge produced and requirement of pH adjustment both before and after treatment.

Calcium Phosphate

A fluoroapatite (FAP) precipitation process, which involves the addition of calcium and phosphate and seeding either with hydroxyapatite or bone char to facilitate crystal growth, was proposed to remove fluoride [6]. The concentration of calcium and phosphate in water should be in excess of stoichiometric amount needed for the precipitation of fluorapatite. The removal of fluoride was effective at pH values greater than 9. Thus, the pH of the influent water needs to be adjusted before treatment. Otherwise, excess amount of calcium and phosphate should be added, if the treatment should be conducted at neutral pH. The reported removal efficiency of fluoride is very low (Table 1) most likely due to the various solid phases that may be involved in the precipitation of phosphates of calcium.

Table 1: Final fluoride concentration after treatment with various chemicals

Chemical	Initial fluoride concentration (mg/l)	Final fluoride concentration (mg/l)	Chemical dose (g/l)	Reaction pH	Reference
$Ca(OH)_2$	25	15.4	1.0	11.0	Shafer and Varuntanya, 1991
$CaCl_2$	25	15.1	1.375	9.5	“
$Al_2(SO4)_3$	25	10.7	0.500	8.5	“
$Ca(OH)_2 + H_3PO_4$	26	12	1.0 + 2.0	10.0	“
$CaHPO_4$	10	9.6	0.1	7.5	“
$CaHPO_4$ (seeded)	10	6.3	0.1	10.7	Pears and Larsen, 1993

Although fluoroapatite is the most thermodynamically stable form of calcium phosphate, experience showed that precipitation may occur in stages that involve sequentially less stable (more soluble) calcium phosphate phases, such as amorphous calcium phosphate, dicalcium phosphate dihydrate, tricalcium phosphate, and octacalcium phosphate [7]. This means that the precipitation of fluoroapatite is preceded by the precipitation of one or more precursor phases in accordance with the Ostwalds rule [8]. Formation of metal calcium carbonate may also interfere. Nevertheless, fluoroapatite precipitation may have great potential for home-based units in developing countries provided that the reactants (Ca and P compounds) are locally available, mainly because the fluorapatite may be disposed safely.

Electrochemical

Defluoridation of water by electrochemical method using aluminum electrodes as anode has been reported [9, 10]. The electrolytic defluoridation is based on the dissolution of aluminum anode and subsequent formation of cryolite/or aluminum hydroxide and other aluminum complexes.

The formation of cryolite may be favored under low pH and high fluoride concentration near the anode, which can be expected in electrochemical systems. The movement of fluoride ions towards the anode under the influence of an electric field facilitates this process. On the other hand, the formation and stability of the aluminum hydroxide is limited to the neutral pH range (5.0-7.6). Therefore, when the alumino-complex finally tend to be aluminum hydroxide, the positively charged complexes may adsorb the negatively charged fluoride ion through Van der Walls attraction and possibly, by hydrogen bonding [10]. As the adsorption capacities of aluminium hydroxide for fluoride is small [11], excess amount of this compound should be produced to bring significant fluoride removal. The optimum electric current density that needs to be applied in order to generate excess aluminum hydroxide is very large [9]. The turbidity of the water was increased up to 122 NTU after electrochemical defluoridation. Therefore, the precipitated aluminum hydroxide and fluoride must be removed by a proper filtration technique.

Table 2 presents the fluoride removal capacity and the corresponding pH range to achieve maximum fluoride removal by various chemical precipitation techniques estimated from the experimental results of different studies. For all multivalent metal compounds, satisfactory fluoride removal was achieved at pH values less than 4. The electrochemical precipitation appears to be superior because optimum removal can be achieved with in the ambient pH range.

Table 2: Fluoride removal capacity of the newly proposed chemical precipitation methods.

Material (Method)	Removal Capacity (mg F^-/g)	Optimum pH	Reference
Calcium phosphate system	130 (Ca) or 173 (P)	> 10.5	Pearce and Larson, 1993
Aluminum oxide	359.5	< 4.0	Tokunaga et al., 1995
Aluminum hydroxide	359.5	< 4.0	”
Bone	150	< 4.0	”
Electrochemical	142.8	5.5-9.0	Mameri et al., 1998

The major problems with electrochemical precipitation are cost of the electric energy, the possible existence of Al^{3+} ion in the treated water, passivation of the anode and the requirement of post filtration unit. Further more, the electrochemical removal of fluoride seems to be technically complex and the operation cost is expected to be high for applications in small community. Nonetheless, possibilities such as the use of renewable solar energy should be evaluated in order to test the applicability of this method.

Ion-exchange Using Bone Char

Bone char is ground animal bones, which have been charred at optimum temperature (about 500 °C) to remove organics. Hydroxyapatite, the major component of bone char is known for its isomorphous substitution and F^- can substitute OH^- in apatite particularly when the bone is calcined at lower temperature to prevent complete dehydroxylation [12, 13].

The media is regenerated by sodium hydroxide [13] or by a mixture of calcium chloride and sodium dihydrogen phosphate [14]. As compared to synthetic resins, the hydroxyapatite may be more selective for fluoride ion because both F^- and OH^- ions have the same charge and ionic radii. It is due to these physical and chemical properties that fluoride ion replaces hydroxide ion in animal bone and cause fluorosis problem. It may also be less expensive compared to other synthetic adsorbents and exchangers, as it is widely available in local areas. Further more, since the solubility of fluoroapatite is low, disposing the spent medium without expensive regeneration might be a more economical approach, particularly in the case of small-scale units.

Adsorption

In the following section various defluoridation methods that are based on adsorption are discussed. The methods are classified based on the material used for adsorption.

Activated Alum Sludge

Alum sludge is a waste product generated during the manufacture of alum from bauxite by the sulfuric acid process [15] studied fluoride removal from aqueous solution by using alum sludge. Their result showed that alum sludge thermally activated at 400 °C for 3 h is effective in fluoride adsorption as compared to untreated dry sludge. The major mineral phases of the heat-treated alum sludge were boehmite, gibbsite, α-quartz, anatase, and hematite. The composition may vary from sample to sample depending on the type of bauxite used for the production of alum. The surface area of treated sample was 119.4 m^2/g. The optimum pH for fluoride adsorption was from 5.5 to 7.0. Fluoride adsorption capacity of about 3.3 mg/g of treated alum sludge was achieved at an initial fluoride concentration of 10 mg/l and adsorbent dose of 3g/l.

Desorption of the retained fluoride may be possible by increasing the pH to a value greater than or equal to about 10. The fluoride retention capacity of this material was comparable with that of activated alumina. From practical point of view, the results obtained using this material are promising. However, the availability of the material is limited to areas where alum-manufacturing industries are existing. In addition, disposal of regenerant waste is a problem.

Zeolites

Zeolites are naturally occurring silicate minerals with an infinitely extended three-dimensional network [16] and are capable of removing trace quantities of cations and anions from aqueous solutions by utilizing the phenomenon of ion exchange [17]. Although there are about 40 natural zeolite species (the general formula is shown in Table 3), only few are tested for the removal of heavy metals and anions such as chromate and fluoride from water [17, 18]. The fluoride removal capability of Zeolites is believed to result from their ion exchange property due to the presence of hydroxide groups on the three dimensional structure.

Maruthamuthu and Sivasany [19] investigated defluoridation of water by stilbite (Ca-type zeolite) and natriolite (Na-type zeolite) and found that the Ca-type zeolite is more effective than the Na-type. This suggests that different Zeolites may have different selectivity for fluoride and therefore, it is possible that a zeolite, which effectively removes fluoride, may exist.

Santiago et al., [20] reported unaltered zeolite to be ineffective and further investigated the use of zeolite tailored with the organic cations, ethylhexadecyl dimethyl ammonium (EHDDMA) and acetyl pyridinium for the removal of chromate anion. Tailoring of Zeolites results in a positively charged species, allowing for the mechanism of anion exchange in which chromate anion is attached to the tailored zeolite. It is also expected that modified zeolite may have a higher removal capacity for fluoride. In addition, further research should be conducted to identify the existence of fluoride ion selective natural zeolites. Because Zeolites have little resistance for abrasion,

Table 3: Minerals for fluoride removal [7, 16]

Mineral	Name	Formula	Remarks
Zeolite group	More than 40 minerals	$(Na_2,K_2,Ca,Ba)[(Al,Si)O_2]n.xH_2O$	Few tested so far
Serpentines	Chrysotile	$Mg_3[Si_2O_5](OH)_4$	Tested
Two-layer clays (kaolinites)	Kaolinite	$Al_4[SiO_{10}](OH)_8$	Tested
	Halloysite	$Al_4[Si_4O_{10}](OH)_8.2H_2O$	Not tested
Expandable three-layer clays	Illite	$K_xAl_4[Si_{1-x}Al_xO_{20}](OH)_4$	Tested
	Talc	$Mg_6[Si_8O_{20}](OH)_4$	Not tested
	Smectites (montmorillonite)	$(Na,K)(Al_{2-x}Mg_x)_2[(Si_{1-y}Aly)_8O_{20}](OH)4.nH2O$	Tested
	Vermicullite	$(Ca,Mg)(Mg_{3-x}Fe_x)_2[(Si_{1-y}Al_y)_8O_{20}](OH)_4.8H_2O$	Not tested
	Chlorite	$(Mg,Al)_{12}[(Si,Al)_8O_{10}](OH)_{16}$	Not tested
Aluminum oxides	Corundum	α-Al_2O_3	Not tested
	Gibbsite	$Al_2O_3.3H_2O$	Not well tested
	Boehmite	γ-AlOOH	Not tested
	Diaspore	α-AlOOH	Not tested
Iron oxides	Goethite	α-FeOOH	Not well tested
	Lepidocrocite	γ-FeOOH	Not tested
	Limonite	$FeOOH.nH_2O$	Not tested

researches should also be directed to develop a suitable porous carrier material or to increase the strength of the material in order to minimize media loss with out a significant decrease in specific surface area.

Serpentine

Serpentine are a group of sheet silicate minerals with silica tetrahedral and a modified brucite layer (The general formula is shown in Table 4). Adikari and Dharmagunawardhne [21] used serpentine as a defluoridating medium and reported that the material can reduce fluoride concentration in water. The maximum fluoride retention capacity was about 100 mg/kg of adsorbent, which is very low compared to materials such as activated alumina.

Weerasooriya et al. [22] carried out further research on the defluoridation using acid treated surpentinites in order to enhance fluoride retention capacity. The powder serpentinite was acidulated with concentrated HCl to a stoichiometric ratio for generating protonated serpntinite (SH). This product was hydrolyzed with dilute base/distilled water, to yield SOH_2^+. The fluoride adsorption capacity obtained in a batch test was about 120 mg/Kg of serpentinite in the pH range of 5.0-5.5. Acid treatment of serpentine has slightly improved fluoride adsorption capacity. The reaction mechanism was identified as surface complex formations involving SOH and SOH_2^+. The maximum fluoride adsorption was observed at a serpentine to acid ratio of 100 g : 120 ml. Competition from other ions may affect defluoridation performance but the extent to which this material is selective to fluoride ion is not known.

Clay

Clays are important constituents of soils with large specific surface area. Clay surfaces tend to have excess surface energy because of an imbalance of chemical forces among surface atoms, and molecules [23]. The major groups of clay minerals widely abundant in soil are kaolinite, illite and montmoriollinite. These clay minerals feature variable exchange capacity for organic and inorganic cations and anions [16]. The exchange capacity can be limited to external surfaces for minerals such as kaolinite and illite. It can be also extended to the interlamellar space when the interlamellar cations can be hydrated in the case of swelling minerals such as montmorillonite. The chemical formula of various clay minerals is shown in Table 4. Finally, other clay mineral species such as sepiolite and palygorskite may present large adsorption capacities because of their structural microporosity [23] but are less common in nature. These natural properties of clay minerals render them attractive for various industrial and water treatment applications. The removal of heavy metals from wastewater by clays has been reported by different studies [24]. Natural and modified clays are also known to remove toxic organic contaminants from water [25]. Oxide clay minerals in general possess proton bearing surface functional groups, which may be similar to that of synthetic exchangers and in addition may contain ion-bearing exchange sites.

In addition to the above reactions, the ion-bearing sites may also be important to bind anion particularly at lower pH. Although many details of the reaction mechanisms remain unclear, it is well established that in mineral-water interfaces, the principal factors controlling the amount of adsorption are the equilibrium solution concentration of the anion and the solution pH [26].

In the past few years, several researches have been conducted in order to evaluate the possibility of applying clay minerals for the removal of fluoride ion from water. An overview of clay materials tested for defluoridation so far follows.

Andosoil

These are relatively young soils derived from volcanic ash, which in part weathered to yield active aluminum in various forms, notably in allophone [27]. The bulk of the parent material consists of volcanic glass, microlites, organic material and clay minerals. A simple method of defluoridation by adsorption on Ando soil in Kenya has been investigated by Zevenbergen et al. [28]. In a batch experiment, the maximum adsorption capacity of fluoride was about 2.66 g F/Kg of soil. This value is high as compared to other clay minerals (See Table 5). Based on experimental results they concluded that the use of Ando soils appears to be an economical and efficient method for defluoridation of drinking water on a small scale in rural areas of Kenya and other regions in the Rift Zone. Ando soils and related soils with volcanic ash influence are abundant in Kenya and other countries along the Rift Valley [27]. Further research is needed to evaluate practical performance, social acceptance and the distribution of this soil in the Rift Valley of Ethiopia.

Fired Clay Pot and Brick

Clays have long been used for making pot, brick and other clay wares worldwide. After limited use, the materials are disposed as waste. Moges et al. [29] investigated the defluoridation of water by chips of clay pot and brick. They found that low temperature fired clay materials have better fluoride retention capacity as compared to untreated raw clay soil. The optimum pH for fluoride removal was about 5.8. The maximum fluoride retention capacity by using fired clay pot chips was 200 mg F/kg and 285 mg F/kg adsorbent in batch and continuous packed column experiments, respectively. In a batch test, the controlling factors of defluoridation were initial fluoride concentration, time of contact and amount and type of adsorbing medium. The equilibration time was undesirably very long, which is partly due to the slow reaction at the interface or due to mass transfer limitation by diffusion as the experiments were conducted under static conditions. The use of such materials is economically attractive for small-community water treatment systems, as they are easily obtainable in local area.

Kaolinite

Kaolinite contains a non-expandable, layer structure with octahedrally coordinated Al^{3+} and tetrahedrally coordinated Si^{4+} in a 1:1 stochiometric ratio. Although it has five types of surface functional groups, the principal surface complexation sites are limited to =SiOH, =AlOH and Lewis acid sites located along edge of the sheets [16].

Jindassa et al., [30] proposed a simple and inexpensive method of defluoridation by the use of kaolinitic clay. They observed that at equal concentration of total fluoride in solution, fluoride retention was greatly reduced at both low and high pH. Fluoride adsorption conformed to Langmuir and Freundlich isotherms in the concentration range from 5 to 25 mg/l. The maximum fluoride adsorption capacity obtained was about 300 mg/kg for an initial fluoride concentration of 25 mg/l. Based on former studies and their results, they suggested that the adsorption mechanism is possibly a combination of ion exchange with OH and formation of cryolite ($NaAlF_6$). They concluded that kaolinitic clay is applicable for defluoridation of potable water at village level. In addition the effect of other ions such as chloride and bicarbonate was minimal.

Further research has been conducted to evaluate the mechanism of fluoride adsorption on to kaolinite by using a surface complexation model (SCM) [31]. It has been confirmed that fluoride retention of kaolinite be related to the aluminols, silanols and Lewis acid sites along the edge of the kaolinite sheets. At the experimental conditions (19 mg/l initial F^- conc., 10 g/l kaolinite and pH 5), the adsorption capacity was about 100 mg/kg. The removal efficiency was increased with decreasing initial concentration. The adsorption capacity is very low. In addition, clay minerals have little resistance for abrasion and low hydraulic permeability. These problems should be properly addressed before applying clay minerals for water treatment.

Bentonite

Srimurali et al. [32] compared the fluoride removal capacities of various materials like kaolinite, Bentonite, charfines and lignite. Among these materials, Bentonite showed high removal capacity (750 mg/kg) followed by charfine (500 mg/kg). The study indicated that removal of fluoride from water depends on the contact time, pH, and adsorbent dose.

Comparison of the Performance of Different Adsorbents

While several materials are being tested as a defluoridating medium, cost and availability are the most important parameters for comparing the usefulness of a material or method. However, cost information is seldom reported, and the expense of individual materials may vary depending on the degree of processing required, the lifetime of the material and local availability. In general, a material can be assumed as low cost if it requires little processing, does not require pH adjustment during treatment, is abundant in nature, or is a by-product or waste material from another industry or activities.

Table . 4 summarizes the fluoride adsorption capacity of different materials and the corresponding optimum pH range. Activated alumina and other related minerals such as geothite and gibbsite were also included in the Table for the purpose of comparison. Clay materials appear to be promising particularly, for small-scale applications. It is reasonable to anticipate that some version of this system could prove very useful. Major drawbacks of using clay minerals as an adsorbent are their low capacity and low hydraulic permeability. Thus, these problems should be addressed properly before choosing a particular clay mineral for the removal of fluoride from drinking water. To improve the adsorption capacity the surface of clay mineral may be modified. It can be modified either to enhance the removal of cations or anions. Other less complex surface modification methods to enhance fluoride adsorption include thermal treatment and acid treatment.

Regarding low permeability, development of porous support material or the use of granular clay calcined in the temperature range of 500 to 600 °C needs further studies. In addition, further understanding of the mechanism of fluoride adsorption is important to the quantitative design of clay mineral adsorption systems particularly in terms of its regeneration and reuse capability. In addition to these developments, further research should be focused on the use of other materials that are expected to have fluoride ion adsorption capacity but not evaluated yet.

Table 4: Comparison of adsorption capacities of different materials.

Material	Optimum pH	Capacity (mg/kg)	Isotherm model	Reference
Charcoal	ambient	5	NA[a]	*Hendrickson and Vik, 1984*
Charifine	3.0	500	NA[a]	*Srimurali et al., 1998*
Plant carbon	-	320	NA[a]	*Hendrickson and Vik, 1984*
Activated carbon	3.0	-	NA[a]	*Sorg, 1978*
Activated alumina	4.5-6.0	1900	Freundlich	*Choi and Chen, 1979*
Activated bauxite	5.5-6.8	760	Freundlich	*Choi and Chen, 1979*
Alum sludge	4.0-6.0	3300	Langmuir	*Sugana et al., 1998*
Zeolite	4.0-5.5	740	Langmuir	*Maruthamuthu and Madras, 1994*
Serpentine	5.0	120	Langmuir	*Weerasooriya et al., 19*
Ando soil	4.5-6.5	2660	Langmuir	*Zebenbergen et al., 1996*
Kaolinite	5.6	300	Freundlich	*Jindassa et al., 1988*
Bentonite	3-7.0	750	Langmuir	*Srimurali et al., 1998*
Clay soil	5.4-7.0	200	NA[a]	*Moges et al., 1996*
Fired clay pot chips	5.4-7.0	285	NA[a]	*Moges et al., 1996*
Brick	5.4-7.0	280	NA[a]	*Moges et al., 1996*
Geothite	3.0-4.0	8550	NA[a]	*Hao and Huang, 1986*
Gibbsite	4.0-5.0	9500	NA[a]	*Hao and Huang, 1986*
China clay	4.0-6.0	460	Langmuir	*Chaturvedi et al., 1988*

[a] Not Available

Table 5: Summary of potentially low-cost methods and future research needs.

Treatment process	Future research needs
Ion exchange (bone char)	Regeneration by surface coating, disposal, social acceptance
Electrochemical precipitation	Additional post-treatment required, existence of Al^{3+} ion in treated water, possibility to use natural energy
Nalgonda Technique	Sludge disposal
Fluorapatite precipitation	The possibility to combine it with other processes, techniques to enhance precipitation efficiency
Adsorption on to clay and zeolite minerals	Adsorption mechanisms, improvement of capacity, development of suitable support material, development of granular activated clay particles, regeneration versus disposal
Other natural minerals	Feasibility of various minerals not tested so far
New adsorbents	Possibility to develop new fluoride ion traps and other composite materials, which may have high capacity and low treatment cost
Combined process	Possibility to develop a combined process based on the different methods discussed so far and evaluation of treatment cost

CONCLUSIONS

Developing countries are facing enormous challenges due to the high prevalence of fluorosis and limitations of technologies appropriate to them. However scattered researches are being conducted in a number of these countries. It has been tried, in this paper, to show most of the low-cost defluoridiation options currently available. Although wide range of materials have been evaluated, proper comparison of the proposed methods is difficult because of inconsistencies in data presentations. In addition, due to the scarcity of consistent cost information, cost comparisons are difficult to make. It is clear that much has been accomplished in the area of low-cost materials; however, much work is necessary to better understand the processes and to demonstrate the technology.

From the literature reviewed, a few methods that stand out for potential application are summarized in Table 6 along with further research needs. The Nalgonda technique has been used in India, Tanzania, Bangeladish, etc. A research to develop low cost, simple, household defluoridiation unit based on Nalgonda Technique, for People in the Ethiopian Rift valley, is being undertaken by Addis Ababa University. Ion exchange by bone char and electrochemical precipitation by using aluminum electrode may have potential applications if the associated limitations are fully addressed. Alternatively, with the aim of fixing fluoride as less soluble inorganic mineral (natural mineral form) and subsequent disposal, chemical precipitation as fluoroapatite may also be a useful approach.

Among the several adsorbents evaluated, natural clays and related minerals are found to be promising. Whether modified or in their natural state, due to their abundance and low cost, clays are a potential alternative for the adsorption of fluoride. However, further research is required to improve the low permeability and relatively low adsorption capacity of clays that prevails in their natural state.

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