CHAPTER 1

Fluoride Removal from Water Using Adsorption Technique

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Contents

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Abstract

Management of contaminants such as fluoride is a major public issue. Fluoride of geogenic origin in groundwater used as a source of drinking water is a major concern because fluoride content above permissible levels is responsible for human dental and skeletal fluorosis. Consequently, water sources containing elevated levels of fluoride have to be treated. Coagulation/precipitation, electrochemical, electrodialysis, reverse osmosis, adsorption and hybrid processes combining adsorption and dialysis are widely used defluoridation techniques. Currently, however, the development of cost effective and clean processes due to economic constraints and stringent environmental policies is desired. Adsorption technique is arguably one of the most versatile of all the defluoridation techniques due to a number of reasons such as cost, diverse end-uses, socio-cultural acceptance, regulatory compliance, environmental benignity and simplicity. For this technique, activated alumina, bone char and clay adsorption media are the most developed. During the past two decades, extensive research has focused on a number of alternative adsorbents, some exhibiting improved fluoride sorption performances while at the same time do not alter the quality of treated water. Studies have also shifted toward systematic modeling to approximate adsorber design parameters. In view of these, this review opens with a description of paradigm shifts in drinking water sources and highlights the genesis and toxicological effects of fluoride in drinking water as a means of defining the existing problem. Next, potential and established techniques for defluoridation are revisited. This is closely followed with a review of defluoridation adsorbents recognized by the World Health Organization and those novel defluoridation adsorbents reported in literature over the last two decades, with special reference to drinking water. Emphasis is laid on their availability, fluoride sorption capacity and mechanisms. In recognizing surface-tailored zeolite as a novel sorbent, detailed analysis of fluoride adsorption behavior is provided for this sorbent. Finally, defluoridation adsorption unit configurations, and challenges to and prospects for their implementation are briefly discussed.

1. INTRODUCTION

Water is a finite and vulnerable natural resource and the bulk of it is stored as saltwater in the oceans [1]. For the saltwater to be used for industrial, agricultural or household purposes, an expensive conversion process would be required. Thus, freshwater, because of its purity, is generally used in human activities as opposed to saltwater. It is estimated that only 3% of the world's water supply is fresh water and of this, only a third is available as either surface water or groundwater. Over the years, the world population has been surging upward, while most economies have stagnated. The increase in population has exerted an enormous pressure on the world's limited freshwater supply. It is estimated that

water use has been growing at more than twice the rate of the population increase [2]. The end result has been overutilization and pollution of the existing water resources.

From time immemorial, surface water played a pivotal role to human life as a source of drinking water because of its easy access compared with any other water source. A few decades ago, the use of contaminated surface water sources was found to contribute to the transmission of waterborne bacterial diseases. Thus, a paradigm shift in water usage from surface to groundwater was inevitable.

Groundwater is one of the most valuable natural resources possessed by many developed and developing nations. It is reliable in dry seasons or droughts because of the large storage, is cheaper to develop, since, if unpolluted, it requires little or no treatment and it can often be tapped where it is needed, on a stage-by-stage basis. As a result, groundwater has become immensely important for human water supply in urban and rural areas in developed and developing nations alike. Countless large towns and many cities derive much of their domestic and industrial water supply from aquifers, both through municipal well fields and through many private bore holes. However, a gloom picture hangs over the use of groundwater in certain regions. Studies have shown that in certain regions, though groundwater has been perceived to be clean, contain contaminants that are deleterious to human health. Amongst the most notable of these contaminants is fluoride [3].

Fluoride in groundwater is mostly of geogenic origin arising from breakdown of rocks containing the fluoride ions. In addition, anthropogenic sources such as infiltration of chemical fertilizers in agricultural areas and liquid wastes from industrial entities also contribute to fluoride ions in groundwater. Over the years, fluoride in drinking water above permissible limits has attracted public health interest. At low concentrations fluoride can reduce the risk of dental cavities. Exposure to somewhat higher amounts of fluoride can cause dental fluorosis. In its mildest form this results in discoloration of teeth, while severe dental fluorosis includes pitting and alteration of tooth enamel. When water containing severely higher concentration of fluoride is ingested for a long period of time, changes to bone, a condition known as skeletal fluorosis, may result. This can cause joint pain, restriction of mobility and possibly increase the risk of some bone fractures.

Putting the above health effects into consideration, there are maximum contaminant levels (MCL) for fluoride in drinking water set by each country depending also partly on its economic and technological powers. For example, in 1974, Tanzania adopted a value of 8 mg/L [4] for rural water supply, in 1985 the USEPA raised the maximum allowable concentration to 4 mg/L, while Canada and the WHO recommend a permissible limit of 1.5 mgF/L. Waters containing fluoride ions above the preceding permissible levels have to be treated. There are several treatment techniques that have been developed or show potential for remedying fluoride-contaminated water. These techniques include: coagulation/precipitation,

the use of membranes, ion exchange, electrodialysis and adsorption, among others. The choice of a treatment technique for a given utility usually depends on the concentration of the ions, chemical species in source water, existing treatment processes, treatment costs, handling of residuals [5] and versatility of a given technique. Because of limitations in terms of cost, production of enormous waste and difficulty in end-use applications of some of the above treatment techniques, an environmentally benign, robust and low-cost technique has to be devised for remedying contaminated water. Proponents of adsorption technology argue that the technique is economical and efficient and produces high-quality water [6]. Thus, there have been a lot of studies on the removal of fluoride by use of various adsorbents [7–23]. More importantly, adsorption technique is versatile and can be used in large-scale central water treatment systems and in the development of a small-scale point-of-entry (POE) or point-of-use (POU) system.

Our main focus for this review is to briefly and critically describe some of the defluoridation techniques as a means of getting a basis to support the adsorption technique, to evaluate the defluoridation adsorbents now being utilized and those novel defluoridation adsorbents reported in literature over the last two decades, with special reference to drinking water. Emphasis is laid toward the adsorbents availability, fluoride sorption capacity and where applicable their kinetic adsorption characteristics and column performances are reported. Detailed characteristics of fluoride adsorption onto surface-tailored zeolite are provided. In addition, various adsorber configurations are reexamined and challenges to and prospects for their application to less developed countries (LDCs) are discussed.

2. TECHNOLOGIES AND POTENTIAL TECHNOLOGIES FOR REMOVING FLUORIDE FROM WATER

An extensive review of the literature has been performed to critically evaluate what technologies are presently being utilized, and what technologies may potentially be applicable to the removal of fluoride from drinking water. A summary of the technologies is presented in the succeeding subsections.

2.1. Non-treatment and blending techniques

In areas where several water sources are available, installation of multiple wells may provide an opportunity for obtaining water with low fluoride levels without necessarily treating the water. These methods ensure that the water entering the distribution network meets the maximum contaminant level, by blending the targeted source waters. Two other strategies are to recharge the aquifer and to treat a side-stream and subsequently blend the treated water with the untreated. This latter strategy reduces the amount of water to be treated and thus decreases

the design flow. One disadvantage of this method is that the MCL can only be achieved if the quality of the source waters is good.

2.2. Precipitation/coagulation

In this method, fluoride removal from water is mediated by calcite, $Mg(OH)_2$, $Al(OH)_3$ or $Fe(OH)_3$ floc formation. The principle involved in this technology is that the fluoride ions adsorb on the flocs and are then subsequently removed either simultaneous or in succeeding treatment units such as sedimentation, fixed bed or microfiltration unit. A lot of studies have been reported on the use of alum [24] (and hence $Al(OH)_3$) and lime [4,25]. In the 70 s, a co-precipitation technique, the so-called ''Nalgonda technique'', was introduced to the Indian population for fluoride removal from drinking water and also has been tested at pilot scale level in LDCs such as Kenya, Senegal and Tanzania. The method involves the addition of alum and lime into water followed by rapid mixing. After some time, the stirring intensity is reduced and this induces floc formation that is subsequently removed by simple settling. According to the report of the National Environmental Engineering Research Institute (NEERI) of Nagpur, India, the technique is applicable to differ-ent levels of water treatment. On a small scale (household), the chemicals are introduced in buckets or drums, while on a medium scale for a small community, a fill-and-draw plant is used. For large-scale operation, a process combining mixing, flocculation and sedimentation is used.

   Although precipitation is an economical and a robust technique in the removal of fluoride from water, the technique has been found to suffer from excessive sludge generation and dewatering such sludge has proven to be difficult since the solid size and content are extremely small and low, respectively; instability of the sludge under adverse environmental conditions has too been reported and in most cases, achieving the maximum contaminant level has been found to be difficult. Considering the fact that chemical handling is involved in precipitation/coagulation technique, this technique may not be popular with many uneducated groups, especially in LDCs. Therefore, the technique is only suited to centralized water treatment system. In line with the above disadvantages, this technique has not been very attractive to many end users.

2.3. Membrane techniques

As the quality of drinking water sources gets worse, the methods of water treatment or the traditional water treatment systems need to be modernized. Pressure-driven membrane systems such as reverse osmosis (RO), nanofiltra-tion (NF) and ultrafiltration (UF) and electric-driven membrane system such as

electrodialysis (ED) are considered as alternative innovative and efficient technology with great future prospects for the purification and reprocessing of water and sewage. Basic advantages arising from the application of membrane processes as compared with traditional water treatment systems are as follows: production of water of invariable quality, smaller quantity of added chemical substances, lower consumption of energy, compactness of the installation, possibility to effect full automation of the process, application in both small and larger scale treatment systems as POE and POU, and simultaneous removal of other dissolved species in water. Owing partly to the above wholesale advantages, several studies have recently been reported on the use of membranes, in particular NF and RO membranes. Pontié *et al*. [26,27] and Diawara *et al.* [28] have presented various aspects of application of NF to defluorinating water, while Arora *et al*. [29] have studied extensively on the use of RO for the treatment of water containing fluoride under various experimental conditions such as feed composition and pH (*see also their contribution in this book*). They found that up to 95% of fluoride could be removed from water. At present, the WHO and United States Environmental Protection Agency (USEPA) classify RO as one of the best demonstrated available technology (BDAT). A full-scale plant operation specifically constructed for fluoride removal is found at Fort Irwin. Interestingly, Lhassani *et al*. [30] have shown that by optimizing the pressure, selective desalination of fluorinated brackish water by NF is feasible and drinking water can be produced at much lower cost than by using RO.

   Although membrane use has received universal acceptance, a number of limitations has slowed its use in some regions. Fouling arising from feed water characteristics is a major problem and due to high quantity of water rejection typically between 35% and 65%, it is not suitable to regions where water is scarce. Moreover, brine discharge from RO plant is highly concentrated and requires treatment. The technique also involves a high investment cost, requires high technology for operation and maintenance and therefore does not suit developing countries.

2.4. Ion exchange (IE)

Ion-exchange resins are most commonly used in water treatment processes to soften the water supply by exchanging sodium ions for "hardness" ions including calcium and magnesium. Ion-exchange filters exchange the major ions present in the water, removing fluoride and other ions in water. Selective fluoride removal can be performed using the calcium form of DOWEX G-26 (H) strong acid cation-exchange resin. The calcium forms an insoluble complex with the fluoride in water with low to high salt concentrations. Soluble anions such as sulfate, arsenic, selenium and nitrate and TDS can compete with fluoride and can affect the run

length ([31]). Thus, if systems contain high levels of suspended solids and pre-cipitated iron that can cause clogging of the IE bed, then pre-treatment may be required. USEPA has proposed passage of water through a series of columns to improve removal and decrease regeneration frequency.

Some of the limitations to the use of ion exchange include the production of a highly concentrated waste by-product stream that poses a disposal problem (this problem can be reduced by brine recycling). Run length is affected by sulfate level. The technology is only recommended primarily for small groundwater systems with low sulfate and low TDS. Another limitation to its use is that it requires a high level of operator skill and therefore not popular with many end-users.

2.5. Electrochemical technique

Electrochemical technique (also electrocoagulation) is a simple and efficient method for the treatment of potable water. This process is characterized by a fast rate of contaminant removal, a compact size of the equipment, simplicity in operation and low capital and operating costs. Moreover, it is particularly more effective in treating wastewaters containing small and light suspended particles, such as oily restaurant wastewater, because of the accompanying electroflotation effect.

The electrochemical technique is in general at a developmental stage and therefore is not an established technology for defluoridation. Some researchers [32,33] have demonstrated that electrocoagulation (EC) using aluminum anodes is effective in defluoridation. In the EC cell, the aluminum electrodes first sacrifice themselves to form aluminum ions. Afterward, the aluminum ions are transformed into $Al(OH)_3$ before being polymerized to $Al_n(OH)_{3n}$. The $Al(OH)_3$ floc is believed to adsorb F^- strongly as shown by the following reaction:

$$Al(OH)_3 + xF^- \Leftrightarrow Al(OH)_{3-x}F_x + xOH^-. \tag{1}$$
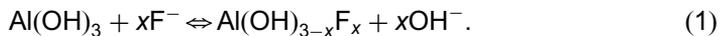
At aluminum cathode, hydrogen gas is released according to the following reaction:

$$2H_2O + 2e^- \Rightarrow H_2 + 2OH^- \tag{2}$$
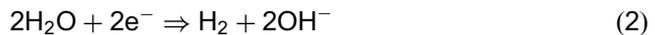
Unfortunately, up to date, no solid evidence was reported to support the hypothesis of the above adsorption mechanism. Moreover, the hydrogen gas produced at the EC cathode prevents the flocs from settling properly on leaving the electrolyzer [34]. In order to overcome this problem, an EC process followed by an electro-flotation (EF) operation can be applied. In this combined process, the EC unit is primarily for the production of aluminum hydroxide flocs. The EF unit would undertake the responsibility of separating the formed flocs from water by floating them to the surface of the cell.

2.6. Adsorption technique

Adsorption in water treatment is a robust technique for removing water-soluble ions, especially when these ions exist in water at low concentrations. Coincidentally, fluoride ions exist in some groundwaters at low concentrations, which are above the permissible limits. The principle behind this technique is that a component (fluoride in our case) is transported by diffusion from the bulk phase to the solid surface where it is bound at the surface or interface between two phases by either chemical or physical forces [35]. Numerous investigations have focused on surface adsorption as a means of removing fluoride from water. As a result of these studies various water treatment plants using treatment media such as activated alumina or bone char have been constructed and are in use in several countries. One example is a water purification plant in Kansas that utilizes activated alumina [36]. Several other smaller fluoride treatment facilities are scattered all over India, Kenya and Tanzania, among other nations.

2.7. Fluoride removal technique screening

The treatment techniques mentioned above are those that are widely reported in literature. Their application in a specific geographical region depends on a number of factors. In discussing these factors, our argument will be biased toward application of the various techniques in LDCs because these regions bear the highest occurrence of fluoride contamination of drinking water. These factors are also the basis of a decision framework for helping utilities determine the most appropriate technique.

2.7.1. Cost

To understand how cost of a given technique is important, we need first to identify the countries that are most affected by fluoride contamination of drinking water. Among these countries are Kenya, Tanzania, Uganda, Ethiopia, India, Mexico, Argentina, Libya, Senegal, Pakistan, Srilanka, New Zealand and China. Most of these countries have low *per capita* incomes and therefore application of a given technique will depend on the cost of the technique. Moreover, the distribution of wealth in some of these countries is such that majority of people live below poverty line. In line with this, only low-cost options that perform adequately well may be applicable. Most literatures indicate that membrane techniques, ion exchange and electrochemical technique are medium to high cost, while adsorption and precipitation/coagulation techniques are low-cost fluoride treatment options.

2.7.2. Regulatory compliance

Currently, the WHO recommends a maximum value of 1.5 mgF/L in drinking water. Countries like India have lowered their permissible limits to 1.0 mg/L. The performance of the technologies considered in this review depends on the quality of the water to be treated. In general, most of these technologies will meet the WHO's maximum allowable concentration (MAC) values. However, precipitation/coagulation method has been found to rarely meet the safe levels of fluoride in drinking water. To achieve safe levels using this technique, a treatment train involving the addition of an adsorption unit or a membrane unit is required. The latter comes with additional cost.

2.7.3. Appropriateness of the technique

A given technology of choice should be tailor-made to suit the local conditions of the region in which it is intended. The local conditions include the fact that most of the contaminated water are obtained from tube wells, that the wells are scattered all over the region where in most cases there is no electricity, that the users are mainly women with no strong education and no sound incomes [37]. In considering these factors, ion exchange, membrane and electrochemical techniques are automatically disqualified, as they require medium- to high-level skills to operate. Moreover, they cannot be applied to areas where there is no supply of electricity.

2.7.4. Environmental burden

In the 21st century, the impetus to protect the environment is very strong. Consequently, the benefits arising from a given technology should not override the environmental load the technology imparts on the environment. Most technologies considered in this review increase environmental load to certain extent. For example, precipitation/coagulation is known to produce a large amount of sludge that has low content of solid and thus difficult to dewater. Adsorption on the other hand produces non-hazardous spent regeneration solution containing a high content of fluoride and thus an additional chemical handling facility would be required. Membrane processes on their part reject a large amount of water, while ion exchange produces highly concentrated brine. Based on these assessments, these technologies will all impact negatively on the environment. Adsorption technique, however, produces little amount of non-hazardous waste.

2.7.5. Public perception and acceptance

Public perception and acceptance is critical to the success of a given fluoride treatment technique. To make a technique popular, there must be an

understanding of local socio-cultural inclination. In general, all the techniques considered here have positive public perception. However, adsorption technique based on bone char adsorbent is known to be unacceptable to several religious groups. Also, some clique of people has mistakenly associated activated alumina (AA) with aluminum poisoning. Thus, they do not believe that water treated with AA is clean to drink.

Considering the above screening strategies as well as the summary in Table 1, it is observed that adsorption technique for fluoride removal from water is an established, low-cost, environmentally benign technique that has public acceptance. Thus, our discussion will henceforth concentrate on adsorptive removal of fluoride from drinking water.

3. DEVELOPMENT OF DEFLUORIDATION ADSORPTION UNIT: ALGORITHM

Most people in LDCs are affected by fluoride-contaminated drinking water supplied by the numerous scattered tube wells. The most feasible solution to this problem is to develop a cost-affective technique with diverse end-uses. As already mentioned in the previous sections, one robust technique is that based on adsorption. The development of an adsorption unit in general requires a number of stages. These are summarized in the Fig. 1 (Adsorption Research Inc. USA). According to the Adsorption Research Inc. (USA), the adsorption unit development stages frequently follow a pattern, with ideas being generated and data being collected, all focused on developing a full-scale process. As Fig. 1 suggests, the process idea in our case is to defluoridate drinking water. Since the technique to be adopted is known, i.e. adsorption, the next stage is to examine the adsorption media. Frequently, a few or even several adsorbent candidates are examined as potential choices. To this end, we have provided in Section 3.1 a description of some of the adsorption media reported in literature over the last two decades.

To evaluate the adsorbents, the relevant factors such as cost implication, availability, performance and regenerability are considered. The performance of an adsorption media for defluoridation is indicated as isotherms and rate data, while costs in general are determined by local availability, regenerability of the adsorption media, whether the media is synthetic or natural, needs further processing before use, among others. Using such factors as mentioned above, it is frequently possible to decide beforehand whether an adsorbent is suitable or not. In order to design an effective adsorption separation or purification unit using a chosen adsorption media, preliminary design information is required [38]. Often, these pieces of information are gathered through the performance of an extensive series of experiments that are time consuming and expensive. The aim of such a study is to predict *a priori* what will happen in a full-scale operation under

Table 1. Summary of fluoride removal technology screening

Screening strategy	Precipitation and coagulation	Membrane processes	Ion exchange	Electrochemical	Adsorption
Cost	Low	High	Medium	May be high	Low
Regulatory compliance	MCL not achievable	MCL achievable	MCL achievable	MCL achievable	MCL achievable
Appropriateness	Nalgonda method applicable to LDCs	Not appropriate to LDCs	Not appropriate to LDCs	Not appropriate to LDCs	Appropriate to LDCs and is versatile
Environmental burden	Difficult to dewater sludge	Water rejection high	Highly concentrated brine	At development stage	Non-hazardous waste
Public perception and acceptance	Acceptable	Acceptable	Acceptable	At development stage	Acceptable

Note: Non-treatment technique is not considered.
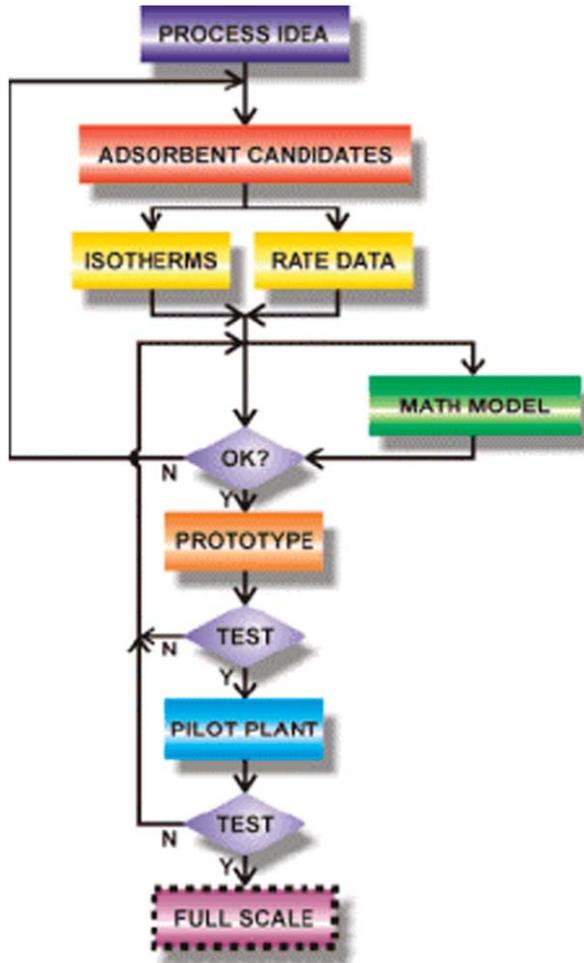
Fig. 1. Adsorption process development flow chart (Adsorption Research Inc., USA).

various design and operating parameters. Among the operating parameters and fluid features that are paramount for a good design are linear flow rate, initial concentration, bed height, size of adsorption media, type of adsorbent, pH and temperature of water. To reduce costs and to save time in doing unnecessarily too many experiments, mathematical models are used to predict the optimum conditions when the above parameters are varied. As an example, using surface-tailored zeolite as an efficient fluoride adsorption media, the modeling approach for batch equilibrium and kinetic data and column breakthrough curves are illustrated in Section 3.2. If factors such as cost, availability, performance and re-generability and/or mathematical model imply that the purification will be

successful, then a prototype system may be built. Otherwise, additional adsorbent candidates would be evaluated. If the prototype tests are successful, a larger pilot plant might be built, for on-site testing. During the on-site tests, field-based performance and acceptability are evaluated. In case the prototype tests are unsuccessful, it is necessary to revise the model conditions or parameters, or possibly to look at other adsorbent candidates. If the pilot plant tests are successful, a full-scale plant could be built. Conversely, it is necessary to revise the model conditions or parameters, or possibly to look at other adsorbent candidates again. Among the configurations (pilot/full-scale configurations, where applicable) that are considered in this review are "tea bag" POU, "coffee filter" POU, household POU, cartridge POU, community-based tube-well-attached defluoridator, household POE and centralized water treatment systems. By virtue of the nature of these configurations, some are extremely simple and their developments do not necessarily follow the algorithm illustrated in Fig. 1.

3.1. Established and potential adsorption media for fluoride

Adsorption technology is frequently used as a robust technique to remove water-soluble ions that are detrimental to human health from aqueous solutions, especially when these ions exist in low concentrations. Thus, a lot of studies have been reported in literature on the use of various adsorbents for fluoride removal from drinking water. The studies have mainly been motivated by the need to have alternative adsorbents that are low in cost, have local availability, require little processing and are superior in performance. Synthetic adsorbents have good capacities for fluoride but are always expensive, while natural materials that are available in large quantities or certain wastes from agricultural or industrial concerns may potentially be low-cost materials. An overview of some of the adsorbents that have been reported in literature over the last two decades are given below.

  (a) *Activated alumina*. AA are commonly used as adsorbents, desiccants and catalysts and therefore the chemistry, size and structure of these aluminas are tailored to specific applications. Based on pH in water, four kinds of AA can be identified. These are: basic (pH 9.5 ± 0.5), neutral (pH 7.5 ± 0.5), weakly acidic (pH 6.0 ± 0.5) and acidic (pH 4.5 ± 0.5) AA. As an adsorbent, AA has been widely applied in the removal of contaminants from water. Removal of fluoride by AA is an established treatment technology and has been and is still practiced both by small- and large-scale water treatment enterprises. The WHO and USEPA classify AA adsorption as one of the best demonstrated available technology (BDAT) for fluoride removal. AA has high affinity for fluoride because in aqueous environment at pH values below its pH_{pzc} – the point of zero charge – it forms protonated ($=Al\text{-}OH_2^+$) and neutral ($=Al\text{-}OH$) aluminol sites, which are

responsible for binding fluoride ions by formation of inner-sphere complexes. Because of the good performance of AA, several researchers have studied its fluoride sorption behavior under varying conditions [36,39–46]. Interestingly, different researchers have obtained different adsorption capacities as shown in Table 2. Usually, the efficiency of the AA for adsorbing fluoride is generally poor on the first adsorption cycle unless the alumina is pre-treated. A pre-treatment that involves allowing a dilute aluminum sulfate solution ($\sim$29 g $Al_2(SO_4)_3$ $18H_2O$/L) to remain in contact with the alumina for 1 h is found to be particularly satisfactory. In another similar pre-treatment of AA to improve its performance, Wasay *et al.* [46] intensively studied the effect of impregnating AA with La (III) and Y (III) ions. They found that the capacity of AA after the impregnation increased twofold. Ku and Chiuo [44] using γ-activated alumina found optimal adsorption (capacity = 16.3 mgF/g) of fluoride to take place in the pH range 4–6.

Although AA is a robust adsorbent for fluoride uptake, it is expensive and its performance is affected by the presence of co-ions in water such as silicates, sulfates, chlorides, bicarbonates and phosphates. The effect of bicarbonate ions on the performance of AA is particularly strong, i.e. the removal efficiency of fluoride by AA decreases significantly with an increase in bicarbonate content. This is partially due to the fact that bicarbonate ions buffer water pH at higher values thus reducing the number of active sites on AA available for binding fluoride. This brings us to another factor (pH) from solution chemistry that induces a negative effect on the performance of AA. The pH has an inhibiting effect of fluoride uptake since solution pH determines the speciation of fluoride, the number and the distribution of active sites on AA. In the acidic media (pH < 7), the fluoride uptake by AA usually decreases with a decrease in pH due to the fact that

Table 2. Summary of adsorption capacities of AA

Source	Material	Capacity (mg F/g)	Mode of operation
Anonymous [36]	Al-pretreated AA	4.6	Column
Ghorai and Pant [39]	Locally (India) available AA	2.41	Batch
Coetzee *et al.* [45]	Type 504C, Fluka	0.5	Batch
Li *et al.* [17]	γ-Al_2O_3	3.70	Batch
Ku and Chiuo [44]	γ-activated alumina	16.34	Batch
Ramos *et al.* [11]	α-alumina	8.42	Batch
Wasay *et al.* [46]	AA	3.3	Batch
Wasay *et al.* [46]	La(III)-pretreated AA	6.3	Batch
Wasay *et al.* [46]	Y(III)-pretreated AA	6.1	Batch
Rubel [61]	AA	0.627–2.627	Pilot plant

HF is weakly ionized (pH < 3.2), and soluble alumino–fluoro complexes are formed resulting in the presence of aluminum ions in the treated water and lowering of the active sites. At near neutral pHs, the uptake of fluoride is maximum. Assuming that the pH_{pzc} of AA is about 8–9 as reported in several literatures, then at near neutral pHs the active sites consist of $=Al\text{-}OH_2^+$ (protonated) and $=Al\text{-}OH$ (non-protonated) aluminol sites. The interaction between fluoride and the protonated aluminol sites leads to the formation of inner-sphere complexes and elimination of water. The reaction can be represented by

$$= Al\text{-}OH_2^+ + F^- \Leftrightarrow\, = AlF + H_2O \qquad (3)$$
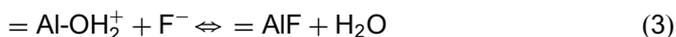
The protonated aluminol sites are the most effective fluoride sorption sites and are usually responsible for the rapid kinetics due to coulombic attraction between the positively charged sites and the negatively charged fluoride species. The reaction with non-protonated sites involves ligand exchange, leads also to the formation of inner-sphere complexes, releases hydroxyl ions, is slow and characterized by a higher activation energy.

$$= Al\text{-}OH + F^- \Leftrightarrow\, = AlF + OH^- \qquad (4)$$

Further increase in pH beyond pH_{pzc} is expected to enhance electrostatic shielding of the active sites and to reduce their number and activity. This argument explains why AA is reported to perform poorly at $pH > pH_{pzc}$.

The use of AA in water defluoridation has been limited to certain extent to countries with well-established economies. AA being synthetic is relatively expensive and may not be locally available in all fluoritic regions. India has an increasing incidence of fluorosis, both dental and skeletal, and with some 62 million people at risk. High-fluoride groundwaters are present especially in the hard rock areas south of the Ganges valley and in the arid northwestern part of the country. Owing to the robust performance of the Indian economy over the years, more and more AA-based tube-wells-attached columns are being used to defluoridate drinking water. Moreover, in recent times, an Indian company called Mytry De-Fluoridation Technologies (MDFFT) has produced and implemented AA-based defluoridation filters. The Mytry filter is a two-bucket system with the upper bucket containing the filter media. Murcott [47] reported that since 2004, the MDFFT had sold 9000 units and produced 50 units daily.

(b) *Bone char*. Bone char, a mixed adsorbent containing around 10% carbon and 90% calcium phosphate, is mainly produced by the carbonization of bones. Structurally, the calcium phosphate in bone char is in the hydroxyapatite form. Bone char has traditionally been used to decolorize sugar solutions in the sugar refining industry for many years. More than four decades ago, it was recognized as a potential medium for partial defluoridation of water. The defluoridation process was reportedly of the ion exchange in which carbonate radical of the apatite, $Ca(PO_4)_6.CaCO_3$, was replaced by fluoride to form an insoluble fluorapatite [48].

Bone char is therefore a well-established adsorbent for water defluoridation. Unfortunately, the treated water in some cases had bad taste. Moreover, socio-cultural acceptance in some communities was lacking, while at the same time cost and availability of raw materials were inhibiting. In 1988, however, the WHO recommended bone char for use in fluoride removal from drinking water in LDCs. Earlier, USEPA [49] reported that a full-scale defluoridation plant was operational in South Dakota, while Phanfumvanit and LeGeros [50] presented a robust bone char-based defluoridation units for individual households. Mwaniki [51] presented more interesting results of fluoride sorption characteristics of different grades of bovine bone char. They found that the 24 h-batch capacity of fluoride depended on the temperature of the heat-treatment of the bones. Black-grade bone char (heat-treated at 350°C) had a capacity of 11.4 mg/g, gray grade (heat-treated at 450°C) had a capacity of 2.4 mg/g, while white grade (heat-treated at 450°C) had a capacity <0.3 mg/g. Although black bone char (BBC) has high capacity for fluoride, Menda [52] reported from a Tanzanian experience that the water quality arising from the use of BBC was low due to bad smell and discolored water.

In a laboratory study, Abdel-Raouf and Daifullah [53] reported that the bone char derived by heating animal bone to 500–600°C could be used to remove fluoride from drinking water. Table 3 summarizes some of the capacities of bone char reported in literature.

Owing to enormous challenges facing Tanzania as most of her groundwaters have excess fluoride levels and most of the population is poor, a robust system of making bone char for water defluoridation has been devised in order to cut the cost of production. It involves charring raw fresh bones in an easy-to-use charcoal-fueled kiln at about 500–600°C. The charred bones are then pulverized into grains of sizes ranging between 0.5 and 2 mm and used in POU systems for treating cooking and drinking water only [4]. In Kenya where fluoride in drinking

Table 3. Summary of adsorption capacities of various grades of bone char

Source	Material	Capacity (mg F/g)	Mode of operation
USEPA [49]	Bone char	2.2	Full-scale plant operation
Mwaniki [51]	Black bone char	11.4	Batch
Mwaniki [51]	Gray bone char	2.4	Batch
Mwaniki [51]	White bone char	0.3	Batch
Abe *et al.* [19]	Bone char	>3	Batch
Mjengera and Mkongo [4]	Locally made bone char	7000 L/4 kg column	Column POU operation

water has also enormously attracted public health attention, the Catholic Diocese of Nakuru (CDN) has extensively researched and is in the implementation phase of a bone char-based household and community filters for water defluoridation. In the latter system, the bone char is either placed into a two-bucket POU system or into a large tank through which water contaminated with fluoride is passed [47].

(c) *Hydroxyapatite*. Hydroxyapatite is a highly crystallized material. One report by Fan *et al.* [16] gives its specific surface area as $0.052\,m^2/g$ and very close to that of calcite, quartz and fluorspar. The uptake of fluoride in hydroxyapatite is dominated by ion exchange. In water defluoridation, the fluoride ions firstly adsorb onto hydroxyapatite surfaces and the adsorbed fluoride is exchanged with OH group at the nearest surface of apatite particles, and then exchanged with the mobile OH group inside the hydroxyapatite particles, resulting in a much higher uptake of fluoride by hydroxyapatite. The exchange process can be represented by

$$Ca_{10}(PO_4)_6(OH)_2 + nF^- = Ca_{10}(PO_4)_6(OH)_{2-n}F_n + nOH^- \qquad (5)$$

As a consequence of the above reaction, the capacity of hydroxyapatite for fluoride was found to be 4.54 [16].

(d) *Carbonaceous materials*. Carbon-based adsorbents have widely been used in adsorption processes for water treatment. Most of these adsorbents have very high internal surface area needed for adsorption. However, the affinity of anions by carbon is quite low. Thus, Ramos *et al.* [11] utilizing the high surface area of activated carbon, and the high affinity and capacity of aluminum toward fluoride ions, produced a novel sorbent, aluminum-impregnated carbon. In a batch study, they found that the aluminum-impregnated carbon had a 3–5 times higher capacity of fluoride than that of plain carbon. Just like with any other sorbent, the performance of aluminum-impregnated carbon was found to be dependent upon the pH of the impregnating solution, temperature of calcinations and solution pH of fluoride-containing water. In another study, Li *et al.* [54] used Al_2O_3-doped carbon nanotubes to remove fluoride from water. Carbon nanotubes are needle-like cylindrical tubules of concentric graphitic carbon capped by fullerene-like hemispheres. Since their discovery [55], great efforts have focused on their synthesis, characterization, theoretical investigation and their applications. Owing to their novel mechanical and electronic properties, large specific area and high thermal stability, they have a tremendous potential for future engineering applications, in such areas as hydrogen storage, field emission, catalyst supports and composite materials, among others. Application of carbon nanotubes as adsorbent in environmental pollution control is an emerging field. For this reason, Li *et al.* [17] prepared aligned carbon nanotubes (ACNTs) by catalytic decomposition of xylene using ferrocene as catalyst and tested the adsorbent in fluoride adsorption. They found a moderate capacity of ACNTs for fluoride. In explaining the mechanism of fluoride uptake by ACNT, they cited the availability of defects and

coats of amorphous carbon. These defects and amorphous carbon offered active sites for fluoride adsorption on the outer surfaces of the ACNTs. Additionally, the inner cavities and the micropores or mesopores composed by internano-tube space between the densely ACNTs may have also contributed to the effective adsorption of fluoride. In a research using various carbonaceous materials such as charcoal, carbon black and activated carbons, Abe et al. [19] found the percentage of fluoride ion removal by the carbonaceous materials to increase with an increase in iodine-adsorption capacity. They explained that it meant that the adsorbability of the fluoride ions onto carbonaceous materials depended upon the specific surface area. Generally speaking, the amount of adsorbates adsorbed onto carbonaceous materials depends upon pore size distribution because adsorption occurs in pores, suggesting a physical adsorption.

Although a lot of research has been reported on the use of various carbonaceous materials in defluoridation, no known column or full-scale plant operation is easily available in open literature. One reason for this is that most carbonaceous materials show poor adsorption capacity (Table 4) for fluoride and therefore only laboratory-scale performances have so far been reported. Amorphous alumina supported on carbon nanotubes on the other hand show high capacity (28.7 mgF/g adsorbent) for fluoride and is therefore a promising material for drinking water defluoridation.

(e) Geomaterials. Geomaterials are low-cost adsorbent resources used in water and wastewater treatment. In addition, they are mostly locally available and require minimal processing, if any, before they are used. Moges et al. [56] intensively investigated both in batch and column operation modes, the fluoride adsorption ability of fired clay chips from a region in Ethiopia. They found that the clay had an appreciable fluoride adsorption capability and could lower the fluoride levels in drinking water to an acceptable value (Table 5).

Table 4. Summary of adsorption capacities of various carbonaceous materials

Source	Material	Capacity (mg F/g)	Mode of operation
Ramos et al. [11]	Plain carbon	0.49	Batch
Ramos et al. [11,82]	Al-impregnated carbon	1.07	Batch
Li et al. [54]	ACNTs	4.1	Batch
Li et al. [17]	Al_2O_3/CNT	28.7	Batch
Abe et al. [19]	Carbon black	0.2	Batch
Abe et al. [19]	Activated carbons	0.34 (coal based)	Batch
Abe et al. [19]	Charcoals	0.07	Batch

Table 5. Summary of adsorption capacities of selected geomaterials

Source	Material	Capacity (mg F/g)	Mode of operation
Moges *et al*. [56]	Fired clay	0.20	Batch
Moges *et al*. [56]	Fired clay	0.285	Column
Zevenbergen *et al*. [7]	Ando soil	5.51	Batch
Srimurali *et al*. [8]	Bentonite	1.15	Batch
Srimurali *et al*. [8]	Charfine	0.95	Batch
Wang and Reardon [57]	Tertiary soil	0.150	Column
Sugita *et al*. [58]	Kaolinite	≈ 0.667	Batch
Das *et al*. [59]	Titanium-rich bauxite	3.7–4.1	Batch

Zevenbergen *et al*. [7] attempted to make use of a locally available Kenyan soil derived from volcanic ash (i.e. Ando soils or soils with andic properties) as a fluoride adsorbent. The Ando soil contains in small quantities aluminum, iron and silica. It is probably these constituents that provide the active sites for fluoride ions. The ability of the Kenyan Ando soil to adsorb fluoride was determined experimentally. The batch capacity for fluoride adsorption was estimated at 5.51 mg/g, using the Langmuir isotherm model. These results were extended to possible technical application using a one-dimensional solute transport model. Based on the results it was concluded that the use of Ando soils appeared to be an economical and efficient method for defluoridation of drinking water on a small scale in rural areas of Kenya and other regions along the Rift Zone. Further research was warranted to evaluate its practical applications and social acceptance. In another study, Srimurali *et al*. [8] tested charfine, lignite, bentonite and kaolinite in fluoride sorption. At optimum conditions using a solution containing 5 mgF/L, the authors found that charfine and bentonite had an appreciable adsorption capacity of 38% and 46%, respectively. They explained, on the one hand, that the mechanism of uptake of fluoride by bentonite proceeded by adsorption onto the lattice structure and possibly by reaction with aluminum silicate, while on the other, fluoride adsorption on charfine proceeded by chemical interaction due to the surface heterogeneity and imperfections contained in charfine.

Limestone is another promising geomaterial for drinking water defluoridation. However, it has only been tested in wastewater containing high concentration of fluoride. In a research work by Reardon and Wang [60], limestone was used in a two-column continuous flow system (limestone reactor) to reduce fluoride concentrations from wastewaters to below the MCL of 4 mg/L for wastewater. Calcite was forced to dissolve and fluorite to precipitate in the first column. The degassing condition in the second column (did not serve to remove fluoride) caused the

precipitation of the calcite dissolved in the first column, thus returning the treated water to its approximate initial composition.

In a study by Wang and Reardon [57], heavily weathered tertiary soil from Xinzhou, China was used as a sorbent for defluoridation of high-fluoride drinking water. The soil was composed of quartz, feldspar, illite and goethite, with Fe oxide content of 6.75%. The authors found the soil's sorption capacity (150 μg/g) to be about a quarter of the low-end range of values reported by Rubel [61] for commercially available AA. The sorption of F^- ions was specific and involved ligand exchange between hydroxyl ions and fluoride ions according to the equation

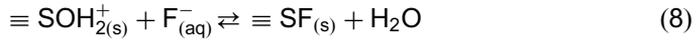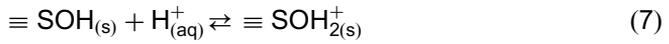$$\equiv FeOH + F^- \Leftrightarrow \ \equiv FeF + OH^- \tag{6}$$

The authors further explored the optimum heating temperature and found that heating the tertiary soil at 400–500°C enhanced the adsorbent's fluoride removal capacity. Moreover, a preliminary column experiment showed that 4.0 kg of 400°C heat-treated soil could treat more than 300 L of 5 mg/L fluoride feed water before the effluent fluoride concentration of 1.0 mg/L was reached. To minimize environmental impact of the used material, a cost-effective regeneration technique was devised and it involved rinsing the soil with sodium carbonate solution, followed with dilute HCl and finally twice with distilled water.

Using coal-based sorbents, Sivasamy et al. [62] evaluated their ability to remove fluoride from water. On equilibrium basis, Langmuir and Freundlich models were used to describe the data points, while the kinetic data points were interpreted in terms of reaction and mass transfer processes. Kaolinite, adioctahedral two-layered (silica and alumina) silicate (1:2 type), has also been tested in drinking water defluoridation. Recently, Sugita et al. [58] and earlier Kau et al. [63] and Weerasooriya et al. [10] presented fluoride adsorption results of kaolinite. The fluoride-binding sites in kaolinite consist of aluminol and silinol sites. The authors explained that the fluoride–kaolinite interaction led to the formations of both the inner- and outer-sphere complexes.

Bauxite ores, abundantly available in many parts of India, usually contain oxides/oxyhydroxides of Al, Fe and Si. The titania content in the bauxite ore depends upon the geological process that controlled the development of bauxite and usually varies in the range of 1–3 wt%. However, bauxite ore from several parts of central India (especially in the states of Jharkhand and Chattisgarh) mainly consists of oxides/oxyhydroxides of Ti and Al and small amounts of Fe and Si. Each of these oxides/oxyhydroxides possesses good adsorption capacity for fluoride as also seen in several recent investigations [9,16,64–66]. In an attempt to devise a simple and cost-effective fluoride removal process using locally available F sorbent (e.g., titanium-rich bauxite (TRB)), a study was designed to evaluate the adsorption capacity and to optimize the fluoride adsorption parameters using TRB so that a suitable adsorption process could be developed in future to abate fluoride from drinking water. The effect of pH, heat-treatment and

regeneration ability of the material were studied. Considering the pH profile and nature of oxides/oxyhydroxides present in TRB, the adsorption of fluoride is represented by the following two-step protonation/ligand-exchange mechanism:

$$\equiv SOH_{(s)} + H^+_{(aq)} \rightleftarrows \ \equiv SOH^+_{2(s)} \tag{7}$$

$$\equiv SOH^+_{2(s)} + F^-_{(aq)} \rightleftarrows \ \equiv SF_{(s)} + H_2O \tag{8}$$

which gives the net reaction

$$\equiv SOH_{(s)} + H^+ + F^-_{(aq)} \rightleftarrows \ \equiv SF_{(s)} + H_2O \tag{9}$$

where $\equiv S$ represents the surface of adsorbent. This two-step mechanism is favorable at pH $<$ 6. However, at pH $>$ 6, fluoride ion is pre-dominantly adsorbed by the following mechanism:

$$\equiv SOH_{(s)} + F^-_{(aq)} \rightleftarrows \ \equiv SF_{(s)} + OH^- \tag{10}$$
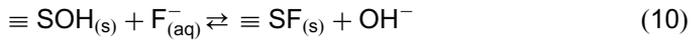
The progressive decrease of fluoride uptake at pH $>$ 6 is mainly due to two factors: the electrostatic repulsion of fluoride ion to the negatively charged surface of the TRB (pH$_{zpc}$ = 7.05–7.5) and the competition for active sites by excessive amount of hydroxyl ions. The adsorption capacities of the geomaterials described above are summarized in Table 6.
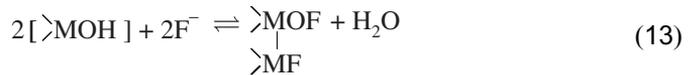
(f) *Waste-derived adsorbents*. Waste-derived adsorbents are considered low-cost alternative defluoridation media. The ability of treated alum sludge to remove fluoride from aqueous solution was investigated by Sujana et al. [9]. Alum sludge is a waste product generated during the manufacture of alum from bauxite. This material mainly consists of aluminum and titanium with small amounts of undecomposed silicates. It is well known that these constituents have fluoride ions affinity. In using this material in fluoride adsorption, the authors argued that they solved two problems, fluoride contamination and waste disposal problems. The fluoride uptake was found to follow the Langmuir isotherm suggesting sorption on

Table 6. Summary of adsorption capacities of selected waste-derived materials

Source	Material	Capacity (mg F/g)	Mode of operation
Sujana et al. [9]	Alum sludge	5.39	Batch
Cengeloglu et al. [13]	Red mud	3.12	Batch
Cengeloglu et al. [13]	Activated red mud	6.29	Batch
Mahramanlioglu et al. [14]	SBE	7.75	Batch
Liao and Shi [67]	Zr(IV)-loaded collagen fiber	43.51	Batch

homogeneous sites, while kinetically the adsorption reaction was first order. Also from an environmental and economic standpoint, spent bleaching earth (SBE), a solid waste from edible oil-processing industry, was tested as a low-cost adsorbent for fluoride adsorption [14]. SBE has two components: residual oil not removed by filter pressing and montmorillonite clay. When not utilized as in this case, the material is normally disposed off directly to landfill either in a dry state or as wet slurry. The material was found to be most effective at pH 3.5 and the adsorption transient curves were best described by second-order kinetics.

Another waste material that has found fluoride adsorption application is the red mud. Just like the alum sludge, red mud (bauxite wastes of alumina manufacture) emerges as an unwanted by-product during the alkaline-leaching of bauxite in the Bayer process. Çengeloğlu et al. [13] reported that about 500,000 m^3 of strongly alkaline (pH $\approx$ 12–13) red mud water was dumped annually into specially constructed dams around Seydiğehir Aluminium Plant-Turkey. Since the plant began to operate, the red mud accumulated and posed severe environmental problem. Consequently, the authors investigated the possibility of utilizing the material in the original or activated form as an adsorbent for the removal of fluoride from aqueous solution. They explained that the uptake of fluoride involved ligand-exchange reaction as follows:

$$MOH + H^+ \rightleftharpoons MOH_2^+ \tag{11}$$

$$MOH_2^+ + F^- \rightleftharpoons MOH_2 - F(\text{or } MF + H_2O) \tag{12}$$

$$2\,[\,{>}MOH\,] + 2F^- \rightleftharpoons \begin{array}{l} {>}MOF \\ | \\ {>}MF \end{array} + H_2O \tag{13}$$

where M represents metal ion (Al, Fe or Si). The first reaction involves the protonation of the neutral sites, usually taking place at pH values below the pH_{pzc} of the adsorption media (red mud). According to the second reaction, fluoride ions interact with the positively charged sites to form either the outer-sphere complexes or inner-sphere complexes with elimination of water molecule. The third reaction involves interaction between fluoride and the neutral sites forming inner-sphere complex.

Collagen fiber, an abundant natural biomass, comes from the skin of animals and has been traditionally used as raw material in leather manufacturing. The collagen molecule is composed of three polypeptide chains with triple-helical structure, and they are aggregated through hydrogen bonds to form collagen fiber. Collagen fiber is water insoluble but is a hydrophilic material. According to the principles of leather manufacture, collagen fiber that has abundant functional groups is capable of chemically reacting with many kinds of metal ions, such as Cr(III), Al(III), Zr(IV). Thus, Liao and Shi [67] prepared a novel adsorbent by impregnating Zr(IV) on collagen fiber, and its adsorption behavior in removing

fluoride from water was investigated. The adsorption capacity was 43.51 mg/g (Table 6) at pH = 5.5. The adsorption isotherms were well fitted with the Langmuir equation. The adsorption capacity increased with an increase in temperature suggesting an endothermic adsorption. These facts imply that the mechanism of chemical adsorption might have been involved in the adsorption process of fluoride on the adsorbent and that fluoride ions formed a monolayer on the surface of the adsorbent. The adsorption kinetics of fluoride onto Zr(IV)-impregnated collagen fiber were described by Lagergren's pseudo-first-order rate model. In addition, results of desorption indicated that this adsorbent was easily regenerated by use of dilute NaOH solution.

In a similar study operated in a batch mode, Oguz [23] used gas concrete waste materials to remove F^- from aqueous solutions under varying experimental conditions such as solution pH and temperature. It was thought that the removal of fluoride by gas concrete took place both by adsorption and precipitation of Al^{3+} and Ca^{2+} salts. As a result of this study, it was concluded that wastes of gas concrete were an efficient adsorbent (about 96%) for the removal of fluoride ions from water.

(g) *Polymeric materials*. Chelating resins have been recognized for their promising metal-adsorption properties. Utilizing their ability to adsorb trivalent metals and their large internal matrices, several author have studied extensively the application of metal-loaded polymeric resins as potential adsorbents for anions: in particular, fluoride. La(III)-loaded PMA resin, Zr(IV)-loaded Amberlite XAD-7, La(III)-AFB resin, Pr(III)-AFB resin [68], Al(III)-AMPA resin [69], La(III)-impregnated silica gel, cross-linked pectic acid (CPA) gel, phosphorylated cross-linked orange juice (POJR) gel, La(III)-loaded 200CT resin, saponificated orange residue (SOJR) are some of the polymeric adsorbents that have been tested for fluoride uptake in acidic to near neutral pH range using a batch mode of operation. For these materials, their capacities are appreciable higher than those of other adsorbents. Because of the metal loading onto the adsorbents, the mechanism of fluoride removal from water is that due to ligand exchange between fluoride ions from water and hydroxyl ions from the resin. Not much is known about the large-scale operation of these adsorbents and nor is their long-term stability well defined from the scanty literature available. However, Fang *et al.* [70] presented column dynamics of fluoride removal from water using La(III)-loaded 200CT resin. They found that the adsorbent could only process 50-bed volumes before breakthrough was reached indicating that the high-batch capacities (Table 7) of these adsorbents are fallacious. Because these kinds of adsorbent are synthetic, they are expected to be relatively expensive.

(h) *Layered double hydroxides*. In nature layered double hydroxides (LDHs) are very rare; however, they can be synthesized in a laboratory by a co-precipitation method. The applications of LDHs as adsorbents to selectively remove anionic organic or inorganic pollutants from aqueous solutions have attracted considerable attention in the recent past [71–79] .The LDHs, also called hydrotalcite-like

Table 7. Summary of adsorption capacities of selected polymeric materials

Source	Material	Capacity (mg F/g) (BV: bed volume)	Mode of operation
Chikuma and Nishimura [68]	Pr(III)-AFB resin	0.5	Batch
Popat et al. [69]	Al(III)-AMPA resin	11.16	Batch
Popat et al. [69]	Al(III)-AMPA resin	86.7 BV	Column
Fang et al. [70]	200CT resin	5.39	Batch
Fang et al. [70]	200CT resin	50 BV at breakthrough	Column
Fang et al. [70]	IR124 resin	42.0	Batch
Fang et al. [70]	CPA gel	39.3	Batch
Fang et al. [70]	POJR gel	22.2	Batch
Fang et al. [70]	SOJR gel	16.15	Batch

compounds or anion clays, consist of brucite-like hydroxide sheets. Many cations can be incorporated in the brucite-like sheets. The general formula is

$$[M_{1-x}^{II}M_x^{III}(OH)_2]^{x+}[(A^{n-})_{x/n} \cdot mH_2O]^{x-} \tag{14}$$
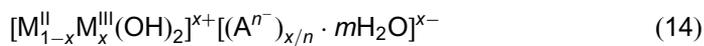
where M^{II} is divalent cation like Mg^{2+}, Zn^{2+}, Cu^{2+}, etc., M^{III} trivalent cations like Al^{3+}, Cr^{3+}, Fe^{3+}, etc. and A^{n-} anion [80]. Owing to the partial substitutions of M^{III} for M^{II}, the hydroxide sheets are positively charged and require intercalation of anions such as CO_3^{2-}, Cl^- or NO_3^- to remain electrically neutral. Studies have shown that LDHs can uptake some inorganic or organic anionic pollutants by exchange with interlayer anions [74,75], but the efficiency of uptake is affected considerably by the properties of interlayer anions. Generally, LDHs have greater affinities for multivalent anions such as CO_3^{2-} and PO_4^{3-} than for monovalent anions. In a recent study by Das et al. [18], calcined Zn/Al hydrotalcite-like compound (HTlc) was used to remove fluoride from aqueous solution. The maximum adsorption took place within 4 h at pH 6.0. The fluoride removal was exothermic in nature, the efficiency increased with an increase in the adsorbent dose, but decreased with an increase in the fluoride concentration. The maximum adsorption capacity was 16.2 mg/g at 30°C.

(i) *Zeolites*. Zeolites are aluminosilicates with a framework structure of $(SiAl)O_4$ tetrahedral containing pores filled with water molecules and exchangeable cations. The ions and molecules of water contained in the voids have a considerable freedom of movement that leads to ion exchange and reversible dehydration. Zeolites are abundantly available in both natural and synthetic form and among them are: Zeolite A, Zeolite X, Zeolite Y, Zeolite F9, Clinoptilolite, Mordenite, HSZ

300HUD, Erionite, Zeolite ZSM-5, Offretite, Type L and Omega. Over the years, zeolites have gained enormous applications especially in sorption processes as evidenced from researches by Song et al. [81], García-Sánchez et al. [82], Färm [83], Doula and Ioannou [84], Majdan et al. [85], Daković et al. [86], Dal Bosco et al. [87], Turan et al. [88] and Wingenfelder et al. [89]. Recent adsorption data of anions by surface-tailored zeolite suggests that this novel media has potential for water treatment [90–95].

By using the wet impregnation method, a novel adsorbent, aluminum-loaded Shirasu-zeolite P_1 (Al-SZP$_1$), was developed for the removal of fluoride ions from aqueous system [96]. The dependence of removal percentage upon aluminum concentration in the loading solution, pH, initial concentration and co-existing anions was investigated. The rate of adsorption of fluoride followed first-order kinetics, equilibrium data described by Freundlich isotherm, while the mechanism was supposedly an ion exchange process between fluoride and the hydroxide groups on the surface of A1-SZP$_1$. In another study, a new adsorbent, cerium(IV) oxide coated on SiMCM-41 ((Ce)SiMCM-41), was prepared by Xu et al. [97] for the removal of fluoride ions from water. Factors investigated were the number of impregnations, Ce/Si ratios, the concentration of F^- ions, pH values and calcination temperatures. The dynamics, isotherms and mechanism of adsorption of F^- ions were discussed. Using a similar impregnation method, Onyango et al. [98–100], have shown that low-silica zeolites can be charge-reversed and used in fluoride removal from water. Table 8 summarizes some of the reported zeolite capacities.

3.2. Characteristics of fluoride adsorption onto surface-tailored low-silica zeolite

In this section, detailed analysis of fluoride adsorption characteristics are provided. Zeolite-adsorption media is chosen for this purpose. Zeolites are well

Table 8. Summary of adsorption capacities of zeolites

Source	Material	Capacity (mg F/g)	Mode of operation
Xu et al. [97]	(Ce)SiMCM-41	114.4	Batch
Onyango et al. [98]	La-exchanged F9	54.3	Batch
Onyango et al. [98]	Al-exchanged F9	39.5	Batch
Onyango et al. [100]	Al-exchanged A4	41.4[a]	Batch
Onyango et al. [100]	Al-pretreated HUD	28.1[a]	Batch
Onyango et al. [100]	Na-Al-pretreated HUD	34.8[a]	Batch

[a] Indicates values are determined from Dubinin–Radushkevitch isotherm.

known for their ion-exchange phenomenon and are an emerging competitive adsorbent. Their role in the conversion of solid and liquid hazardous wastes into environmentally acceptable product is well documented. In water treatment, several zeolites, namely, clinoptilolite, chabazaite, Shirasu-zeolite SZP1, 13X and 5A have been identified as potential adsorption media. Synthetic zeolites are useful because of their controlled and known physicochemical properties relative to those for natural zeolites [95]. More importantly, low-silica synthetic zeolites provide relatively higher number of ion-exchange sites. This latter property was utilized to create a novel adsorbent for fluoride.

3.2.1. Surface modification of zeolite

One disadvantage of using zeolites in anions adsorption inheres in their negative zeta potential in solution over a wider pH range. The preceding factor (negative charge) results in coulombic repulsion between the zeolite surfaces and adsorbing anions. Thus, to effectively use zeolites in anions adsorption, their surfaces need to be tailored in such a manner as to create surface-active sites that are efficient and specific to target anions. By a wet impregnation method using Al^{3+} ions the net surface charge of zeolite can be altered as shown in Fig. 2 [98].

Figure 2 above shows a typical plot of changes in electrokinetic properties of zeolite F9 (Na-form, Si/Al ratio $= 1.23$) and its modified forms suspensions in 10 mM NaCl as a background electrolyte. Zeolite F9 contains sodium oxide, silicon oxide and aluminum oxide and therefore it is a mixed oxide adsorbent. It is shown in Fig. 2 that zeolite F9 is negatively charged over the whole pH range tested and therefore has no pH_{pzc}. By contrast, when Na^+ ions were exchanged for Al^{3+} ions, the zeolite particles were charge-reversed and the pH_{pzc} was found to be 8.15. At this pH, the positively charged aluminol sites (Zeo-$AlOH_2^+$) and those due to unexchanged sodium, if any, are basically equal to the negatively charged sites mainly from silica and hydroxylized aluminol sites. Also indicated in the figure is the field pH range (6.5–8.5) of drinking water over which defluoridation is desired.
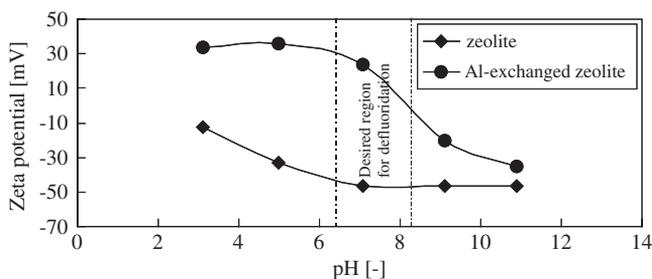

Fig. 2. Changes in electrokinetic properties of zeolite F9 and its modified form, Al^{3+}-exchanged zeolite.

Over this pH range, the number of active sites in Al-exchanged zeolite F9 is expected to reduce substantially as can be deduced from the fall in zeta potential. Using the surface-modified zeolite, batch equilibria and kinetics and column dynamic were studied.

3.2.2. Batch fluoride adsorption equilibrium

Figure 3 summarizes the typical equilibrium data for fluoride sorption on 0.150–0.300 mm surface-tailored zeolite F9. Only the low-concentration range was considered where the Henry's law is applicable. Co-incidentally, fluoride ions exist in natural systems, such as groundwater, at low concentrations. It is observed that the data fit well to the linear isotherm suggesting sorption onto sites with high capacity for fluoride. From Fig. 3, the linear isotherm constant, K ($= 2.337$ L/g), was obtained and coupled into the diffusion model, equation (16).

3.2.3. Prediction of mass transfer processes

Adsorption process involves the transfer of a species from the bulk solution to the adsorbent surface, then to the interior matrix of the adsorbent where the species is bound onto the active sites. Figure 4 shows the effect of varying initial fluoride concentration from 5 to 20 mgF/L. The quantities of fluoride removed from the solution increased with an increase in initial concentration. Diffusion is a passive transport process driven/governed by the concentration gradient at the solution/sorbent interface. At higher initial concentration, the driving force, which is the difference between the bulk-phase concentration and the sorbed-phase concentration, is expected to be higher. This leads to larger uptake in both the early and longer contact times, for higher initial concentration.

During transport, both external and intraparticle mass transfer resistances play a role to a varying degree. A first step in adsorber design is to predict or
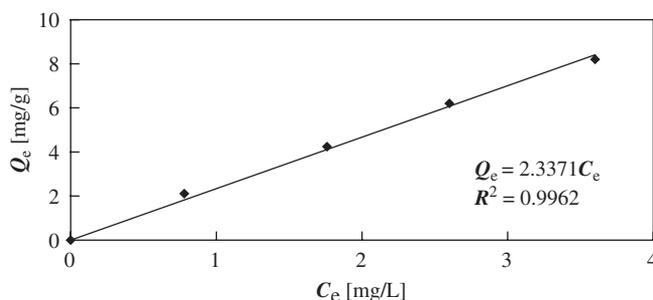

$$Q_e = 2.3371 C_e$$
$$R^2 = 0.9962$$

Fig. 3. Linear adsorption isotherm. Initial fluoride concentration ranged from 5–20 mg/L.
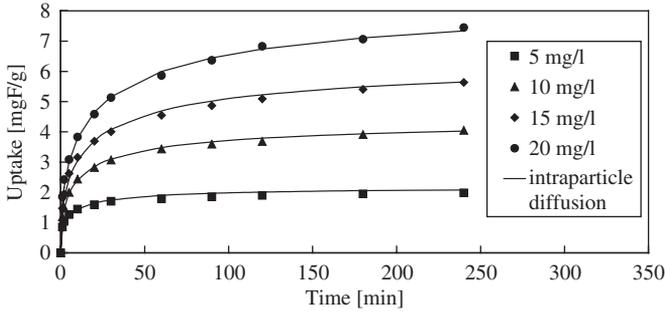
Fig. 4. Effect of initial concentration on fluoride uptake: particle size, 0.150–0.300 mm; sorbent dose, 2 g/L; agitation speed, 300 rpm and solution temperature, 295.1 K.

determine these resistances. Thus, a batch operation mode was adopted to determine the film and intraparticle diffusion coefficients under varying initial fluoride concentration (5–20 mg/L), as an example. The mass transfer values obtained from such study can then be used as first estimates in mechanistic modeling of columns. The evaluation of external resistance to mass transfer was done, by determining the film diffusion coefficients according to a simple method proposed by Mckay [101]. The method involves the calculation of the initial slope of the concentration against time curve and substituting the obtained value into Equation

$$\left.\frac{\mathrm{d}(C_t/C_o)}{\mathrm{d}t}\right|_{t=0} = -k_f S_A \tag{15}$$

where k_f is the film diffusion coefficient (cm/s) and S_A the specific surface area of the zeolites (cm^{-1}). The specific surface area is expressed as

$$S_A = \frac{6m_s}{\rho_p d(1 - \varepsilon_p)} \tag{16}$$

where m_s is the zeolite mass per unit volume (g/cm^3), ρ_p the density of zeolite (g/cm^3), d the average zeolite size (cm) and ε_p the porosity. The film diffusion coefficients determined according to equation (15) are summarized in Table 9. The magnitude of k_f values was in the range 2.07×10^{-2}–3.08×10^{-2} cm/s. This range of k_f values is high implying less external resistance to mass transfer. Moreover, they are comparable to those reported by Mahramanlioglu *et al.* [14] and Ghorai and Pant [39] for fluoride adsorption on SBE and AA, respectively, and indicate the rapidity with which fluoride ions were transported to the external surface of the zeolites.

   In general, as an adsorbate is transported in the internal matrix of adsorbent, there is tendency of adsorbate–adsorbate interaction in the pores and hopping, from site to site, of adsorbed species along the wall of the adsorbent. These phenomena give rise to pore and surface diffusion resistances to intraparticle

Table 9. Summary of mass transfer parameters for batch fluoride adsorption

Initial concentration (mg/L)	Mass transfer parameters			
	K_f (cm/s)	D_e (cm^2/s)	$N_{Bi} = k_f\, r_o/D_e$ (−)	$\Delta q\%$
5	3.05×10^{-2}	1.11×10^{-9}	»100	4.66
10	2.07×10^{-2}	5.27×10^{-10}	»100	1.45
15	2.45×10^{-2}	3.22×10^{-10}	»100	2.16
20	3.08×10^{-2}	2.68×10^{-10}	»100	1.48

mass transfer. Thus, a parallel pore–surface diffusion model for a differential radial shell of zeolite adsorbent is given by

$$\varepsilon_p \frac{\partial c}{\partial t} + \rho_p(1 - \varepsilon_p)\frac{\partial q}{\partial t} = D_p \varepsilon_p \frac{1}{r^2}\frac{\partial\left(r^2 \frac{\partial c}{\partial r}\right)}{\partial r} + \rho_p D_s \frac{1}{r^2}\frac{\partial\left(r^2 \frac{\partial q}{\partial r}\right)}{\partial r} \tag{17}$$

where c and q are the pore- and adsorbed-phase concentrations, respectively, D_p and D_s the pore and surface diffusion coefficients, ε_p the particle porosity, ρ_p the particle density, r the radial dimension and t the time. In this model it is assumed that a local equilibrium exists between the adsorbing fluoride ions and those in pore phase for $0 \leq r \leq r_o$ and that equilibrium is described by a linear isotherm as described in Section 3.2.2. Analytical solution of the above equation is given by Crank [102]:

$$Q_{av,t} = Q_e \left\{ 1 - \sum_{n-1}^{\infty} \frac{6\alpha(\alpha + 1)\exp(-\beta_n^2 k't)}{9 + 9\alpha + \beta_n^2 \alpha^2} \right\} \tag{18}$$

where r_o is the mean particle radius, $Q_{av,t}$ is the average amount adsorbed in the pore and surface, Q_e the equilibrium concentration and β_ns are the positive non-zero roots of

$$\tan \beta_n = \frac{3\beta_n}{3 + \alpha\beta_n^2} \tag{19}$$

and $\alpha = 1/\rho K$ represents the sorbent load factor and $k' = D_e/r_o^2$ represents the intraparticle diffusional time constant, D_e (combines pore and surface diffusion coefficients) is the effective intraparticle diffusion coefficient and ρ equal to sorbent mass to particle-free volume. The intraparticle resistance to sorbate transport is determined by intraparticle diffusion coefficient, D_e. Thus, the D_e values were determined, by minimizing the normalized standard deviation ($\Delta q\%$) and are summarized in Table 9. As the initial concentrations were raised, the effective diffusion coefficients decreased in a non-linear fashion. McKay and Al-Duri [103] found a non-linear decrease in effective diffusivity with an increase in dyes concentration and attributed this to surface diffusion effects. To the contrary,

Ma *et al*. [104] attributed a decrease in diffusivity with an increase in initial concentration to pore diffusion effects. Because zeolites are bi-dispersed sorbents, both surface and pore diffusions may dominate different regions. In micropores, surface diffusion may be dominant, while pore diffusion may be dominant in macropores. This, therefore, supports the use of a lumped parameter (D_e). To explore further the relative importance of external mass transfer *vis-a-vis* internal diffusion, Biot number ($N_{Bi} = k_f\, r_o/D_e$) was considered. Table 9 summarizes the N_{Bi} values for the four initial concentrations. The N_{Bi} values are significantly larger than 100 indicating that film diffusion resistance was negligible.

3.2.4. Defluoridation in zeolite column

In liquid-phase adsorption separation and purification process, there are a number of configurations such as batch, fixed bed and fluidized bed that are applicable for a given utility. Among these, fixed bed is the most commonly used configuration in drinking water treatment. The advantages of using fixed-bed adsorbers in water treatment inhere in the high quality of drinking water produced, their simplicity, ease of operation and handling and regeneration capacity. Moreover, for such configuration, both POU system that can serve an individual household and POE system that can serve a small or large community are possible. Thus, a number of researchers have studied defluoridation of drinking water using various adsorption media in fixed-bed column. Rubel [61] and Ghorai and Pant [22] using AA and Mjengera and Mkongo [4] using bone char showed that fixed-bed configuration is a feasible defluoridation unit.

In order to design an effective adsorption separation or purification unit, preliminary design information is required [38]. Often, these pieces of information are gathered through the performance of an extensive series of pilot-plant experiments that are time consuming and expensive. The aim of such a study is to predict *a priori* what will happen in a full-scale column under various design and operating parameters. Among the operating parameters and fluid features that are paramount for a good design are: linear flow rate, initial concentrations, bed height, particle size, adsorbent types, pH and temperature, among others. To cut costs and to save time in doing unnecessarily too many experiments, Ko and co-workers [38] suggest that models should be used to predict the optimum conditions when the above parameters are varied. Models may broadly be divided into empirical, simplistic and mechanistic models. In mechanistic models for fixed-bed adsorber, all the fundamental mass transport mechanisms, including external film, pore and surface diffusions, axial dispersion and reaction kinetics have to be accounted for. Unfortunately, the solution of a number of differential equations involved often require numerical techniques and thus require high-level expertise. In addition, these solutions also require accurate correlations for mass transfer parameters to describe external film, internal pore diffusion and the

equilibrium relationship between sorbate and sorbent [38]. Because of the above limitations, several simplified design models such as the empty bed contact time (EBCT), the bed depth service time (BDST) and empirical design model such as the two-parameter model are some of the common approaches usually applied. These kinds of the so-called "short-cut" models ensure that pilot-plant testing is used largely for verification rather than information gathering, thus, saving time and money. In this communication, therefore, fluoride removal using fixed-bed column is undertaken at different bed heights and initial fluoride concentrations. The results are interpreted using EBCT approach, and BDST and two-parameter models.

(a) *The bed depth service time model*. The laboratory-scale fixed-bed column used in this study was 15 cm long with 2.1 cm internal diameter containing granular surface-tailored zeolite of 0.150–0.355 mm size. Fluoride-spiked solution was pumped to the column in an upward-flow mode. The effects of two variables, bed height and initial fluoride concentration, on breakthrough curves are reported.

The BDST model is based on the assumption that reaction kinetics plays a limiting role in adsorption. Therefore, the starting point in BDST modeling approach is to consider the reaction kinetics. As already mentioned, both the protonated and neutral aluminol surface sites are the fluoride-adsorption sites. These surface groups are located at the 0-plane. Fluoride ion being an inner-sphere complex-forming species, interacts with the active sites in the region bounded by the adsorbent surface (0-plane) and inner Helmholtz plane (IHP) of the Stern layer, as illustrated in Fig. 5.

Mechanistically, the interaction between fluoride and the active sites follows second-order kinetics. If we let S_t to be the total number of sites, SF the sites occupied by fluoride, and S_t-SF the sites available for reaction, then the rate of reaction, r_s, is given by

$$r_s = \frac{d[SF]}{dt} = k_a[F^-][S_t - SF] - k_d[SF] \qquad (20)$$
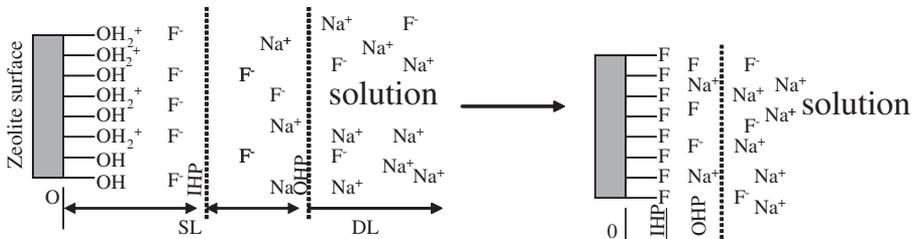

Fig. 5. Illustration of the scheme of surface-tailored zeolite–water interface with adsorbing fluoride ions found in the region bound between planes 0 and IHP. The interaction leads to the formation of inner-sphere complexes of surface-tailored zeolite/fluoride. Sodium ions do not penetrate the IHP.

or simply

$$\frac{dq}{dt} = k_a c(q_m - q) - k_d q \tag{21}$$

where $[SF] = q$, $[S_t] = q_m$, $[F^-] = c$, k_a is the forward rate constant and k_d the backward rate constant. If the zeolite–fluoride bonding is strong, then $k_a \gg k_d$. Moreover, Bohart and Adams [105] simplified the above expression for ion exchange as follows:

$$\frac{dq}{dt} = -k_a q c \tag{22}$$

In carrying out material balance over a small control volume of a fixed bed, it is considered that fluoride removal is solely by adsorption onto the zeolite particles. Additionally, the system is assumed to be isothermal, non-equilibrium and non-adiabatic single-component fixed-bed adsorption. For the control volume (Fig. 6), $A_x dz$, for a limiting situation $z \rightarrow 0$, the material balance is given by

$$\frac{\partial C_z}{\partial t} = D_L \frac{\partial^2 C_z}{\partial z^2} - u \frac{\partial C_z}{\partial z} - C_z \frac{\partial u}{\partial z} - \frac{(1 - \varepsilon)}{\varepsilon} \rho_s \frac{\partial q}{\partial t} \tag{23}$$

where A_x is the cross-sectional area of the bed, z the axial dimension, D_L the axial dispersion coefficient, C_z the concentration, w (Fig. 6) the bed weight, u the linear velocity, ε the bed porosity and ρ_s the particle density. For mathematical expediency, axial dispersion is assumed negligible and for dilute solution u is assumed to be constant, and therefore a combination of equations (22) and (23) gives

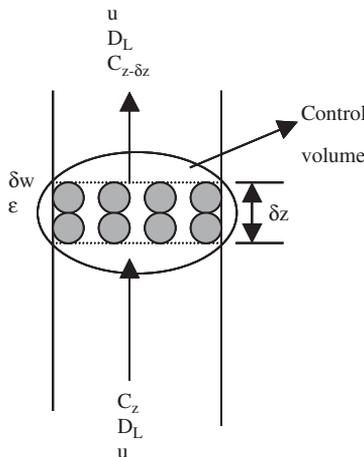$$\frac{\partial C_z}{\partial t} + u \frac{\partial C_z}{\partial z} = -k_a q c \tag{24}$$

Fig. 6. Control volume of a fixed bed over which material balance is carried.

If the volumetric sorption is expressed by N_o (gF/L), then the solution of equation (24) over the bed length is given by a simplistic model, well known as the BDST, expressed as

$$\ln\left(\frac{C_o}{C_t} - 1\right) = \ln\left(e^{k_a N_o Z/u} - 1\right) - k_a C_o t \tag{25}$$

The linearized form of the above equation is given by

$$t = \frac{N_o Z}{C_o u} - \frac{1}{k_a C_o}\ln\left(\frac{C_o}{C_b} - 1\right), \quad \text{for } C_t = C_b \text{ (breakthrough concentration)} \tag{26}$$

Application of the BDST model (equation (25)) to simulate breakthrough curves of fluoride adsorption onto zeolite in a fixed bed is shown in Fig. 7. The BDST model satisfactorily simulates the experimental data points. It is observed that as the bed height is raised, it takes longer time for a given concentration to exit due to increases in the number of active sites and possibly due to increase in contact time. The BDST model was further considered in the linearized form according to equation (26) and as shown in Fig. 8, in which the service time is correlated with the bed depth. A highly significant linear regression line was obtained. From the linear plot, for $C_b = 1.5$ mg/L (WHO permissible limit), the rate constant k_a was found to be 8.3×10^{-4} L/mg/min. The critical bed depth was also determined. The critical bed depth (Z_0) represents the theoretical depth of adsorbent necessary to prevent the sorbate concentration to exceed the limit concentration C_b. From equation (26) when $t = 0$, we have

$$Z_0 = \frac{u}{k_a N_o}\ln\left(\frac{C_o}{C_b} - 1\right) \tag{27}$$

The critical bed depth (Z_0) was found to be 0.8 cm. When the column capacity at breakthrough was compared with batch capacity at the same concentration, the
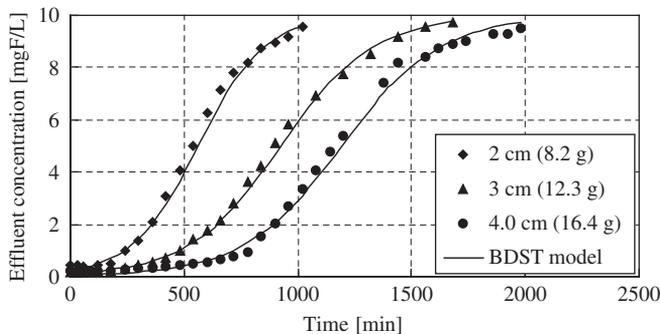

Fig. 7. Effect of bed height on fluoride removal from water. BDST model simulation is represented by continuous line. Initial concentration = 10 mg/L; flow rate ≈ 9.8 mL/min; particle size = 0.150–0.355 mm; and pH = 6.2–6.4.
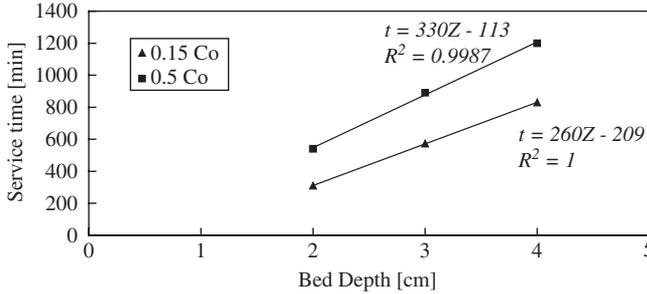
Fig. 8. BDST: fixed bed design.

former was found to be higher. This and other useful pieces of information are summarized in Table 10.

In another experimental run, the initial fluoride concentration was varied from 5 to 20 mg/L as shown in Fig. 9. It is observed that the higher the concentration, the steeper the slope of breakthrough curves, hence a reduction in zone spreading time. Also, the breakthrough curves shift towards the origin with increase in initial concentration. These observations are due to the fact that at higher concentration, the active sites are quickly filled up. From this figure and model simulation, the times required for the exit concentration to rise to breakthrough point ($C_b = 1.5$ mg/L) and 50% of initial concentration at the exit and column capacity were determined and are summarized in Table 10.

In optimizing fixed bed, it is important to know how the EBCT affect the adsorbent exhaustion rate (AER) (AER: mass of adsorbent per volume of water treated at breakthrough). Thus, AER was determined at various adsober heights and initial concentrations. On the one hand, it was found that an increase in bed height resulted in a decrease in AER, while on the other, an increase in initial concentration resulted in a corresponding increase in AER (Table 10). The former suggests that within the range of heights used in this study, a longer bed is preferred, while from the latter, it can be concluded that lower concentrations lead to processing of more bed volumes.

(b) *The two-parameter model*. A simple two-parameter model is an empirical expression for modeling breakthrough curves and it takes the form [106]

$$\frac{C_t}{C_o} = \frac{1}{2}\left(1 + \text{erf}\left[\frac{(t - t_o)\exp(\sigma(t/t_0))}{\sqrt{2}\sigma t_0}\right]\right) \tag{28}$$

where erf[x] is the error function of x, defined by

$$\text{erf}[x] = \frac{2}{\sqrt{\Pi}}\int_0^x \exp(-\eta^2)\,\text{d}\eta \tag{29}$$

where t is the column residence time, t_0 the time at which the effluent concentration is half the influent concentration and σ represents the standard deviation

Table 10. Summary of BDST and EBCT data

| Variable	Lowest concentration (mg/L)	Time to breakthrough, C_b (min)	Time to 0.5 C_o (min)	Capacity at C_b (mg/g)	Batch capacity at C_b (mg/g)	EBCT (min)	AER (g/L)
Effect of Bed depth							
2 cm	0.42	310	540	3.72	3.49	0.69	2.70
3 cm	0.19	573	891	4.64	3.49	1.06	2.13
4 cm	0.21	830	1200	4.79	3.49	1.39	2.02
Effect of initial concentration							
5 mg/L	0.23	1211	1524.5	3.79	3.49	1.06	1.04
10 mg/L	0.19	573	891	4.64	3.49	1.06	2.13
20 mg/L	0.28	307.5	473	4.93	3.49	1.06	3.84
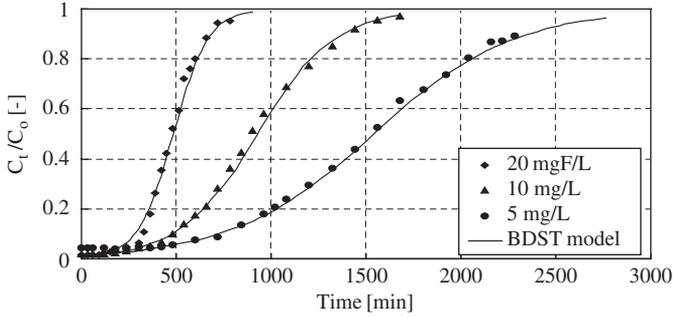
Fig. 9. Effect of initial concentration on fluoride removal from water. BDST model simulation is represented by continuous line. Bed height $= 3\,$cm, flow rate-$\approx 9.8\,$mL/min; particle size $= 0.150$–$0.355\,$mm; and pH $= 6.2$–6.4.

which is a measure of the slope of the breakthrough curve. Chu [106] further suggests that the use of simpler and more tractable models that avoid the need for numerical solution appears more suitable and logical and could have immediate practical benefits. In general, such a model is easier to use and more efficient from a computational point of view compared to the use of full mechanistic models which are much more complicated mathematically. For these reasons, we also explored the possibility of simulating the breakthrough curves using the two-parameter model (equation (28)), by considering the effects of bed height and initial fluoride ions concentration.

The model parameters σ and t_0 for the adsorption of fluoride onto surface-tailored zeolite were determined by matching equation (28) with experimental data. This was done by minimizing the objective function, ϕ, expressed as

$$\phi = \sum \frac{\left|C_{\mathrm{ecp}} - C_{\mathrm{cal}}\right|}{n} \tag{30}$$

where C_{exp} and C_{cal} are the experimental and calculated values of concentration at the column exit and n is the number of data points. In Figs. 10 and 11, the breakthrough curves determined using the best-fit values of σ and t_0 are represented by continuous lines. As was with the case of BDST model, the data points are well represented with the two-parameter model. When the height of the bed and the initial concentration were increased, σ decreased (Table 11). The parameter t_0 on the other hand increases with an increase in bed height and a decrease in initial concentration.

Although both the BDST and two-parameter models fit the experimental data points so well, care should be taken when they are being used in fixed-bed design. Consequently, Chu [106] in contradicting an early work of Ko *et al.* [38], suggests that these models should not be used to predict breakthrough *a priori*. The modeling approach presented here is thus for the purpose of illustration only.
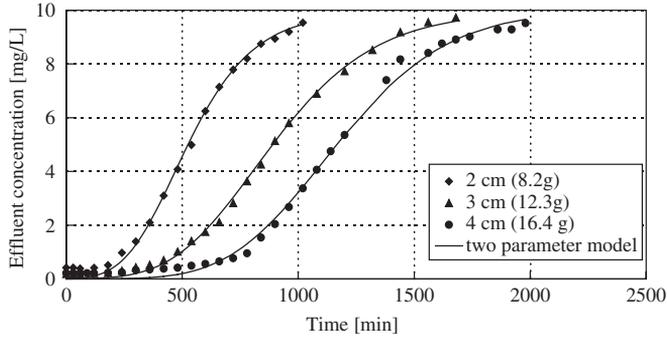
Fig. 10. Effect of bed height on fluoride removal from water. Two-parameter model simulation is represented by continuous line.
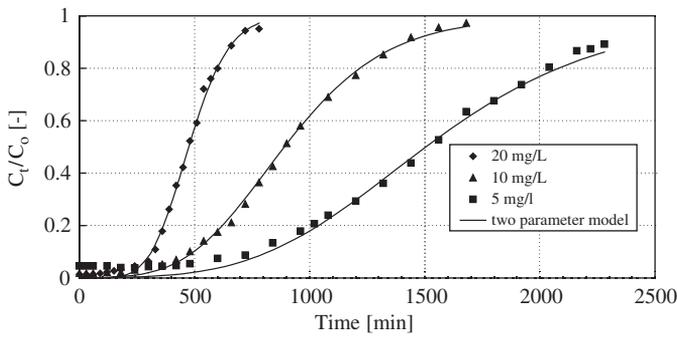

Fig. 11. Effect of initial fluoride concentration on fluoride removal from water. Two-parameter model simulation is represented by continuous line.

A better approach would be to correlate the model parameters with several process variables before the model can be used to design and scale-up the column.

3.3. Configurations and modes of operation of adsorbent-based defluoridation units

Once an adsorption media is chosen and where applicable, model simulations are satisfactory, the next step would be to consider various defluoridator configurations. There are several attractive water treatment configurations based on adsorption technique. These configurations are also principally applicable to water defluoridation. The choice of a given configuration will depend on the amount of water to be treated, the knowledge base of the general population of a given region where the configuration is to be applied, performance and costs of

Table 11. Summary of two-parameter model data

Bed height (cm)	Model parameters	
	σ (−)	t_0 (min)
2	0.315	525
3	0.293	890
4	0.250	1167
Initial concentration (mg/L)		
5	0.300	1505
10	0.293	890
20	0.230	473

adsorption media and of developing a given defluoridation unit. Established and potential defluoridation configurations and their modes of operation are described below.

3.3.1. "Tea bag" POU system

Fluoride-related health hazards are associated with the use of fluoride-contaminated water for drinking and cooking. This corresponds only to 2–4 L per capita per day. Fluoride removal in rural areas in LDCs, where centralized water treatment and distribution facilities are unavailable, should consequently be carried out at a household level and the system applied should be simple and affordable. In this regard, "tea bag" POU system becomes handy. Although this kind of system has not been specifically reported for water defluoridation, it has been tested for arsenic [37,107]. It is therefore a short-term potential technique worth considering. In this technique, adsorption medium is placed in a tea bag-like packet, which is subsequently placed in a bucket of water to be treated. To ensure faster defluoridation kinetics, the bag should be swirled inside the water. It therefore operates like a batch reactor and hence requires a relatively longer adsorption time to achieve the permissible levels. Since the swirling motion is supposed to be human-powered, the technique would require a material with very fast kinetics or very fine adsorption media.

3.3.2. "Coffee filter" POU system

This is also a simple and potential adsorbent-based technique that is worth considering as a short-term solution to fluorosis pandemic. Laboratory trials for the removal of arsenic from water have been reported [107]. Principally, the operation of this kind of defluoridation unit is similar to that of a coffee filter.

Accordingly, water to be treated is passed through adsorption media contained in a filter paper. In doing so, the adsorption media retains fluoride ions, while clean water passes through the filter. Thus, because of the dynamic nature of this process, the adsorption time is relatively shorter than that of the "tea bag" POU system. This kind of system may be handy when only a small amount of water for drinking and cooking is needed. One disadvantage of such a system is that the quality of treated water cannot be guaranteed since its performance depends on the ingenuity of the user.

3.3.3. Household defluoridation POU unit

The use of household defluoridation POU units has increased in recent times in several developing countries such as Kenya, Tanzania and India. As the name suggests, the units are mostly small and can only treat a small amount of water to serve a household. These units operate under the same principle as fixed beds; water to be defluoridated is passed in an upward or downward flow through a small column or bucket containing adsorption media. The designs, however, vary from region to region. The mostly reported adsorption media for this kind of defluoridator are AA and bone char. In India, for example, a Mytry defluoridation filter, which is a two-bucket system with the upper bucket containing AA has been developed and implemented. Murcott [47] reported that since 2004, the MDFFT had sold 9000 units and produces 50 units daily.

In the same country, UNICEF launched an AA household defluoridator unit shown in Fig. 12 [108]. The unit basically consists of two chambers, upper bucket containing adsorption media and lower chamber where the treated water is collected. The upper chamber is fitted with a simple flow control device (removable circular ring) at the bottom. The average flow is 10 L/h. The main component of this unit is a PVC casket containing 3 Kg of AA giving a bed depth of 17 cm. A perforated plate of either stainless steel or tin metal is placed on the top of AA bed to facilitate uniform distribution of raw water. The lower chamber of the defluoridator is fitted with a tap to draw the treated water. Since adsorption media efficiency reduces during operation, regeneration is required for economic and environmental impacts reasons. Thus, exhausted AA can be regenerated by dip-regeneration method. In this method, the casket containing exhausted AA is placed in a plastic bucket containing 8 L of 1% NaOH for 4 h. The casket is then transferred to a bucket containing water and is rinsed by occasional lifting. Thereafter, the casket is placed in a plastic bucket containing 8 L of 0.20% H_2SO_4 for 4 h. Other reports indicate that AA can be regenerated by aluminum sulfate solution [31]. Once regeneration is done, the AA is washed till the pH rises above 7.0 and is then ready for the next defluoridation cycle.

Aluminum oxide present in soil has been utilized to make brick pieces of 15–20 mm sizes that are effective in drinking water defluoridation. When the
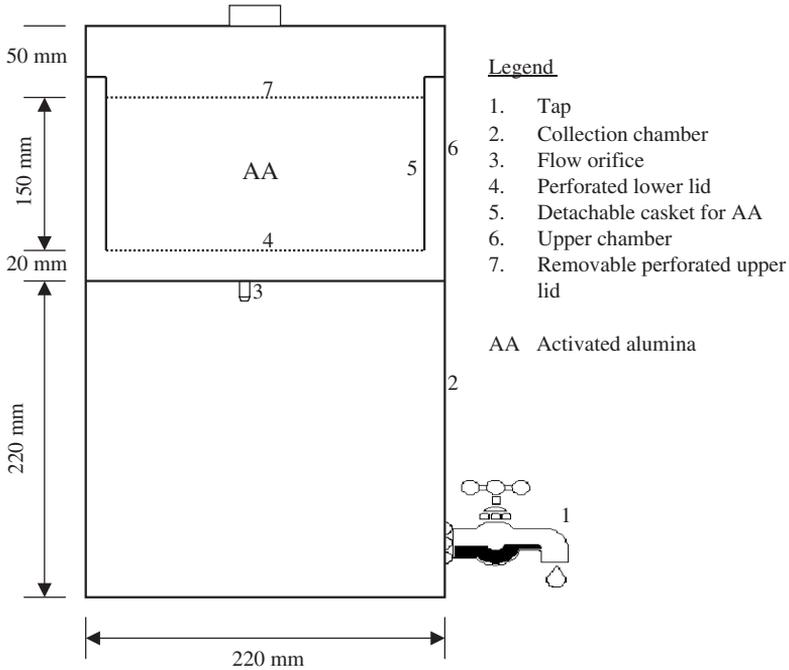
50 mm

150 mm

7

AA   5

6

4

20 mm

3

220 mm

2

1

220 mm

Legend

1.   Tap
2.   Collection chamber
3.   Flow orifice
4.   Perforated lower lid
5.   Detachable casket for AA
6.   Upper chamber
7.   Removable perforated upper
     lid

AA   Activated alumina

Fig. 12. Household-level AA filter [108].

bricks are burnt in a kiln, they become activated. A defluoridation unit using brick pieces has been developed. The unit consists of two PVC concentric pipes, the inner being 20 mm diameter serves as the raw water inlet, while the outer one has a diameter of 225 mm. The bricks are packed in the space between the inner and outer pipes and raw water is allowed to come in contact with the bricks from the bottom of the unit through a perforated plate. This unit is estimated to treat 16 L of water for drinking and cooking. Currently, the unit retails at an equivalent of USD 14 and can operate for 3 months before replacement of the media.

Moges *et al.* [56] and Agarwal *et al.* [109] have reported that ground-fired clay pot could effectively defluoridate drinking water. However, the process is extremely slow. The use of mud pots dates back to ancient times. When mud pots are fired, they become activated and have affinity for fluoride ions. The ability to remove the fluoride ions, however, depends on the alumina content of the soils used for molding the pots. These kinds of pots are cost effective and their use do not require any know-how. They are estimated to retail at USD 0.33/pot.

In Tanzania where fluorosis is also endemic, a household bone char filter column defluoridator has been developed [4]. This unit is slightly differently configured from those described above. It has two separate detached sections. The upper section holds water to be treated, while the lower section is column-like and contains the adsorption media. Water from the upper section is passed by gravity

to the bottom of the column and by upward flow the water is contacted with the adsorption media. Treated water is directly withdrawn from the top of the column.

The disadvantage of household water treatment systems relative to those of centralized water treatment systems is that it is difficult to monitor the performance of the units since they would be scattered in rural settings that are not easily accessible.

3.3.4. Cartridge POU system

Cartridge POU systems are common in regions with tap water. They are relatively expensive and are not common in developing countries. The cartridges are usually installed under the sink to treat water for cooking and drinking. The Environmental and Research Technology – India has however developed over and under the counter kitchen units that do not require any electricity to operate and can be easily moved from one place to another. The adsorption media used is AA packed in a $3'' \times 9\,3/4''$ cartridge for optimum use. This cartridge can last for 6 months when used to treat water containing 10 ppm fluoride and 12 months when the fluoride content is 5 ppm, calculated on a daily consumption of 20 L of water per family. Recently also, an attempt has been made by Mavura *et al*. [110] to construct a cartridge to be used for the defluoridation of drinking water. This cartridge packed with bone char material can be fixed onto a domestic faucet as a flow-through defluoridation unit. The construction material was PVC of various sizes made from a $3/4''$ pipe. The efficiency of fluoride removal was determined for the following parameters: cartridge length, flow rate of water, compactness of bone char material and particle size with the aim of determining the optimum conditions for a good cartridge.

3.3.5. Household POE systems

When a water system serves a few dozen homes or less, POE water treatment systems may provide a low-cost alternative to centralized water treatment. In POE systems, rather than treating all water at a central facility, treatment units are installed at the entry point to individual households or buildings. POE systems can save the cost of installing expensive new equipment in a central water treatment facility. Moreover, POE systems can also save the considerable costs of installing and maintaining water distribution mains when they are used in communities where homeowners have individual wells. Lahlou [111], however, reports that AA-based POE system may be relatively expensive in terms of initial operating and maintenance costs compared with other POE systems. Regulators often have significant objections to using POE devices. Concerns include the difficulty and cost of overseeing system operation and maintenance when

treatment is not centralized, and liability associated with entering customers' homes. These objections have merit, particularly as system size increases and the complexity of monitoring and servicing the devices increases. Using centralized water treatment should be the preferred option, and POE or POU treatment should be considered only if centralized treatment is not possible. In general, POE systems for drinking water defluoridation suit mainly developed countries or those countries in economic transition.

3.3.6. Community-based tube-well-attached defluoridator

Tube-well-attached defluoridator is increasingly becoming popular among the rural population in several LDCs and thus is a community-based water treatment solution. This kind of unit (Fig. 13) is used to treat water serving several households or institutions like schools. In India, a fluoride treatment plant using AA housed in a column operated in a down-flow mode is reported. The water from the tube-well hand pump enters the unit at the bottom and flows upward through the AA media onto which fluoride is adsorbed. Up-flow mode has also been reported by Daw [112]. The adsorption media requires regular monitoring, so that once the breakthrough point is exceeded, regeneration is effected. The frequency of regeneration depends on the raw water fluoride concentration and flow rate.
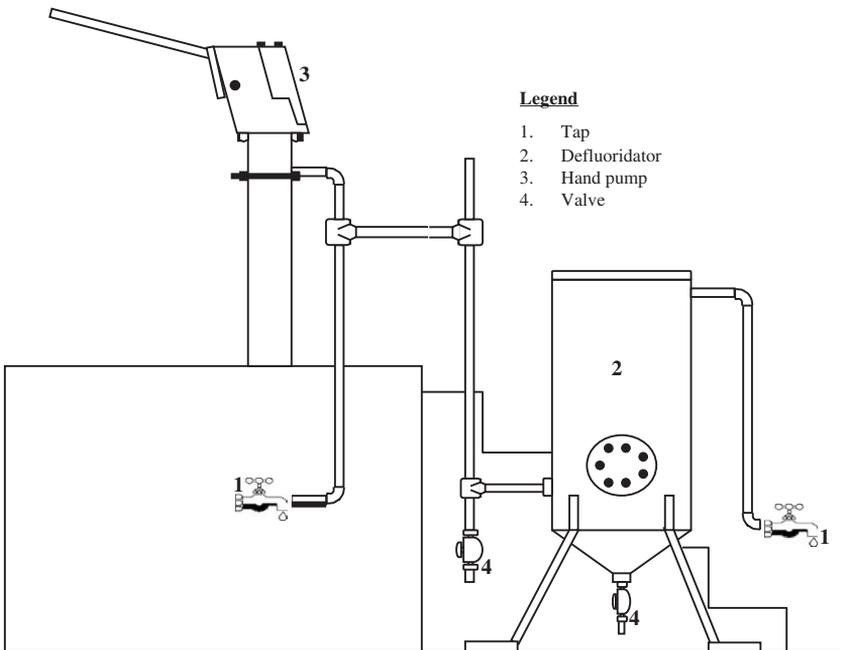

Legend

1. Tap
2. Defluoridator
3. Hand pump
4. Valve

Fig. 13. Hand pump-attached defluoridation unit [112].

After exhaustion, the AA media is regenerated and restored with sulfuric acid and caustic soda. The process of regeneration and restoration requires skilled personnel, for which village-level volunteers can be trained.

3.3.7. Centralized water treatment

Fluoride can also be removed from a centralized water treatment point. This is common in developed or countries in economic transition and provides a long-term solution to fluoride problem in drinking water. A full-scale water purification plant based on AA-adsorption media was reported to be in operation in Kansas, USA. In this technique, all water to the distribution system is treated irrespective of its intended use. Thus, it is unrealistic way of defluoridating water since the main concern is usually fluoride ions contained in drinking water. From the technical point of view, however, centralized water treatment guarantees the quality of drinking water since the performance of the defluoridation plant can easily be monitored. Wider application of this technique for the sole purpose of removing fluoride from water is not widely reported in literature.

3.4. Implementation of defluoridation units: challenges and prospects

In most third world countries as opposed to the developed nations, most people live in the rural areas where water is scarce, the available sources are scattered, the areas are inaccessible and the locals are ill educated. Moreover, it is estimated that several hundreds of millions of people rely on unsafe drinking water containing contaminants such as fluoride. The contaminants are known to cause chronic poisoning. Efforts should thus be made to enlighten the rural population about the dangers of consuming fluoride-containing water. Also, effective technologies for community and household water treatment and storage, in combination with improved hygiene should be instituted [113]. Water technologies aim to make water clean, available, sustainable and economical. Several community and household configurations based on adsorption technique have been designed (Section 3.3) that can suit different geographical regions. Unfortunately, only three adsorbents are currently well recognized by WHO. These are AA, bone char and clay-based adsorbent. AA is relatively expensive and has low capacity for fluoride, while bone char has limited acceptance in certain regions due to religious reasons. Fortunately, indications are that some economies are growing up rapidly and several other good performing adsorbents (Section 3.1) are now available in abundant quantities and some at reduced cost since they are derived from waste materials. However, as indicated in the previous sections, not so much is known about their performance in the field since they have only been

tested under laboratory conditions. More work is thus required to ascertain their performances.

Experience has shown that community water treatment systems hardly pass the test of time. This is partly due to a lack of sense of ownership by the user communities, resulting in indifferent attitude toward the operation and maintenance of these plants [112]. Defluoridation plants are no exception. To succeed, a holistic participatory approach should be adopted in dealing with defluoridation plants/units. The local government, private sector, community-based organizations (CBOs) and the local water users should form a concerted effort in mitigating the fluoride problem and implementing treatment technologies. In this regard, the local government should devise a cost-sharing method in which, say, they provide maintenance personnel but impose some tariffs to water users. Additionally, public–private partnership should be encouraged. Women being the main users of fluoride treatment technologies in rural areas should not be isolated but should participate fully. Indian experience in arsenic treatment technologies has shown that technical solution alone will rarely lead to a sustainable solution [47]. Thus, local knowledge and ingenuity should be inputted into implementation phase to reach higher success rates because they address the problems or issues specific to the community.

4. CONCLUSIONS

This paper provided an overview of the defluoridation techniques with accompanying decision framework for helping utilities determine the most appropriate technique. We biased our discussions towards applications of these techniques to LDCs where fluoride occurrence and distribution is a major issue. Consequently, adsorption technique was vouched for its low cost in general, versatility and environmental benignity, and formed the main focus of our discussion. The emphasis was placed on established and potential adsorption media that are in use or those reported in literature over the last two decades. An attempt was made to critically evaluate the performances of selected adsorption media, in-terms of batch capacity, batch kinetics and column adsorption characteritics, where applicable. It was shown that several adsorption media are attractive for water defluoridation. However, there was paucity of information regarding field application of most adsorption media, the quality of treated water, the stability of the adsorption media and the long term availability. Moreover, the use of adsorption as a drinking water treatment technique faces major challenges such as dependeces of perfomance on solution pH, fast breakthrough by established adsorption media and accumulation of bacteria in the media. An emerging novel adsorbent, surface tailored zeolite, was discussed in more details using recent laboratory data.

The use of adsorbent based POU or POE system was described as an attractive defluoridation configuration that should be given more impetus in LDCs. Though a lot of challenges exist to implementation of defluoridators, it was suggested that a holistic participatory approach by all stakeholders be adopted in fluorotic areas in remedying fluoride contaminated drinking water.

APPENDIX: LIST OF ACRONYMS

POE	point-of-entry
POU	point-of-use
LDC	less developed countries
NEERI	National Environmental Engineering Research Institute
RO	reverse osmosis
NF	nanofiltration
UF	ultrafiltration
ED	electrodialysis
USEPA	United States Environmental Protection Agency
BDAT	best demonstrated available technology
IE	ion exchange
EF	electroflotation
AA	activated alumina
BBC	black bone char
ACNT	aligned carbon nanotubes
MCL	maximum contaminant level
TRB	titanium-rich bauxite
SBE	spent bleaching earth
LDH	layered double hydroxides
EBCT	empty bed contact time
BDST	bed depth service time
MDFFT	Mytry De-Fluoridation Filter Technologies

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Note from the Editor

See also in this series the chapter by M. Pontié *et al*. on nanofiltration processes.