



Review

Review of fluoride removal from drinking water

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ABSTRACT

Fluoride in drinking water has a profound effect on teeth and bones. Up to a small level (1–1.5 mg/L) this strengthens the enamel. Concentrations in the range of 1.5–4 mg/L result in dental fluorosis whereas with prolonged exposure at still higher fluoride concentrations (4–10 mg/L) dental fluorosis progresses to skeletal fluorosis. High fluoride concentrations in groundwater, up to more than 30 mg/L, occur widely, in many parts of the world. This review article is aimed at providing precise information on efforts made by various researchers in the field of fluoride removal for drinking water. The fluoride removal has been broadly divided in two sections dealing with membrane and adsorption techniques. Under the membrane techniques reverse osmosis, nanofiltration, dialysis and electro-dialysis have been discussed. Adsorption, which is a conventional technique, deals with adsorbents such as: alumina/aluminium based materials, clays and soils, calcium based minerals, synthetic compounds and carbon based materials. Studies on fluoride removal from aqueous solutions using various reversed zeolites, modified zeolites and ion exchange resins based on cross-linked polystyrene are reviewed. During the last few years, layered double oxides have been of interest as adsorbents for fluoride removal. Such recent developments have been briefly discussed.

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1. Introduction

The fluoride occurs mainly as sellaite (MgF_2), fluor spar (CaF_2), cryolite (Na_3AlF_6) and fluorapatite [$3\text{Ca}_3(\text{PO}_4)_2 \text{Ca}(\text{F},\text{Cl}_2)$]. As fluor spar it is found in sedimentary rocks and as cryolite in igneous rocks. These fluoride minerals are nearly insoluble in water. Hence fluorides will be present in groundwater only when conditions favour their dissolution or high fluoride containing effluents are discharged to the water bodies from industries.

Fluoride in drinking water has a profound effect on teeth and bones. Fluoride displaces hydroxide ions from hydroxyapatite, $\text{Ca}_5(\text{PO}_4)_3\text{OH}$, the principal mineral constituent of teeth (in particular the enamel) and bones, to form the harder and tougher fluoroapatite, $\text{Ca}_5(\text{PO}_4)_3\text{F}$. Up to a small level this strengthens the enamel. However, fluoroapatite is an order of magnitude less soluble than hydroxyapatite, and at high fluoride concentration the conversion of a large amount of the hydroxyapatite into fluoroapatite makes the teeth and (after prolonged exposure) the bones

denser, harder and more brittle. In the teeth this causes mottling and embrittlement, a condition known as dental fluorosis. With prolonged exposure (Dissanayake, 1991) at higher fluoride concentrations dental fluorosis progresses to skeletal fluorosis (Table 1). Fluoride is thus considered beneficial in drinking water at levels of about 0.7 mg/L but harmful once it exceeds 1.5 mg/L which is the World Health Organisation limit being followed in most of the nations (WHO, 1985; Smet, 1990) and is also the Australian recommended limit (NHMRC, 2004). The difference between desirable doses and toxic doses of fluoride is ill-defined, and fluoride may therefore be considered as an essential mineral with a narrow margin of safety (WHO, 1984).

With the increase in industrial activities water bodies with excess levels of fluoride are becoming a matter of great concern. High fluoride concentrations in groundwater, up to more than 30 mg/L, occur widely, notably in the United States of America, Africa and Asia (Czarnowski et al., 1996; Azbar and Turkman, 2000; Wang et al., 2002; Agarwal et al., 2003; Moges et al., 1996; Gaciri and Davies, 1992; Chernet et al., 2002; Mjengera and Mkongo, 2002; Moturi et al., 2002; Apambire et al., 1997). Long back it was estimated (WHO, 1984) that more than 260 million people worldwide consume drinking water with a fluoride content of >1.0 mg/L. The majority of these people live in tropical countries where the problem is exacerbated by the need to drink more water because of

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Table 1
Effect of prolonged use of drinking water on human health, related to fluoride content (Dissanayake, 1991).

F ⁻¹ concentration, mg/L	Health outcome
<0.5	Dental caries
0.5–1.5	Optimum dental health
1.5–4.0	Dental fluorosis
4.0–10	Dental and skeletal fluorosis
>10.0	Crippling fluorosis

the heat. It is thus absolutely essential to bring down the fluoride levels to acceptable limits for which tremendous research and development efforts are being put all over the world. The present paper reviews the techniques available and ongoing efforts for fluoride removal from drinking water.

2. Methods of defluoridation from aqueous solutions

The objective in fluoride removal is to treat the contaminated water so as to bring down fluoride concentration to acceptable limits. The defluoridation techniques can be broadly classified into two categories, namely membrane and adsorption techniques. (High concentrations of fluoride in industrial effluents are usually brought down to ~ 30 mg/L following precipitation method making use of calcium/magnesium/barium hydroxide slurry to reject fluoride as CaF₂, MgF₂ or BaF. This method is not being discussed in the present review.)

2.1. Membrane techniques

Membrane techniques comprising of reverse osmosis, nanofiltration, dialysis and electro-dialysis are briefly discussed in the following sections:

2.1.1. Reverse osmosis and nanofiltration

Reverse osmosis produces water of extremely high purity. Some applications of reverse osmosis to purification of water are discussed by Schneider and Middlebrooks (1983), Fu et al. (1995), and Arora et al. (2004). Ndiaye et al. studied fluoride removal from effluents using RO technique (Ndiaye et al., 2005). It was observed that the rejection of fluoride ion was typically higher than 98%, considering that the RO membrane was fully regenerated after each set of experiments.

Nanofiltration makes use of the same overall phenomenon as reverse osmosis. For nanofiltration, the membranes have slightly larger pores than those used for reverse osmosis and offer less resistance to passage both of solvent and of solutes. As a consequence, pressures required are much lower, energy requirements are less, removal of solutes is much less exhaustive, and flows are faster. The selectivity of nanofiltration relative to reverse osmosis is a particular advantage, and much experimental and theoretical research is being devoted to obtaining a clearer idea of the mechanism of solute retention to facilitate production and selection of targeted membranes as well as optimisation of conditions (Diawara, 2008; Hu and Dickson, 2006; Bason et al., 2006; Szymczyk and Fievet, 2005; Szymczyk et al., 2006; Lefebvre et al., 2004; Lefebvre and Palmeri, 2005; Paugam et al., 2004; Cervera et al., 2003; Palmeri et al., 1999). Retention of solutes is attributed mainly to steric and charge effects (Diawara, 2008) and although fluoride is a very small ion it is more strongly hydrated than other monovalent anions because of its high charge density, and the consequent steric effect leads to fluoride being more strongly retained on nanofiltration membranes than competing monovalent anions such as chloride or nitrate, a particular advantage in

defluoridation of brackish waters. Lhassani et al. (2001) studied the selective demineralization of water by nanofiltration especially with respect to its application to the defluoridation of brackish water. Drioli et al. (1999) have comprehensively reviewed the use of nanofiltration membranes in water and wastewater treatment.

Tahaikt et al. (2007) carried out fluoride removal operations on underground water using a nanofiltration pilot plant with two modules. The performances of two commercial spiral membranes were proved. The influence of various experimental parameters such as initial fluoride content, pressure and volume reduction factor was studied. Further the authors (Tahaikt et al., 2008) compared the performance of three commercial membranes in fluoride removal by nanofiltration using commercial modules in pilot scale. Many configurations were tested: simple pass, double pass with one type of membranes and combination of two types of membranes and supplied batch configuration. The water parameters were followed as a function of the running conditions (time, pressure, fluoride content, etc.) in order to follow the behaviour of the membranes tested.

2.1.2. Dialysis and electro-dialysis

Dialysis separates solutes by transport of the solutes through a membrane rather than using a membrane to retain the solutes while water passes through it as in reverse osmosis and nanofiltration. The membrane pores are much less restrictive than those for nanofiltration, and the solute can be driven through by either the Donnan effect (Donnan, 1911) or an applied electric field. Hichour et al. (1999) studied the Donnan dialysis process in a counter current flow system in which the anion-exchange membrane was loaded with sodium chloride and the feed was 0.001 M NaF together with other sodium salts. Fluoride migrated into the receiver as other ions migrated into the feed. This technique was later used to defluoridate solutions made to simulate high fluoride African groundwaters (>30 mg/L fluoride) and whatever other ions were present the fluoride in the feed could be brought below 1.5 mg/L (Hichour et al., 2000). Later, combining dialysis with adsorption, the group added aluminium oxide and zirconium oxide to the receiver to force the Donnan equilibrium in the direction of fluoride flow out of the feed. In this way it was possible to maintain a flow of feed while leaving the receiving solution in place or renewing only in batches. The cation composition remained unchanged, whereas anions, except chloride, were partially eliminated and substituted by chloride ions, giving a fluoride concentration of 1.5 mg/L (Garmes et al., 2002).

The removal of fluoride from diluted solution with Neosepta AHA anion-exchange membrane has been studied by Donnan dialysis (Durmaz et al., 2005). The effects of concentration, pH, and accompanying anion on feed phase and receiving phase composition were investigated. The results obtained for AHA membrane were compared with Neosepta AFN and polysulfone SB-6407 membranes. The transport efficiencies of the membranes were found to be in the order AFN > AHA > SB-6407.

The transport of fluoride through Neosepta-ACM anion-exchange membrane was studied as a function of feed phase and receiver phase concentration and co-existence anions under Donnan dialysis condition (Tor, 2007). It was observed that the transport of fluoride was maximum at pH 6 of feed phase and at pH 1 of receiver phase. Recently the fluoride ion removal from aqueous solution has been reported with plasma modified and pristine AFX anion-exchange membranes (Alkan et al., 2008) by Donnan dialysis (DD) method as a function of concentration, pH and membrane structure. The flux values and recovery factors for plasma modified AFX membrane were higher than that of pristine membrane which was explained on the basis of change of wettability and morphology in the plasma modified membrane.

Electro-dialysis is the removal of ionic components from aqueous solutions through ion exchange membranes under the driving force of an electric field. Annouar et al. compared defluoridation using natural chitosan as an adsorbent, in comparison with electro-dialysis, and found both approaches to bring the fluoride level to within WHO guidelines (Annouar et al., 2004). In a further project for defluoridation of Moroccan groundwater, the group improved the efficiency of the process by linking electro-dialysis in tandem with chitosan adsorption. The group also worked for several years on the defluoridation and general purification of brackish groundwater in Morocco and showed that electro-dialysis can defluoridate water with 3000 mg/L total dissolved salts and 3 mg/L fluoride (Sahli et al., 2007). Recently Kabay's group studied the optimisation of fluoride removal by electro-dialysis, evaluating the separation performance in terms of mass transfer and energy consumption. The separation performance increased when the initial concentration of fluoride in the feed solution was increased and when the applied potential was increased. However, they did not find a change in performance with changes in feed flow rate, and they found that separation of fluoride was influenced by chloride but not by sulphate ions (Kabay et al., 2008). Lahnid et al. (2008) have recently made an economic evaluation of fluoride removal by electro-dialysis.

2.2. Adsorption technique

Although membrane methods have successfully reduced fluoride concentration to acceptable levels, surface adsorption retains a major place in defluoridation research and practice because of its general greater accessibility and lower cost. Thus even in the past decade, when interest in alternative defluoridation approaches has been increasing rapidly, many researchers have continued to explore the development of low-cost and effective adsorbents and to improve the efficiency of all adsorbents (Biswas et al., 2007; Jamode et al., 2004).

The nature of adsorption of fluoride on some adsorbents, especially clays which contain oxides of iron, aluminium and silicon, has been reviewed by Puka (2004) as background for his own experimental studies to improve the understanding of fluoride-adsorbent interactions. Theoretically, the adsorption of fluoride on to solid particles normally takes three essential steps (Fan et al., 2003):

- (i) diffusion or transport of fluoride ions to the external surface of the adsorbent from bulk solution across the boundary layer surrounding the adsorbent particle, called external mass transfer;
- (ii) adsorption of fluoride ions on to particle surfaces;
- (iii) the adsorbed fluoride ions probably exchange with the structural elements inside adsorbent particles depending on the chemistry of solids, or the adsorbed fluoride ions are transferred to the internal surfaces for porous materials (intra particle diffusion).

Evaluating an adsorbent for practical purposes, however, requires consideration of adsorption capacity in dilute solutions, pH, time for fluoride removal, stability of adsorbent, regeneration, and loading capacity in presence of other anions and cation and finally the overall cost for fluoride removal. Not all research papers report on all these factors and indeed various adsorbents cannot be readily compared with respect to adsorbent loads, initial fluoride concentrations, and the varied dependent parameters reported. Even for example the temperature to which titanium-rich bauxite is heated to prepare an activated adsorbent has such a profound effect on adsorption that a difference of 90 °C in calcination

temperature can have the effectiveness of the resulting adsorbent in lowering the concentration of fluoride in water (Das et al., 2005).

A wide variety of adsorbents have been used for the removal of fluoride from water. These include activated, and impregnated alumina (Das et al., 2005; Lounici et al., 1997; Mohapatra et al., 2004; Wasay et al., 1996a; Yang et al., 1999), rare earth oxides (Raichur and Basu, 2001), activated clay (Agarwal et al., 2003; Puka, 2004), impregnated silica (Wasay et al., 1996b), carbonaceous materials (Abe et al., 2004; Li et al., 2003a,b; Ramos et al., 1999), solid industrial wastes like red mud, spent catalysts and fly ash (Cengeloglu et al., 2002; Lai and Liu, 1996; Piekos and Paslawaska, 1999; Chaturvedi et al., 1990), zeolites and related ion exchangers (Rao and Bhaskaran, 1988) biosorbents (Mohan et al., 2007) alum (Piñón-Miramontes et al., 2003), alum sludge (Sujana et al., 1998) and modified chitosan (Jagtap et al., 2009) in addition to those considered under the heading of membrane techniques and more recently including layered double hydroxides.

While many adsorption systems have been studied, few adsorbents take the concentration of fluoride down to or below the 1.0–1.5 mg/L level which is required for drinking water and for effluent water that could find its way into drinking water sources (Tripathy et al., 2006). However, less stringent limits for effluent that is not to be released in sensitive locations are readily reached. For example in New South Wales a fluoride concentration of 20 mg/L is the maximum concentration permissible before the waste becomes a controlled liquid waste requiring a licence for transport and disposal (EPA, 1999).

2.2.1. Alumina and aluminium based adsorbents

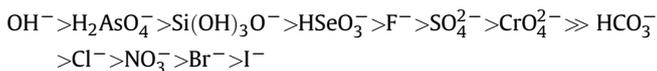
2.2.1.1. Alumina. In early experiments Farrah et al. (1987) investigated the interaction of fluoride ion with amorphous aluminium hydroxide ($\text{Al}(\text{OH})_3$), gibbsite (naturally occurring aluminium hydroxide) and aluminium oxide (Al_2O_3) over a range of pH values from 3 to 8 and F^- concentrations from 0.1–1 mM (~1.9–19 mg/L). At pH < 6 and total F:Al ratios >2.5, most of the amorphous $\text{Al}(\text{OH})_3$ gel dissolved through formation of Al-F complexes, with the distribution of fluorine being determined by the equilibrium F^- value. At lower F:Al ratios, some solid persisted in the pH 4–7 region and strongly sorbed F^- from solution. Maximum uptake occurred in the pH range 5.5–6.5 (up to 9 mol/kg ~ 170 mg/g). At lower pH, uptake declined because of preferential formation of complexes; at higher pH, OH^- displaced F^- from the solid, and the amount of F^- sorbed or converted to complexes declined rapidly towards zero between pH 6 and 8. Similar pH trends were observed using $\alpha\text{-Al}_2\text{O}_3$, except that both substrate solubility and the adsorptive capacity was less. At a fixed pH (between 5 and 7.5) uptake varied in accordance with a Langmuir equation (maximum capacity approx. 19 mg/g). The amount of substrate converted into $\text{Al}^{3+}\text{-F}^-$ complexes in acid media increased with increasing acidity and increasing initial fluoride concentration. Gibbsite displayed the same dissolution trends, but reacted at a much slower rate. Little F^- was sorbed by this substrate (10–20 mmol/kg or 0.2–0.4 mg/g). The study has confirmed the ability of fluoride to mobilize Al and the capacity of $\text{Al}(\text{OH})_3$, to scavenge F^- from aqueous phases in the pH 4–7 region. Hao et al. (1986) reported the adsorption characteristics of fluoride onto hydrous alumina.

To be an effective adsorbent, alumina must be activated by heating. This typically entails being prepared by pyrolysis of (usually) gibbsite, $\text{Al}(\text{OH})_3$, or materials containing gibbsite, either slowly which gives rise to a substantially crystalline product or rapidly (flash calcination) at a high temperature (Rozić et al., 2001, 2006). Slow decomposition is usually achieved by steam whereas rapid decomposition takes place in flue gases at 400–800 °C and exposure times of 1 s or less. Alumina rapidly activated in this way by Rozić's group was transitional alumina (transitional between

gibbsite and Al_2O_3) with 0.2–1 mol water of crystallisation per mole of aluminium oxide. This product was less crystalline as compared either to gibbsite or alumina prepared by slow calcination. It is the less crystalline product that is the most rapid and effective adsorbent for fluoride, as it has a surface area well over 200 m^2 per gram of alumina.

Shimelis et al. (2006) also showed the importance of activation, comparing untreated hydrated alumina (UHA) and thermally treated hydrated alumina (THA) obtained from hydrolysis of locally manufactured aluminium sulphate. The parameters considered were contact time, adsorbent dose, thermal pre-treatment of adsorbent, initial fluoride concentration and pH. Fluoride adsorption efficiencies were found to increase with increase in the thermal treatment temperature up to 200 °C, but further increase in temperature resulted in decreased removal efficiency. High defluoridation efficiency was achieved using both UHA and THA within a pH range of 4.0–9.0. The adsorption data at ambient pH were well fitted to the Freundlich isotherm model with a loading capacity of 23.7 mg/g and 7.0 mg/g THA and UHA, respectively.

The selectivity sequence of anion adsorption (Johnston and Heijnen, 2002) on activated alumina in the pH range of 5.5–8.5 has been reported to be:



Activated alumina can be regenerated by flushing with a solution of 4% sodium hydroxide which displaces fluoride from the alumina surface (Schoeman and MacLeod, 1987). This procedure is followed by flushing with acid to re-establish a positive charge on the surface of the alumina. A major disadvantage of adsorption on activated alumina is that pH needs to be on the acid side of 7 and dissolution of some aluminium oxide/hydroxide is inevitable, releasing toxic aluminium ions (Turner et al., 2005).

The efficacy of alum-impregnated activated alumina (A/AA) in removal of fluoride from water was found to be 92.6% at pH 6.5, contact time 3 h, A/AA dose of 8 g/L, when 25 mg/L fluoride was initially present (Tripathy et al., 2006). This left 1.9 mg/L fluoride in solution. The EDAX analysis showed that the uptake of fluoride at the A/AA/water interface is due only to surface precipitation.

2.2.1.2. Alumina plus manganese dioxide. Maliyekkal et al. (2006) reported that a new adsorbent manganese oxide-coated alumina (MOCA) was able to bring fluoride concentration below the statutory 1.5 mg/L for drinking water and was faster-acting than activated alumina and had a greater fluoride load capacity (2.85 mg/g compared with 1.08 mg/g for activated alumina). Tripathy and Raichur (2008) found that manganese dioxide-coated activated alumina could bring fluoride concentration down to 0.2 mg/L when the initial concentration of fluoride in water is 10 mg/L. Maximum adsorption relative to adsorbent dose took place at pH 5.5. From observation of kinetics and zeta-potential measurements, isotherm modelling and energy-dispersive X-ray analysis (EDAX) the authors concluded that the uptake of fluoride occurred through physical adsorption as well as initial intra particle diffusion at the porous surface. The adsorption of fluoride was found to decrease in the presence of other ions.

Teng et al. (2009) prepared and characterized hydrous manganese oxide-coated alumina (HMOCA). Both batch and column adsorption experiments were carried out to evaluate the adsorption behaviour. Effect of competing anions revealed to have an adverse effect of fluoride uptake. The effluent fluoride containing 5.0 mg/L was defluoridated in column giving <1 mg/L in the treated solution.

2.2.1.3. Alumina plus magnesium oxide. Recently Maliyekkal et al. (2008) described a magnesia-amended activated alumina (MAAA) prepared by impregnating alumina with magnesium hydroxide and calcining the product at 450 °C. MAAA adsorbed fluoride from drinking water more effectively than activated alumina. More than 95% removal of fluoride (10 mg/L) was achieved within 3 h of contact time at neutral pH, bringing concentration down to only 0.5 mg/L. Adsorption of fluoride on to MAAA was found to be pH-dependent and a decrease in sorption was observed at higher pH. The maximum sorption capacity for fluoride was 10.12 mg/g. Most of the co-existing ions found in the natural water source studied had negligible effect on fluoride sorption by MAAA. However, higher concentrations of bicarbonate and sulphate reduced the fluoride sorption capacity.

2.2.1.4. Alumina plus iron oxide. When aluminium and iron(III) hydroxides are co-precipitated from a chloride mixture in equimolar quantities using ammonia, the resulting mixed hydroxide, after aging and drying, is a better adsorbent for fluoride than either aluminium hydroxide or iron(III) hydroxide (Biswas et al., 2007). This suggests that the hydroxides are bonded and not acting independently, and physical measurements of the materials supported the conclusion that there was a new compound. Fourier transform infrared (FTIR) spectra indicate the presence of the Fe–O–Al bond. Scanning electron microscopy (SEM) showed an almost irregular surface morphology with high porosity, indicative of a high surface area. The monolayer adsorption capacity of the mixed hydroxide, derived from Langmuir isotherms, was greater than for the pure hydroxides. Chubar et al. (2005) studied the anion adsorption capacity of an adsorbent precipitated from equimolar aluminium and iron(III) chloride by addition of ammonia. The anions investigated were fluoride, chloride, bromide and bromate. At pH 4, fluoride was the most strongly adsorbed at 88 mg per gram of adsorbent. Similar observations have been made in investigating adsorption of As(III) and As(V) anionic species. Sujana et al. (2009a) prepared a series of amorphous Fe–Al oxides with different molar ratios and studied the fluoride uptake behaviour by varying experimental parameters.

Farrah and Pickering (1986) studied the interaction of dilute fluoride solutions with hydrous iron oxides. Dey et al. (2004) presented the hydrous ferric oxides as a scavenger of fluoride from contaminated water. Tang et al. (2009) have reported a detailed study on fluoride uptake by using commercial granular ferric hydroxide. Experimental parameters including pH, ionic strength and major co-existing anion like phosphate, carbonate, sulphate and chloride were varied to study the adsorption behaviour. Inner sphere complexation of fluoride was confirmed from the XPS studies.

2.2.1.5. Alumina plus calcium minerals. The Nalgonda technique, named after the village in Andhra Pradesh, India, where the method was pioneered, is based on adsorption of fluoride on flocs of aluminium hydroxide as they are formed in solution. Long back Nawlakhe et al. (1975) reported on this technique. Two chemicals, alum (aluminium sulphate or potassium aluminium sulphate) and lime (calcium oxide) are rapidly mixed with the fluoride-contaminated water. Induced by subsequent gentle stirring, “cotton wool”-like flocs develop (aluminium hydroxides) which carry most of the dissolved fluoride and are removed after being allowed to settle. The Nalgonda technique has been introduced in many countries, e.g. India, Kenya, Senegal and Tanzania.

Simple inexpensive set-ups, suitable in third world households, have been outlined by Dahi et al. (1996). The operation can be carried out on a large or small scale, and the technique is suitable for either community or household use. One household version

uses a pair of 20-litre buckets, with a settling time of one hour but not more than two hours: after coagulation and settling are complete, the treated water is withdrawn through a tap 5 cm above the bottom of the first bucket, safely above the sludge level, and stored for the day's drinking in the second bucket. Dahi has described the operation of the Nalgonda technique in the Tanzanian village of Ngurdoto. The concentration of fluoride in the raw water, which is pipe schemed spring water, had been subjected to both seasonal as well as non-seasonal variations, between 12.5 and 8.8 mg/L. The adopted dosages of 12.8 g alum and 6.4 g lime in the villagers' 20-L buckets had been reducing the fluoride concentration to 2.1 ± 0.7 mg/L which was still above the WHO-recommended limit of 1.5 mg/L. Although it has been claimed the Nalgonda process to be the most effective technique for fluoride removal, critics have identified disadvantages. For example Meenakshi and Maheshwari (2006) have listed the following, some of which may be shared by all other attempts to date to detoxify water where community resources are scarce.

- (i) The process removes only a smaller portion of fluoride (18–33%) in the form of precipitates and converts a greater portion of ionic fluoride (67–82%) into soluble $Al^{3+}-F^{-}$ complex ions which are themselves toxic (Apparao and Kartikeyan, 1986).
- (ii) The concentration of the SO_4^{2-} ion from the aluminium sulphate coagulant reaches high levels, and in a few cases it crosses the maximum permissible limit of 400 mg/L.
- (iii) The residual aluminium in excess of 200 ppb in treated water is believed to cause dementia and also affects musculoskeletal, respiratory and cardiovascular systems (Nayak, 2002)
- (iv) Many users do not like the taste of the treated water.
- (v) Regular analysis of feed and treated water is required to calculate the correct dose of chemicals to be added, because the water matrix fluctuates with time and season.
- (vi) The maintenance cost of a community plant is high. On an average as experienced in the recent years, a plant of 10,000 L per day capacity requires Rs. 3000 every month.
- (vii) The process is not automatic. It requires a regular attendant during treatment process.
- (viii) Large space is required for drying of sludge.
- (ix) Silicates have adverse effect on defluoridation by Nalgonda technique. Temperature also affects the defluoridation capacity.

2.2.1.6. Bauxite. Das et al. (2005) studied the adsorption of fluoride on thermally activated titanium-rich bauxite (TRB). Thermal activation at moderate temperatures (300–450 °C) greatly increased the adsorption capacity of TRB. Adsorption was rapid and maximum level was attained within 90 min. The uptake of fluoride increased with increasing pH, reaching a maximum at pH 5.5–6.5 and thereafter decreased. The presence of common interfering ions in drinking water did not affect the uptake of fluoride from aqueous solution indicating fluoride-specific sorption behaviour of TRB.

2.2.1.7. Red mud. Aluminium and iron oxides are major components of red mud, and this mixed adsorbent has been studied extensively as an adsorbent for anionic pollutants, especially anions from arsenic(III) and arsenic(V), because of its availability and low cost (White et al., 2003; Mohan and Pittman, 2007). Table 2 shows a typical composition of an Australian red mud. As recovered from the Bayer process, red mud is too alkaline (pH 10–12) for use as an adsorbent for anions. The alkalinity can be reduced by washing with seawater (White et al., 2003; McConchie et al., 2000; Genç-Fuhrman, 2004), and on a laboratory experiments the pH can be adjusted with strong acid or base. Washing, acid-activating and

Table 2

Components of red mud from Alcoa's Kwinana bauxite refinery, Western Australia (White et al., 2003).

Chemical	Formula	% w/w
Aluminium oxide	Al_2O_3	17–22
Calcium oxide	CaO	4–5
Iron oxide	Fe_2O_3	25–35
Silicon dioxide	SiO_2	25–30
Sodium carbonate	Na_2CO_3	2.8
Sodium oxide	Na_2O	2–3
Titanium oxide	TiO_2	2–4

drying red mud (Cengeloglu et al., 2002) produced an adsorbent that would avoid the need for bulk acidification of water to be defluoridated. The authors separated treated red mud into two batches. The first was washed with water until neutral, and the second, after washing, was soaked in 5.5 M HCl and then washed again with water. Both were dried, and each gave a neutral solution when suspended in water. After treatment for two hours at the optimum pH of 5.5, the activated red mud could remove only 77% of 21 mg/L fluoride, leaving 2.7 mg/L fluoride in solution which was still higher than the acceptable levels. Tor et al. (2009) have recently reported batch and column adsorption experiments carried out on granular red mud (GRM). The experimental conditions were optimized and data fitted to isothermic and kinetic models. The column data was fitted to Thomas model and a good agreement was achieved for the predicted and experimental values. The regeneration of adsorbent was accomplished by pumping 0.2 M of NaOH through the loaded GRM-column.

2.2.1.8. Lateritic ores. Nickel laterites and chromite mine overburden usually contain high content of iron and small amounts of alumina, chromium, cobalt, nickel, manganese. Due to their high iron content in the form of goethite, some studies have been reported for fluoride adsorption (Sarkar et al., 2006). Recently Sujana et al. (2009b) have compared the fluoride uptake capacity of various goethite containing geo materials of India. Effect of various experimental parameters such as time, temperature, pH, adsorbent and adsorbate concentration has been reported. The kinetic, isothermic and thermodynamic parameters were evaluated. Groundwater samples were also tested for fluoride removal.

2.2.2. Clays and soils

The first comprehensive study of fluoride adsorption on to minerals and soils was published in 1967 (Bower and Hatcher, 1967). Since then there have been a large number of studies including the use of Ando soils of Kenya (Zevenbergen et al., 1996), Illinois soils of USA (Omueti and Jones, 1977), Alberta soil (Luther et al., 1996), illite-goethite soils in China (Wang and Reardon, 2001), clay pottery (Chaturvedi et al., 1988; Hauge et al., 1994), fired clay (Bårdsen and Bjorvatn, 1995), fired clay chips in Ethiopia (Moges et al., 1996), bentonite and kaolinite (Kau et al., 1997; Srimurali et al., 1998), and fly ash (Chaturvedi et al., 1990).

2.2.2.1. Clay. Bower and Hatcher (1967) had indicated that the adsorption of fluoride on to minerals and soils is accompanied by the release of OH^{-} ions. It was also found that the fluoride adsorption is concentration-dependent and it is described by the Langmuir adsorption isotherm. The structure of the clay plays a key role in determining the charge on the clay surface and type of exchange that can occur with ions in solution (Puka, 2004). In general the more positive the surface the better the sorption will be for negatively charged ions, such as fluoride. Adsorption capacity is strongly pH-dependent as pH modifies the charges on edge

positions in phyllosilicates and also those of variably charged minerals such as gibbsite, haematite and goethite. Charges are generally positive under acid conditions and negative in an alkaline environment. The specific pH range for positive and negative surface charge will depend on the pKa values of the conjugate acids of the metal hydroxides present. With hitherto little-researched South African clays as examples, Puka has carried out and reported a major study on the relationship between the clay composition, the pre-treatment of the clay, and its fluoride adsorption characteristics (Puka, 2004).

2.2.2.1.1. Fired clays. Many researchers have studied the removal of fluoride using fired clays (Hauge et al., 1994; Bårdsen and Bjorvatn, 1995; Moges et al., 1996). Hauge's group investigated the effect of firing temperature on fluoride adsorption by pottery. The rate and capacity of F⁻ binding in the clayware varied with the firing temperature. Clay fired at approximately 600 °C was most effective. Temperatures over 700 °C caused a decline in F⁻-binding, and pottery fired at 900 °C and above seemed unable to remove F⁻ from water. Pots fired at 500 °C or less cracked in water.

2.2.2.1.2. Coated clays. Chemical pre-treatment which includes the use of dilute sodium carbonate and hydrochloric acid improves the adsorption capacity of many clays and soils (Srimurali et al., 1998). Further improvement can be achieved by chemical coating introduced by stirring the pre-treated clay with solutions containing ions such as Al³⁺ or Fe³⁺ and adjusting pH to precipitate the adsorbed cations as hydroxides. Studies on the surface coating of clays and soils have been reported by Coleman and Thomas (1964), Agarwal et al. (2003), Zhuang and Yu (2002) and Puka (2004).

Working with South African clays, Puka (2004) first removed any natural fluoride by ion exchange with hydroxide, after which the clay samples were pre-treated using sodium carbonate solution followed by dilute hydrochloric acid, and finally washed, dried and ground to <2 µM. The pre-treated clays to be amended with surface coatings were stirred with 1 M solutions of aluminium or iron(III) salts, followed by rigorous washing with deionised water. Table 3 summarises the results obtained after coating the clay minerals kaolin and bentonite with aluminium and iron(III) hydroxides. The results were compared with those obtained for the uncoated materials, showing the advantage of coating and the greater enhancement brought about by aluminium compared with iron.

The removal of fluoride from aqueous solution by using montmorillonite (treated with hydrochloric acid) was studied by Tor (2006). Influence of contact time, pH, initial fluoride concentration and adsorbent dosage on the adsorption were investigated. The results were interpreted using the well known kinetic and isothermic models. The adsorbed fluoride could be easily desorbed by washing the adsorbent with a solution having pH of 12.

2.2.2.1.3. Related low-cost materials. Srimurali et al. (1998) investigated the removal of fluoride using low-cost materials such as kaolinite, bentonite, charfines, lignite and nirmali seeds. Their results show that fluoride adsorption using nirmali seeds and lignite is low (6–8%). The removal of fluoride by kaolinite is slightly better (18.2%) while charfines and bentonite give higher fluoride removal capacity of 38 and 46% respectively. Kau et al. (1997) also

found bentonite to have a higher fluoride adsorption capacity than kaolinite. Fluoride removal using China clay was studied by Chaturvedi (Chaturvedi et al., 1988). Low fluoride concentration, high temperature and acidic pH are factors favoured the adsorption of fluoride. It was concluded that the alumina constituent of the China clay is responsible for fluoride adsorption. In 1990, Chaturvedi went on to study the defluoridation of water by adsorption on fly ash. Again low fluoride concentration, high temperature and acidic pH favoured the adsorption of fluoride (Chaturvedi et al., 1990).

2.2.2.2. Soils. Several research groups have studied the adsorption of fluoride on soils (Wang and Reardon, 2001; Bjorvatn et al., 1997; Zevenbergen et al., 1996; Chhabra et al., 1980; Omuetti and Jones, 1977). Chhabra et al. (1980) investigated the effect of varying levels of exchangeable sodium on the adsorption of fluoride onto sodic soils. At equilibrium fluoride concentration, a decrease in adsorption of fluoride with increase in the soil exchangeable sodium percentage was observed. Omuetti and Jones (1977) studied the adsorption of fluoride by Illinois soils. They reported that at low concentrations fluoride adsorption onto soils was described by both Langmuir and Freundlich isotherms. It was also suggested that fluoride adsorption on soils was due to the presence of amorphous aluminium hydroxides. Bjorvatn et al. (1997) studied the defluoridation of water using soil samples from Ethiopia. It was reported that five soil samples from highland areas around Addis Ababa reduced the fluoride content of the water from about 15 to 1 mg/L. From this study, it was concluded that the highland soil may be useful for removal of excessive fluoride from drinking water. Zevenbergen et al. (1996) studied the defluoridation of water using the Ando soil of Kenya. It was concluded that the use of Ando soils appears to be an economical and efficient method for defluoridation of drinking water.

2.2.3. Calcium

Fan et al. (2003) studied fluoride adsorption on to a number of minerals such as fluorite, calcite, quartz, iron activated quartz and compared their fluoride uptake capacities. Fan et al. (2007) took advantage of the extremely sensitive analysis available for the radioisotope ¹⁸F (10⁻¹³ mg) to look closely at the deposition of fluoride on calcite, hydroxyapatite and fluorite along with quartz and iron(III)-activated quartz from very dilute solutions (0.025–6.34 ppb). Their experimental data suggested that among the selected materials, calcite is a surface fluoride adsorbent within that low fluoride concentration range and less effective than all the other solids except untreated quartz. The fluoride did not appear to exchange with carbonate beyond an initial surface reaction. Turner et al. (2005) extended this lead to a range of fluoride concentrations in which (unlike Fan's conditions) the solubility product of calcium fluoride is readily exceeded. Results indicated that fluoride adsorption occurs immediately over the entire calcite surface with fluorite precipitating at step edges and kinks, where dissolved Ca²⁺ concentration is highest. Surface-sensitive techniques, including atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS) as well as ζ potential measurements, confirmed that although precipitation occurred so did adsorption. Calcium fluoride precipitation alone, although it has been utilised widely with calcium salts other than calcite in an effort to raise calcium activity enough to precipitate maximum fluoride (Glover and Sippel, 1962; Simonsson, 1979; Farrah et al., 1985; Saha, 1993; Phantumvanit and Legeros, 1997; Yang et al., 1999; Reardon and Wang, 2000), suffers from the difficulty in obtaining equilibrium fluoride concentrations less than 0.42 mM (8 mg/L) because of solubility constraints, and requirement for a pH above 9, which is unacceptable for the regulatory authorities (Turner et al., 2005). Badillo-Almaraz et al.

Table 3

Fluoride adsorption at pH 6 by kaolin and bentonite coated with aluminium and iron(III) oxides compared with natural samples (Puka, 2004).

Clay mineral	Coating	% Fluoride adsorbed
Kaolin	No coating	45.1
	Al oxide	72.3
	Fe oxide	61.3
Bentonite	No coating	49.6
	Al oxide	95.3
	Fe oxide	80.4

(2007) reported that the best pH range for adsorption on hydroxyapatite is 7.0–7.5, when the mineral adsorbs 19 mg fluoride per 1 g solid.

Larsen and Pearce (2002) developed a procedure for defluorinating water which could be used in the home. It made use of calcite and brushite, a mineral of formula $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$, believed to be a precursor of apatite and found in guano-rich caves. Equal charges of 300–500 mg brushite and calcite were stirred with 1 L of the fluoride-contaminated water and the suspensions boiled in an electric kettle, left to cool and the calcium salts to sediment. Solution ion concentrations were determined and sediments were examined by X-ray diffraction. In distilled water initially containing 5, 10 and 20 mg/L fluoride the concentration was reduced to 0.06, 0.4 and 5.9 mg/L, respectively. Using a local tap water which contained 2.6 mmol/L (104 mg/L) calcium the final concentrations were 1.2, 2.5 and 7.7 mg/L, respectively. The runs without calcite gave results similar to those with calcite.

2.2.4. Carbon

The three best-known allotropes of carbon are diamond, graphite and fullerene. Diamond is not relevant to adsorption of fluoride, but graphite and fullerene can be good adsorbents when suitably treated and amended.

2.2.4.1. *Graphite.* Abe et al. (2004) have reported the fluoride uptake capacity of various carbon based adsorbents in the order bone char > coal charcoal > wood charcoal > carbon black > petroleum coke. Bhargava and Killedar (1992) studied the fluoride adsorption on fishbone charcoal through a moving media adsorber. Daifullah et al. (2007) studied fluoride adsorption on activated rice straw which produced a low density and highly porous activated product. The activated rice straw carbon was treated with the strong oxidants nitric acid, hydrogen peroxide and potassium permanganate. The adsorption capacity was greatly increased relative to similarly activated carbon which had not been treated with oxidants. This effect was more marked if activation had been carried out at 750° than for carbons activated at lower temperatures. The effect of permanganate was greatest, followed by that of nitric acid. Hydrogen peroxide had some effect but much less than the other oxidants.

Recently Gupta et al. (2007) applied waste carbon slurries from fuel-oil energy generators for defluorination down to levels within the WHO guideline of <1.5 mg/L. Solid from the slurry was activated by heating in air at 450 °C, and washed with sodium hydroxide solution to remove ash and then with fluoride-free water. The product was dried at 100 °C. The resulting material contained 92.0% carbon, 0.45% aluminium and 0.6% iron. Both adsorption of fluoride and regeneration by removing fluoride were sharply pH-dependent with optimum pH 7.6. The rate-controlling step was diffusion into the pores of the adsorbent. Adsorption capacity of this material was reported to be much less than that of bentonite clay, bleaching earth and zeolite but it had the advantage for its availability as a waste material.

2.2.4.2. *Alumina-impregnated graphitic carbon.* Ramos et al. studied adsorption of fluoride from an aqueous solution on plain and alumina-impregnated activated carbons, prepared by stirring with an aluminium nitrate solution at a fixed pH, followed by calcination under nitrogen at temperatures ≥ 300 °C (Ramos et al., 1999). The adsorption of fluoride on impregnated carbon was shown to be dependent upon both the pH of the impregnating solution and the temperature of calcination. Impregnated carbon was shown to have a fluoride adsorption capacity of 3 to 5 times that of plain activated carbon. With the increase in calcination temperature from 300 to 1000 °C, uptake of fluoride decreased.

2.2.4.3. *Carbon nanotubes.* Exploring the application of carbon nanotubes to adsorbing fluoride, a team led by Yan-Hui Li (Li et al., 2003a) prepared aligned carbon nanotubes (ACNT), by the decomposition of xylene, catalysed by ferrocene. The authors found this material to adsorb 4.5 mg/g fluoride from 15 mg/L fluoride at pH 7, and the adsorption capacity to increase with increasing acidity owing to the increasing positive charge on the surface. The adsorption isotherms generated under identical conditions for activated carbon, $\gamma\text{-Al}_2\text{O}_3$, a typical soil and carbon nanotubes showed that the order of adsorption was: carbon nanotubes > soil > $\gamma\text{-Al}_2\text{O}_3$ > activated carbon.

2.2.4.4. *Alumina-impregnated carbon nanotubes.* Li's group also investigated adsorption of fluoride on alumina supported on carbon nanotubes (Li et al., 2001, 2003b). The nanotubes were prepared by pyrolysis of a propylene-hydrogen mixture with Ni particles as the catalyst. The recovered and washed product was ball-milled and then stirred with a calculated quantity of aluminium nitrate solution. Heating at 500 °C under nitrogen for two hours yielded a sponge-like alumina supported on carbon nanotubes, which was ground and sieved to appropriate particle size. Constant charges of adsorbent (0.2 g per 100L solution) were shaken for 12 hours with sodium fluoride solutions after pH was adjusted with small amounts of sodium hydroxide or nitric acid. The effect of pH on adsorption isotherms was determined. The adsorption capacity of the Al_2O_3 /carbon nanotubes was found to be 13.5 times higher than that of AIC-300 carbon, four times higher than that of $\gamma\text{-Al}_2\text{O}_3$ and also higher than that of IRA-410 polymeric resin

2.2.5. Zeolites

During several years' study of zeolites for removing arsenate and fluoride as well as other contaminants from water, Onyango et al. (2004) prepared charge-reversed zeolite in which Na^+ was replaced by ion exchange with trivalent ions. They started with a commercial sodium ion-loaded zeolite (pore size 0.9 nm, silica/alumina ratio 1.23) similar to that used in removing Ca^{2+} and Mg^{2+} by ion exchange. This was immersed in solutions of Al^{3+} or La^{3+} to attach the trivalent ions at the zeolite surface. By measuring pH at point of zero charge (pH_{PZC}), at $\text{pH} < \text{pH}_{\text{PZC}}$ and at $\text{pH} > \text{pH}_{\text{PZC}}$ they were able to show that the Na^+ -loaded zeolite carried a negative surface charge over all pH values, but the zeolites loaded with the trivalent ions showed a different behaviour. In the case of Al^{3+} -modified zeolite the pH_{PZC} was 8.15 with positively charged Z-AlOH_2^+ at the surface balanced by negative centres due to O atoms and to hydroxylated aluminium ions. When Al-exchanged zeolite was suspended in water and the amount of solid increased from zero to 10% the pH decreased from 5.7 to 5.2–5.32, demonstrating that the surface was positive. On the other hand, when the unmodified zeolite was treated in the same way the pH increased from 5.7 to 8.1–8.2, and with the La^{3+} -loaded zeolite on the pH increased to 7.6, showing that the surface was negatively charged and accepted H^+ from the solution. Careful analysis of adsorption of fluoride using different isotherms based on different assumptions led the authors to conclude that adsorption on Al^{3+} -exchanged zeolite was by ion exchange whereas that on La^{3+} -exchanged zeolite was by electrostatic attraction.

Subsequently the authors focused on Al^{3+} -loaded low-silica zeolites as adsorbents for fluorides (Onyango et al., 2005, 2006), and were able to show that charge-reversed zeolites were able to defluorinate water to below WHO's maximum allowable concentration (MAC) of 1.5 mg/L. Aluminium-pre-treated zeolites were prepared from commercial synthetic zeolites F-9 (Na^+ form; Si/Al ratio 1:1.23; pore size: 0.9 nm), A4 (Na^+ form; Si/Al ratio 1:1; pore size: 0.38 nm), Na-enriched HSZ 300HUD (Na^+ form) and HSZ

300HUD (H^+ form), Si/Al ratio: 1:2.75–3.25). All the prepared samples showed maximum fluoride adsorption in the pH range of 4–8. Samatya et al. (2007) have compared high-silica zeolite charge-reversed by Al^{3+} , La^{3+} and ZrO^{2+} . Clinoptilolite-type natural zeolite (pore < 45 μm , Si/Al ratio 1: 0.175) was pre-conditioned with nitric acid solution before loading with Al^{3+} , La^{3+} , or ZrO^{2+} .

2.2.6. Synthetic resins

Chikuma and Nishimura (1990) studied the fluoride removals by a chloride-loaded anion exchanger, Amberlite IRA-400. The chloride ions held on the surface of this resin were exchanged for fluoride ions in aqueous solution. However Ku et al. (2002) have noted that anion-exchange resins are more vulnerable to interference than cation-exchange resins. Lopez et al. (1992) had made similar observations, finding that on Amberlite IRA-410 anionic resin the order of selectivity was sulphate > chloride > bicarbonate > hydroxide > fluoride.

Seeking data from which to predict optimum conditions for a column-based defluoridation process, Ku et al. also studied fluoride adsorption on Amberlite IR-120 resin which had been amended by adsorption of aluminium(III) (Ku et al., 2002). The optimum pH for adsorption of fluoride was 7, with satisfactory defluoridation taking place in solutions on the acid side of 7 but dropping off sharply as pH was increased above this.

Luo and Inoue (2004) compared the fluoride-adsorbing capacities of M^{3+} -loaded Amberlite-type cation-exchange resin Amb200CT bearing a range of trivalent cations. The adsorption capacity of fluoride ion for different metal(III)-loaded Amb200 resin was in the order $La(III) \geq Ce(III) > Y(III) > Fe(III) \sim Al(III)$ (in contrast to the order found on low-silica zeolite by Onyango's group). At pH 4–7 this resin, amended with lanthanum(III), was able to reduce fluoride concentration below WHO's recommended upper limit of 1.5 mg/L.

2.2.7. Layered double hydroxides (LDHs)

Application of layered double hydroxides for defluoridation of water is attracting increasing attention as LDHs are prepared in aqueous medium from low-cost precursors and can be easily regenerated (Mandal and Mayadevi, 2008a; Pavan et al., 2000; Das et al., 2003). Lv and Duan's group made a systematic study of the influence of calcining and of adsorption conditions on the removal of fluoride from water (Lv, 2006; Lv et al., 2006a,b). Calcination temperatures chosen for batches of CLDH of Mg/Al ratio 2.0 were 200 °C, 400 °C, 500 °C, 600 °C and 800 °C. The adsorption capacity was a maximum after calcination at 500 °C, and above that temperature surface area and fluoride adsorption capacity rapidly decreased. The conditions for these experiments were 6 h exposure at a maintained pH of 6, this pH being found to be optimum. With Mg/Al ratios of 3.0 and 4.0 the adsorption capacity was less than for the ratio of 2, which can be ascribed to the charge on the metal hydroxide layer decreasing with increasing proportion of Mg^{2+} . At optimum conditions, maintained pH 6, Mg/Al ratio 2, calcination temperature 500 °C, 1.8 g/L adsorbent at a dose of 2.1 g/L extracted 80 mg fluoride per 1 g solid from 100 mg/L fluoride over 6 h at 30 °C. Of special significance in the defluoridation of drinking water, in further experiments they reduced fluoride concentration from 50 mg/L to 1 mg/L and from 20 mg/L to 0.4 mg/L. The results of X-ray diffraction, FT-IR and TG-MS demonstrated that the adsorption phenomenon is accompanied by rehydration with concomitant uptake of fluoride ions to rebuild the initial layered structure.

Although acid assists the adsorption process by protonating and removing carbonate, once the pH reaches 5 or lower the acid starts to dissolve the metal hydroxide layers and adsorption capacity decreases (Lv et al., 2007). It also significantly protonates fluoride ion, lowering its chemical potential. However, efficient defluoridation of a well water containing 5 mg/L fluoride, at an initial pH of

5 and no pH adjustments during the adsorption process, has been reported by Diaz-Nava et al. With the final fluoride concentration falling to 0.15 mg/L after 1 h. in the presence of 10 g/L calcined (500 °C) hydrotalcite (Diaz-Nava et al., 2003). This adsorptive capacity in solutions with an initial pH of 5, well below the optimum pH 6 but without pH maintenance during adsorption, can be attributed to release of OH^- during the reconstitution of the layered double hydroxide.

Das et al. (2003) studied the physicochemical characterization and adsorption behaviour of calcined Zn/Al hydrotalcite-like compound towards removal of fluoride from aqueous solution. The adsorbent was characterized by XRD and FTIR and fluoride adsorption behaviour was studied by varying experimental parameters including time, pH, temperature, adsorbent and adsorbate concentrations. It was found that a pH of 4–6 was optimum for fluoride removal from aqueous solutions. The adsorbent could be regenerated by dilute alkali solution.

To eliminate the energy requirement of calcinations, Mandal and Mayadevi (2008a) studied adsorption by as-prepared Zn–Al LDH in comparison with the calcined product. Adsorbents with Zn/Al 0 (pure $Zn(OH)_2$), 3.47, 0.97, 0.34, 0.17 and (pure $Al(OH)_3$) were tested without calcination. The uptake capacities were in the order $Zn/Al = 0.97 > 0.34 > 0.17 > 3.47$ and below these were $Al(OH)_3 > Zn(OH)_2$. The most effective of these, Zn/Al = 0.97, was calcined at a range of temperatures to compare the capacity. When compared with the 80 mg/g archived by Lv et al. (2006a), these results show that the capacity is much lower, and the effect of calcination is relatively small. This can be seen as a difference between magnesium and zinc as the divalent metal component. A further difference is the preference for a M^{2+}/M^{3+} ratio of less than 1 for Zn as against 2 for Mg, but as Mandal and Mayadevi did not include a ratio of 2 in their study this comparison remains tentative. As researchers in this field have commented (Lv et al., 2007; Mandal and Mayadevi, 2008a), much research remains to be done into the optimisation of LDH adsorption of fluoride under field conditions.

In a recent development, Mandal and Mayadevi have investigated the possibilities of cellulose-supported uncalcined layered double hydroxides (CSLDHs) for defluoridation (Mandal and Mayadevi, 2008b). Three samples of cellulose-supported Zn–Al (Zn/Al = 1) LDHs were synthesised by varying the LDH loading on cellulose. The fluoride adsorption properties of CSLDHs were found to be superior to those of reported adsorbents, including activated alumina and carbon nanotubes. Defluoridation capacity of the CSLDHs was 2–4 times higher than that of unsupported LDH.

3. Conclusion

A brief review on fluoride removal for drinking water has been presented. The fluoride removal methods have been broadly divided in two sections dealing with membrane and adsorption techniques. Reverse osmosis, nanofiltration, dialysis and electro-dialysis have been discussed under membrane techniques. Adsorption which is a conventional technique deals with adsorbents such as: alumina/aluminium based materials, clays and soils, calcium based minerals, synthetic compounds and carbon based materials. Studies on fluoride removal from aqueous solutions using various reversed zeolites, modified zeolites and ion-exchange resins based on cross-linked polystyrene and layered double hydroxides are also reviewed. Research and development efforts made in the field of fluoride remediation have been reviewed.

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