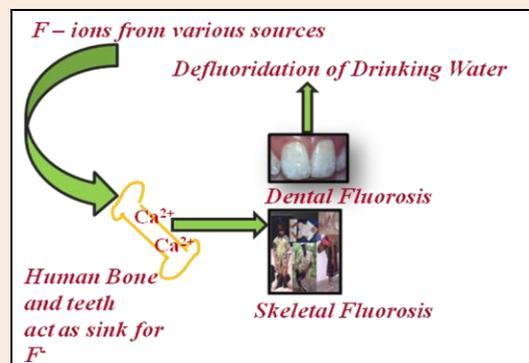


## Review Article

## A Critical Review on the State-of-Art of Water Pollution by Heavy Metals and Fluoride Ions and Defluoridation Techniques

Jaya Bajpai<sup>1</sup>, A. K. Bajpai<sup>1</sup>, Amita Chhatri<sup>2</sup>, Smarika Lawrance<sup>2\*</sup> and Anjali Dsouza<sup>2</sup><sup>1</sup>Department of Chemistry, Government Model Science College, Jabalpur, Madhya Pradesh, India<sup>2</sup>Department of Chemistry and Biochemistry, St. Aloysius College, Jabalpur, Madhya Pradesh, India**Abstract**

In countries like India, the severe contamination of drinking water with excess fluoride has acquired the dimensions of a socio-economic rather than a public health problem triggering interest in defluoridation research. Fluoride has shown affinity for positively charged calcium in teeth and bones due to its strong electro-negativity, which results in dental, skeletal, and non-skeletal forms of fluorosis, in children as well as adults. Various methods of defluoridation are currently in use viz. nanofiltration, reverse osmosis, dialysis and electrodialysis, coagulation, adsorption etc. Among these methods, adsorption technique is economical, efficient and produces high-purity water. The efficiency of this technique mainly depends on nature of the adsorbents as well as experimental conditions. The present article reviews the current scenario of water pollution caused by fluoride and other toxic metal ions and available remediation technologies.



**Keywords:** Fluoride, defluoridation, adsorption, fluorosis

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**Introduction****Water Pollution**

Environmental pollution is the unfavorable alteration of our surroundings. It is the introduction of contaminants into the environment that causes harm or discomfort to humans or other living organisms thus damaging the environment. Pollution can be from chemical substances or energies such as noise, heat or light. Pollutants can be naturally occurring substances or energies but are considered contaminants when in excess of natural levels [1].

Among various types of pollutions the water pollution may be defined as any change in physical, chemical or biological properties of water [2]. Water is essential for life on earth. Ninety-seven percent of the water on the earth is salt water. Two percent of the water on earth is glacier ice at the north and south poles and only less than one percent of all the water on earth is fresh water that is actually available for drinking, agriculture, domestic and industrial consumption. Moreover, the rest is locked up in oceans as salt water, polar ice caps, glaciers and underground reservoirs. Rapid industrialization and population growth have increased water demands but the supply is limited. This available limited quantity of water is also polluted by variety of pollutants. The major sources of water contamination (**Figure 1**) are domestic, industrial and agricultural, as well as solid waste pollution, thermal pollution, shipping water pollution and radioactive wastes [3].

The crisis of water shortage is still one of the most important global challenges of the twenty first century. In quantitative term, although 75 percent of the earth surface is covered by water, fresh water has the share of only 3 percent of this amount, from which only one percent is available for different human uses Based on the reports of

World Health Organization (WHO), nearly 85 percent out of 1.5 billion population of the world has no access to healthy and uncontaminated water and live in small communities who need safe drinking water [4]. The ever-growing population, unplanned urbanization, rapid industrialization and unskilled utilization of natural water resources have led to the destruction of water quality in many parts of the world. In many developing countries, groundwater provides drinking water for more than one-half of the nation's population, and is the sole source of drinking water for many rural communities and some large cities. However, due to industrial, agricultural and domestic activities, a variety of chemicals can pass through the soil and potentially contaminate natural water resources and reservoirs. In recent years, various toxic chemicals/compounds have been widely detected at dangerous levels in drinking water in many parts of the world posing a variety of serious health risks to human beings. Keeping the view of serious health problems to human beings due to elevated concentration of toxic pollutants, there is an urgent need for developing cost effective and environmentally friendly processes to remove them from drinking water and to safeguard the health of affected citizens [5].



**Figure 1** Diagrammatic representation of major sources of water contamination

## Types of Pollutants

### Metal ions

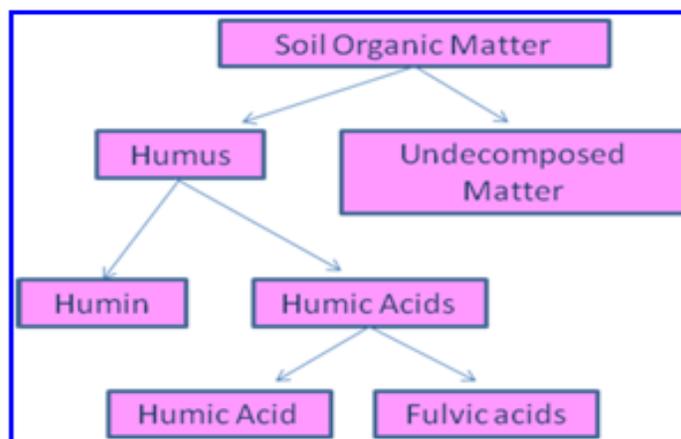
Heavy metals are a general collective term usually applied to the elements such as Hg, Pb, Cr, Cu, Ni, Cd and Co. These metals are major pollutants in ground water, industrial effluents, marine water and even treated waste waters [6]. Environmental contamination by heavy metals is a widespread problem, with sources of pollution arising from industrial activities. The toxicity due to these metals are of significant importance as they are non-biodegradable and once released into the environment, they can only be diluted or transformed, but not destroyed [7]. They pose a serious risk to the environment and endanger public health and the environment as well. Therefore, they must be removed from water and wastewaters before discharge [8]. Heavy metals have often been detected in industrial wastewaters, which mainly originate from metal plating, mining activities, smelting, battery manufacturing, tanneries, petroleum refining, paint manufacturing, pesticides, pigment manufacturing, printing and photographic industries, etc [9]. Inorganic anions are one of the important classes of aquatic pollutants and have been found in potentially harmful concentrations in numerous drinking water sources. The removal of these pollutants from drinking water supplies is an emerging issue [10] although removal of inorganic anions such as fluoride [11, 12], nitrate [13-15], phosphate [16,17], bromide [18] and iodide [19] has been studied extensively.

## Organic Pollutants

In many industries, waste water streams may contain organic compounds which are necessary to be removed before they are discharged or recycled. Usually high and even low concentrations of these compounds may be dangerous for environment. Most of these organic compounds under conditions of high pressure and temperature will be dissolved in the water; thus traditional treatment methods like gas stripping, solvent extraction and activated carbon adsorption may not be efficient or even economical [20]. The removal of organic contaminants from aquatic systems is crucial. Even when not toxic they often produce aesthetically undesirable problems such as colour, odour and taste. Most of these organic compounds are toxic and pose a threat to human health, even at very low levels. To date the removal of organic pollutants to microgram per litre ( $\mu\text{L}^{-1}$ ) and nanogram per litre ( $\text{ng L}^{-1}$ ) levels remains a challenge to scientists, local governments and industries [21].

## Natural Organic Matter (NOM)

Natural organic matter (NOM) is defined as a complex matrix of organic materials present in all natural waters. As a result of the interactions between the hydrological cycle and the biosphere and geosphere, the water sources used for drinking water purposes generally contain NOM. Thus the amount, character and properties of NOM differ considerably in waters of different origins and depend on the biogeochemical cycles of the surrounding environments [22]. The range of organic components of NOM may vary also on the same location seasonally, due to for example rainfall event, snowmelt runoff, floods or droughts. Floods and droughts are the main impacts of climate change on water availability and quality. It has been suggested that these changes may be the reason for an increase in the total amount of NOM, which has been noted to occur on several areas around the world during the past 20 years [23]. The mixture of organic compounds of NOM are divided into hydrophilic and hydrophobic fractions [24,25]. The hydrophilic fractions of NOM are composed mostly of aliphatic carbon and nitrogenous compounds, such as carboxylic acids, carbohydrates and proteins. Hydrophobic NOM primarily consists of humic and fulvic acids (humic substances) (**Figure 2**) and is rich in aromatic carbon, phenolic structures and conjugated double bonds [26].



**Figure 2** Flow chart depicting the decomposition of NOM

NOM significantly affects many aspects of water treatment, including the performance of the unit processes, application of water treatment chemicals and biological stability of water. As a result, NOM acts upon potable water quality by contributing to annoying colour, taste and odour problems, and as a carrier of metals and hydrophobic organic chemicals. In addition, NOM is responsible for the majority of the coagulant and disinfectant use in water treatment. It has a tendency to interfere with removal of other contaminants, it is responsible for fouling of membranes and it contributes to corrosion and acts as a substrate for bacterial growth in the distribution system [27]. NOM has been noted to be the major contributor to the disinfection by-product (DBP) formation.

## Disinfection By Products (DBP)

DBPs have become a focus of attention in water treatment, since they have been reported to have adverse health effects [28]. More than 600 compounds of DBPs have been identified, among which trihalomethanes (THMs) and haloacetic acids (HAAs) are the most common [29]. The hydrophobic and high molar mass (HMM) fraction of NOM is considered to be the more important source of DBP precursors than the hydrophilic fraction and low molar mass (LMM) compounds. However, also hydrophilic compounds are found to contribute to the formation of DBPs, especially in low humic waters, and in addition, bromine and iodine are noticed to be highly reactive with hydrophilic NOM [30]. Thus, optimization of water treatment should be done in order to remove both hydrophobic and hydrophilic organic compounds that can mitigate the formation of DBPs.

## Pollution due to Ions:

### Cationic Pollution

#### Chromium

Water pollution by chromium is of considerable concern, as this metal has found widespread use in electroplating, leather tanning, metal finishing, nuclear power plants, textile industries, and chromate preparation. Chromium exists in two oxidation states as Cr(III) and Cr(VI). The hexavalent form is 500 times more toxic than the trivalent. It is toxic to microorganisms, plants, animals and humans. Human toxicity includes lung cancer, as well as kidney, liver, and gastric damage [31]. International Agency for Research on Cancer has determined that Cr(VI) is carcinogenic to humans [32]. Chromium can be released to the environment through a large number of industrial operations, including metal finishing industry, iron and steel industries and inorganic chemicals production. Extensive use of chromium results in large quantities of chromium containing effluents which need an exigent treatment. The permissible limit of chromium for drinking water is 0.1 mg/L (as total chromium) in EPA standard (United States Environmental Protection Agency). In addition, World Health Organization standard for Cr(VI) concentration in drinking water is 0.05 mg/L [33].

#### Nickel

Nickel is a versatile metal and has several applications including its use in the metallurgic industry for the production of iron-based alloys, however, its use in the electroplating industry and as a material for the production of paints and batteries is of prime interest [34]. The extensive use of nickel in several activities reveals that considerable amount of nickel can find its way to the aquatic environment or to biological wastewater treatment plants [35]. For example, significant amounts of nickel have been detected in groundwater contaminated by leachate from landfills where batteries were discharged. Biological wastewater treatment methods only partially remove nickel from the final effluents, thus hindering reuse of wastewater and posing a serious threat to human health and the environment. The chronic exposure of humans to high nickel concentrations may cause cancer of lungs, nose and bone [36] and consequently, there is a need to remove this toxic metal from wastewater effluents. The US EPA (US Environmental Protection Agency) has set specific nickel limits for wastewater effluent which are 2 mg/l for short-term effluent reuse and 0.2 mg/l for long-term effluent reuse [37].

#### Lead

Lead contamination of drinking water occurs as a result of corrosion and leaching from Pb/Sn soldered joints associated with the copper service lines commonly used in household plumbing [38]. A large number of industries such as battery manufacturing, petroleum, paint, ceramics, electric cable insulation, pesticides and plastics uses lead in various operations. The industrial wastewater contains varying quantities of lead and contaminates the water. Some lead is also present in the runoff waters originating from various sources. The runoff in the lead mining areas is very high in lead concentration. Current drinking water standard for lead as per are USEPA, WHO and BIS (Beauro of

Indian Standard IS: 10500-1983) are 0.05 mg/l, 0.1 mg/l and 0.05 mg/l respectively; but a level of 0.02 mg/l has been proposed and is under review.[39]

### Arsenic

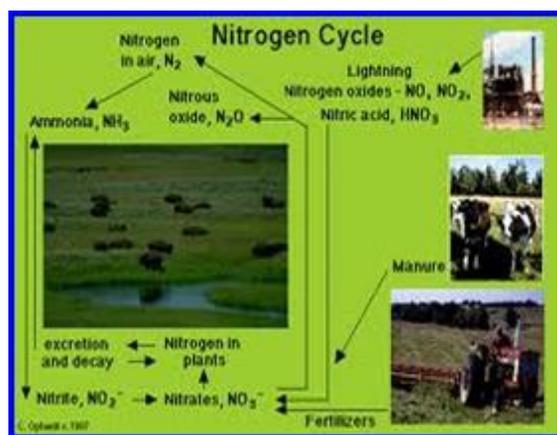
Arsenic is the 20th most abundant element in the earth's crust and, thus, widely distributed in the environment (especially as arsenopyrite or as metal arsenate). It is introduced into water through natural and anthropogenic sources [40, 41], dissolution of mineral ores, industrial effluents and agricultural activities, and also atmospheric deposition [42]. The most common species present in water are the inorganic species As (V), predominant in well-oxygenated waters, and As (III), predominant in groundwater [43]. In the reduced state, As (III), is much more toxic, more soluble, and more mobile than the oxidized As (V) [44]. The presence of arsenic in drinking water, even at low concentrations, is a threat to human health [45].

### Anionic Pollution

#### Nitrate

An elevated concentration of nitrate in groundwater is a serious and increasing problem which is mainly due to run off or seepage of chemical fertilizers from the agricultural fields. Other possible sources of nitrate (**Figure 3**) in groundwater include biological fixation, geological deposits, waste dumps, animal feed lots and defective systems [46]. The guidelines for drinking water prescribed by the WHO for nitrate is 50 mg dm<sup>-3</sup> [47].

Increased nitrate concentrations in public water supplies presents a potential health hazard due to reduction to nitrite in the gastrointestinal human tract. Nitrite causes methemoglobinemia (cyanosis or 'blue baby syndrome') and both nitrate and nitrite have the potential to form carcinogenic N-nitroso compounds [48]. Pregnant women also have greater susceptibility to the toxic effects of nitrates due to lower levels of metHb reductase. Other factors affecting susceptibility to methaemoglobinaemia may include lower levels of gastric acid and thus higher levels of gastric bacteria which enhance the reduction of nitrates to nitrites. There is also some concern around nitrates and gastric cancer, congenital malformations and cardiovascular problems in humans, but there has been no definitive confirmation related to any of these issues [49].



**Figure 3** Sources of nitrate

### Bromide and Iodide

The presence of bromide anions in water resources generates bromate anions during water treatment with oxidizing agents. Bromate anions are highly toxic for humans and, according to the World Health Organization (WHO), 25 µg/L is the maximum concentration permitted in drinking water. The presence of iodide anions in drinking water generates iodomethanes (I-THMs), which have a low taste and odor threshold [50].

## Phosphate

Phosphorus is the 11th most abundant element on the surface of the earth and is most commonly found as phosphate. Many phosphorus compounds cause serious health problems. On the other hand, it plays an important role in biochemical processes and it is a key factor in the eutrophication of surface water [51, 52]. Phosphorus exists in a wide variety of physicochemical parameter forms in natural waters, and they are highly mobile within aquatic ecosystems [53]. Efficient receptors of phosphate anions may afford new methods for their detection, separation, quantification, or transportation. However, most receptors devised for phosphate anions are organic molecules that work only in non-aqueous media via hydrogen bonding interaction [54].

## Chromate and Dichromate

Chromate and dichromate anions are important pollutants because of their high toxicity [55, 56] and presence in soils and waters [57]. Hexavalent chromium (Cr (VI)) compounds are known human carcinogens and have been shown to cause different types of DNA damages, with chromates and dichromates being both mutagenic and genotoxic. Chromate and dichromate ( $\text{CrO}_4^{2-}$  and  $\text{Cr}_2\text{O}_7^{2-}$ ) are dianions with oxide functionalities at their periphery. Nevertheless, since the periphery of the anions has oxide moieties, these are potential sites for hydrogen. The maximum permissible levels of Cr (VI) in potable and industrial wastewaters are 0.05 and 0.25 mg/L, respectively [58]. Due to its high solubility, Cr (VI) is very toxic to living organisms compared to Cr(III) [59].

## Fluoride

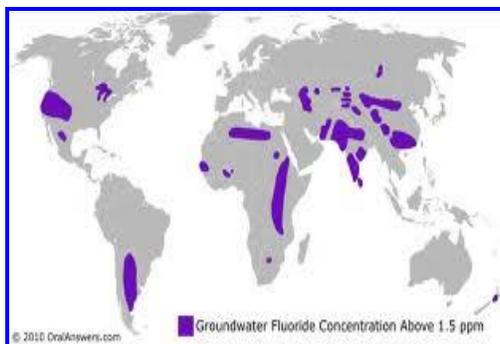
Fluorine, the 13th most abundant element of the earth's crust, represents about 0.3g / kg of earth's crust. It occurs mainly in the form of chemical compounds such as sodium fluoride or hydrogen fluoride, which are present in minerals fluorospar, fluorapatite, topaz and cryolite (**Table 1**). In India, fluorite and topaz are widespread and contain a high percentage of fluoride. Fluoride pollution in the environment occurs through two channels, namely natural and anthropogenic sources [60]. Minerals containing fluoride are given in the Table 1.

**Table 1** Fluoride bearing minerals

Mineral	Chemical Name	Chemical formula	% Fluorine
Sellaite		$\text{MgF}_2$	61 %
Villianmite		$\text{NaF}$	55 %
Fluorite (Fluorspar)		$\text{CaF}_2$	49 %
Cryolite		$\text{Na}_3\text{AlF}_6$	45 %
Bastnaesite		$(\text{Ce,Lu}) (\text{CO}_3)\text{F}$	9 %
Fluorapatite		$\text{Ca}_3(\text{PO}_4)_3\text{F}$	3-4 %

## Toxic Effects of Fluoride

The presence of fluoride in drinking water has dual significance. At lower concentrations, it guards our teeth against cavities [61] but at higher concentrations imparts 'fluorosis' in varying proportions [62, 63]. Of late, excess fluoride in drinking water is reported from more than 35 countries around the globe with India and China, as seen in **Figure 4**, being the worst affected [64].



**Figure 4** Fluoride affected areas in the world depicted with blue

In countries like India, the severe contamination of drinking water with excess fluoride, acquired the dimensions of a socio-economic rather than a public health problem triggering defluoridation research. The World Health Organisation has specified the tolerance limit of fluoride content of drinking water as 1.5 mg/L [65]. Fluoride is attracted by positively charged calcium in teeth and bones due to its strong electro-negativity, which results in dental, skeletal, and non-skeletal forms of fluorosis, in children as well as adults. Fluoride normally enters the environment and human body through water, food, industrial exposure, drugs, cosmetics, etc., however, drinking water is the single major source of daily intake [66].

## Health Impacts of Fluoride

### Dental fluorosis

Due to excessive fluoride intake, enamel loses its lustre. In its mild form, dental fluorosis as seen in **Figure 5** is characterized by white, opaque areas on the tooth surface and in severe form, it is manifested as yellowish brown to black stains and severe pitting of the teeth. This discoloration may be in the form of spots or horizontal streaks [67]. The degree of dental fluorosis depends on the amount of fluoride exposure up to the age of 8–10, as fluoride stains only the developing teeth while they are being formed in the jawbones and are still under the gums. The effect of dental fluorosis may not be apparent if the teeth are already fully grown prior to the fluoride over exposure. Therefore, the fact that an adult shows no signs of dental fluorosis does not necessarily mean that his or her fluoride intake is within the safety limit.



**Figure 5** Dental fluorosis

## Skeletal fluorosis

Skeletal fluorosis (**Figure 6**) affects children as well as adults. It does not easily manifest until the disease attains an advanced stage. Fluoride mainly gets deposited in the joints of neck, knee, pelvic and shoulder bones and makes it difficult to move or walk. The symptoms of skeletal fluorosis are similar to spondylitis or arthritis. Early symptoms include sporadic pain, back stiffness, burning like sensation, pricking and tingling in the limbs, muscle weakness, chronic fatigue, abnormal calcium deposits in bones and ligament. The advanced stage is osteoporosis in long bones and bony outgrowths may occur. Vertebrae may fuse together and eventually the victim may be crippled. It may even lead to a rare bone cancer, osteosarcoma and finally spine, major joints, muscles and nervous system get damaged.

## Other problems

This aspect of fluorosis is often overlooked because of the notion prevailing that fluoride only affects bones and teeth [68]. Besides affecting the dental and skeletal system, various other adverse health effects namely muscle fibre degeneration, low haemoglobin level, deformities in RBCs, excessive thirst, gastrointestinal discomfort, etc., are also observed due to excess fluoride intake. The problem of excess fluoride in drinking water is prevailing in 25 nations across the world and it is estimated that more than 200 million people are bound to consume fluoride contaminated water [69]. Excess fluoride concentration in water affects plants and animals also. Fluoride ion inhibits plant metabolism leading to necrosis, needle scratch and tip burn diseases. In animals, it interferes with carbohydrates, lipids, proteins, vitamins, enzymes and mineral metabolism at higher dosage. [70].



**Figure 6** People affected with skeletal fluorosis

## Techniques of Defluoridation

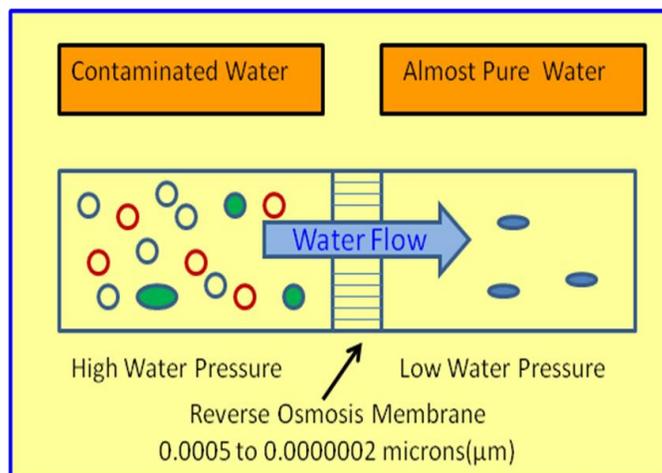
### Membrane Process

#### Reverse Osmosis

There are two types of membranes that can remove fluoride ions from water: Nanofiltration (NF) and Reverse Osmosis (RO). RO membrane process has emerged as a preferred alternative to provide safe drinking water without posing the problems associated with other conventional methods. RO is a physical process in which the contaminants are removed by applying pressure on the feed water to direct it through a semi-permeable membrane. The process is the reverse of natural osmosis as a result of the applied pressure to the concentrated side of the membrane, which overcomes the natural osmotic pressure. The process is represented diagrammatically in **Figure 7**.

RO membrane rejects ions based on size and electrical charge. The factors influencing the membrane selection are cost, recovery, rejection, raw water characteristics and pretreatment. Efficiency of the process is governed by different factors such as raw water characteristics, pressure, temperature and regular monitoring and maintenance, etc.

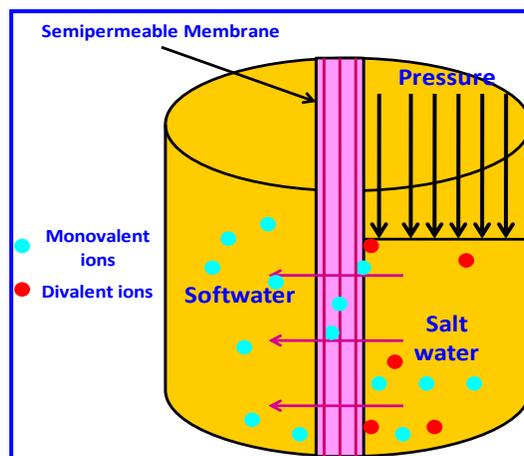
The progressive technical improvements in design and materials of the membranes have made the water treatment process economically competitive and highly reliable. Also, the capital and operational costs of RO plant go on decreasing with increasing plant capacity Reverse osmosis produces water of extremely high purity [71-74].



**Figure 7** Diagrammatic representation of reverse osmosis technology

### Nanofiltration

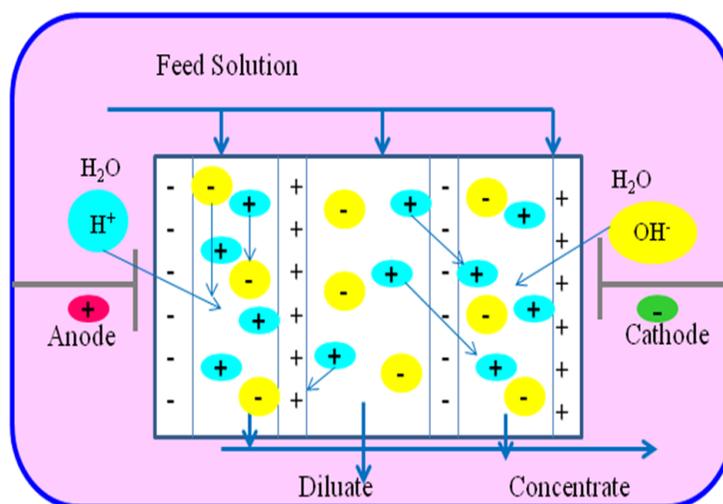
Nanofiltration makes use of the same overall phenomenon as reverse osmosis. For nanofiltration, the membranes have slightly larger pores than those used for reverse osmosis and offer less resistance to passage both of solvent and of solutes (**Figure 8**). As a consequence, pressures required are much 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 [75-83]



**Figure 8** Diagram showing nanofiltration technology

Retention of solutes is attributed mainly to steric and charge effects [84] 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.

## Dialysis and Electrodialysis



**Figure 9** Diagrammatic representation of electrodialysis

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 or an applied electric field (**Figure 9**). Electro-dialysis is the removal of ionic components from aqueous solutions through ion exchange membranes under the driving force of an electric field [85-88].

## Coagulation–precipitation

Lime and alum are the most commonly used coagulants. Addition of lime leads to precipitation of fluoride as insoluble calcium fluoride and raises the pH value of water upto 11–12.



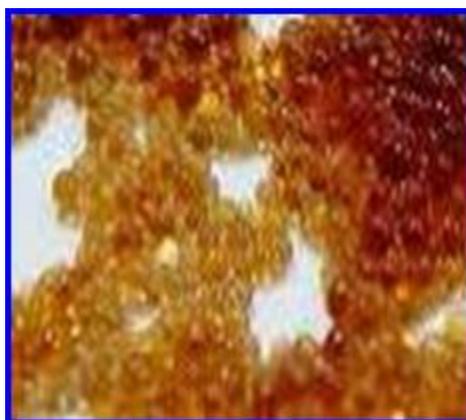
As lime leaves a residue of 8.0 mg F<sup>-</sup>/L, it is used only in conjunction with alum treatment to ensure the proper fluoride removal [89-91]. As a first step, precipitation occurs by lime dosing which is followed by a second step in which alum is added to cause coagulation. When alum is added to water, essentially two reactions occur. In the first reaction, alum reacts with some of the alkalinity to produce insoluble aluminium hydroxide [Al(OH)<sub>3</sub>]. In the second reaction, alum reacts with fluoride ions present in the water. The best fluoride removal is accomplished at pH range of 5.5–7.5 [92].

## Nalgonda Technique

The Nalgonda technique of defluoridation is based on combined use of alum and lime in a two-step process and has been claimed as the most effective technique for fluoride removal [93,94]. 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 aluminium fluoride complex ion, and therefore this technology is erroneous. Also, as the soluble aluminium fluoride complex is itself toxic, adoption of Nalgonda technique for defluoridation of water is not desirable [95]. The residual aluminium in excess of 0.2 mg/L in treated water causes dangerous dementia disease as well as pathophysiological, neurobehavioural, structural and biochemical changes. It also affects musculoskeletal, respiratory, cardiovascular, endocrine and reproductive systems [96].

## Ion Exchange Resin

It is reported that fluoride removal by means of ion-exchange( **Figure 10**) technology using anion-exchange resins is difficult, since the order of selectivity for anionic species by anion-exchange resins is as follows: citrate >  $\text{SO}_4^{2-}$ ,  $\text{C}_2\text{O}_4 > \text{I}^- > \text{NO}_3^- > \text{CrO}_4^{2-} > \text{Br}^- > \text{SCN}^- > \text{Cl}^- > \text{formate} > \text{acetate} > \text{F}^-$ . Consequently the cation/chelating type resins were equally employed for sorption of fluoride. Research work on fluoride removal has been carried out using metal-loaded cation exchangers including inorganic cation exchangers such as silica gel and alumina where high-valence metals such as iron (III), lanthanum (III), cerium (IV), and zirconium (IV) have been loaded as metals [97-98].



**Figure 10** Ion exchange resin

## Adsorption

Among the methods, adsorption technique is economical, efficient and produces high-quality water. The efficiency of this technique mainly depends on nature of the adsorbents [99]. The other important factors influencing adsorption process and capacity of the adsorbent includes pH, interference from other counter-ions in the medium, initial adsorbate concentrations and temperature. The pH of the system derives significance as it controls the electrostatic interactions within the system, thereby affecting the adsorption capacity and removal rate [100]. Theoretically, the adsorption of fluoride on to solid particles normally takes three essential steps [101].

- (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 [102]. Several adsorbent materials have been tried in the past to find out an efficient and economical defluoridating agent. The most commonly used adsorbents are activated alumina and activated carbon [103]. Several natural, synthetic low cost adsorbents have also been tried in the past [104-109].

## Conclusion

Presence of excessive fluoride is the cause of fluorosis and other related disorders in human beings, animals and plants. The World Health Organization has specified the tolerance limit of fluoride content of drinking water as 1.5 mg/L. Fluoride contamination in ground water is a world-wide issue, and some cost effective and efficient technologies are required to eliminate excess fluoride in water. The occurrence of high fluoride concentrations in ground- water and risk of fluorosis by human consumption of fluoride rich water is a problem faced by many Asian countries, notably India, Sri Lanka, and China. Conventionally various defluoridation techniques are used viz reverse osmosis, nanofiltration, dialysis etc. but adsorption technique is economical, efficient and produces high-quality water. Thus we can conclude that the need of the hour is to develop techniques based on adsorption and promote the use of natural, easily available and biodegradable adsorbents

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