Eco. Env. & Cons. 28 (February Suppl. Issue) : 2022; pp. (S251-S257)

ISSN 0971–765X

DOI No.: http://doi.org/10.53550/EEC.2022.v28i02s.041

A Review of techniques to eliminate fluoride from water

Amit Punia[1], M.S. Narwal[2] and A.K. Berwal[3]

[1]Centre of Excellence for Energy and Environmental Studies,
[2]Mechanical Engineering Department, D.C.R.U.S.T., Murthal, Sonepat, Haryana, India
[3]Centre of Excellence for Energy and Environmental Studies,
D.C.R.U.S.T., Murthal, Sonepat, Haryana, India

(Received 6 June, 2021; Accepted 27 July, 2021)

ABSTRACT

This study illustrates the fluoride elimination from drinking water that can be accomplished by various processes, for example, Ultrafiltration, Electro-dialysis, Coagulation/Precipitation, Phytoremediation, Electro-dialysis, Ion-exchange, and Reverse Osmosis processes, ion exchange process, adsorption techniques and so on. Among these process, membrane and ion exchange processes are most expensive. Nalgonda procedure and adsorption techniques are extremely followed worldwide. Nalgonda practice is one of the well known strategies normally utilized for defluoridation of water in some countries such as Tanzania, India and Kenya. Among various processes utilized for the removal of fluoride, the adsorption technique had been frequently used for the elimination of fluoride. The adsorption technique is low cost and offers acceptable results. The adsorption process is broadly used because of its, straight forwardness. It is evident from the literature study that various techniques have signified novel caliber for the elimination of fluoride. The Cost effective and optimum techniques should be adopted among the available processes to control the water contamination.

Key words: *Phytoremediation, Fluoride elimination, Ultrafiltration adsorption, Novel caliber.*

Introduction

Definition of water was given by Dr. S. W. Taylor, a famous bacteriologist and an ex-Director, Metropolitan Water Board, London, the U.K. in the examination of water supply as follows: "Water which is collected from an appropriately protected source and exposed to an adequate system of purification, free from visible suspended matter, color, odor, and taste, devoid of an objectionable bacteria indicative of the presence of disease-producing organisms and contain no dissolved matter of mineral or organic origin which in quality would render it dangerous to health and will not dissolve substances harmful to wellbeing" (Sharma, 2014).

Groundwater plays an significant role as an indispensable and fundamental component of the environment and our life support system. From about 2.5 % freshwater, only 20 % is available as groundwater, which is vital. The presence of certain properties which is not possessed by the surface water makes it of high importance (Goel, 2006).

Groundwater is commonly an inexhaustible source. However, the natural supply of groundwater in hard rock is restricted in existence. Moreover, the quality of accessible freshwater resources is in

([1]Research Scholar, [2]Prof., [3]Prof. & Chairman) danger. Management of groundwater is the most important issue as it is stretching out the least negative impact on the environment while exploiting it for the maximum economic benefits. Groundwater equilibrium is decreasing gradually around the world. Fundamentally three issues overwhelm over groundwater utilizes, as decrease due to over drafting, water-logging because of lacking seepage framework due to industrial, agricultural, and other man-made activities. Practically, water quality relies on the physical condition and the source of water movement. As the water travels; through the hydrological cycle different synthetic, natural and physical cycles change its unique quality or through the response with soil, rocks and organic matter. Natural and man-made activities alter groundwater quality directly or indirectly (USEPA 1990).

Methods for Defluorodation of Water

The various fluoride removal techniques include Ultrafiltration, Electro-dialysis, Coagulation /precipitation, Phytoremediation, electro-dialysis, ion-ex-

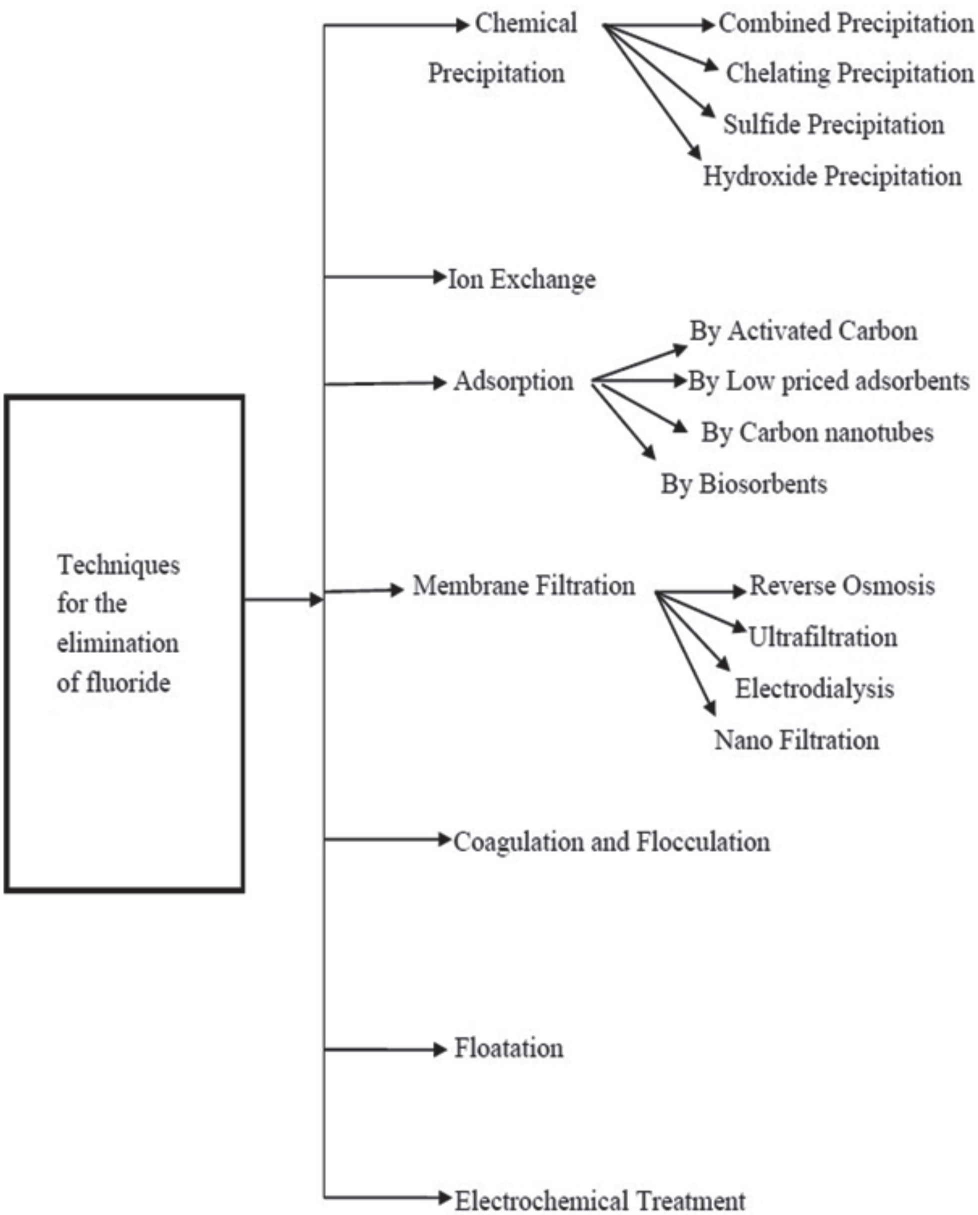

Fig. 1. Techniques for the elimination of fluoride from impure water

change, and reverse osmosis processes shown in figure (Dysart, 2008; Maheshwari, 2006; Fawell *et al.*, 2006). Various conventional methods for the elimination of fluoride from water are summarized as follows:

1. Ultrafiltration (UF)

It is fundamentally a pressure-driven membrane activity that utilizes permeable membranes for heavy metals and fluoride removal. It is a significant purification method for water which is utilized for high-purity water generation. It is a separation process utilizing membranes of pore sizes (0.1 to 0.001 micron). This process eliminates heavy metals, colloidal substances, natural and inorganic polymeric particles. In this process, water and lighter substances permeate from the membrane but heavy particles, macromolecules, and colloids are held. The electrical charge and surface area of the particles may influence the filtration efficiency. Ultrafiltration is very useful process for industrial purposes. Ultrafiltration is broadly used for sea water desalination, defluoridation of groundwater and wastewater treatment.

2. Electro-dialysis

The ionic substances (heavy metals or fluoride) are isolated by semi-permeable membranes which are ion-selective and transfer the cations and anions towards respective electrodes under the influence of an electrical potential. The formation of metal/fluoride hydroxides is the disadvantage of this method which clogs the membrane. The major limitations are the constant power supply and high energy requirements. Annouar *et al.* (2004) compared the process of electro-dialysis with adsorption of fluoride using natural chitosan as an adsorbent and found that both practices were useful to remove fluoride from contaminated water and bring the fluoride level within permissible limits. In rural area, electrodialysis is unfit because this process needs electricity. Adhikary et al. performed the experiments for the treatment of brackish water having fluoride concentration above 10 ppm and TDS upto 5000 ppm. After process, they found that, TDS and fluoride level reaches of 600 ppm and 1.5 ppm, these values are acceptable for drinking purposes which are suggested by BIS standard. This process an energy necessity of < 1 KWh/Kg of salt removes from the brackish water (Adhikary *et al.* 1989).

Kabay *et al.* investigated the elimination of fluoride from impure water by electrodialysis under various operating variables like feed flow rate, applied voltage and effects of fluoride concentration. It was found that the performance was not affected by change in feed flow rate. Ergun *et al*. (2008) performed the experiments for elimination of fluoride from using electrodialysis process. The amount of fluoride present in water sample was 20 mg/l. They found that this process decrease the amount of fluoride content in drinking water it to 0.81 mg/l fit for drinking reason (Ergun *et al.,* 2008).

The merits and demerits of the electro-dialysis are given below:

Merits

1. The electro-dialysis is low-priced process.
2. This method requires low amount of chemicals.
3. Water recovery rate of electro-dialysis process is high.

Demerits

1. The electro-dialysis is low-priced process only separate Ionic elements.
2. Electricity is required for electro-dialysis process.

3. Ion exchange

Metal/fluoride ions are exchanged in this process with ions in dilute solutions held by electrostatic forces. This process is used to separate and purify metals. In this cycle, contaminated water has continually experienced a bed of ion-exchange rosin in an up-flow or down-flow direction till the resin is depleted, e.g., all active sites have been occupied by pollutants. Fluoride can be taken out using unequivocally basic anion-exchange rosin, e.g., chloride-fluoride resin. The resin's fluoride ions were replaced by chloride ions. This cycle continues till all sites of the resin are filled. The backwashing of resin was done by water supersaturated with dissolved salt of sodium chloride. Fluoride ions are replaced by new chloride particles. The main driving force is the strong electro-negativity of the fluoride ions for the replacement of chloride ions (Meenakshi and Viswanathan, 2007).

Ho *et al.* applied titanium oxohydroxide for the elimination of fluoride in ion exchange process. They found that the prepared titanium oxohydroxide material have smallest particle size, high uniformity and high fluoride removal capacity. The cost of this process is very high and membrane fouling arises is the another problem (Ho, *et al*., 2004).

The merits and demerits of the ion-exchange are given below:

Merits

1. The fluoride removal capacity of ion-exchange is 90-95%.
2. Retains the superiority of water.

Demerits

1. The ion-exchange practice is extremely expensive.
2. The high price of rosin.

Reverse osmosis (RO)

Reverse osmosis is a process where heavy metals or fluoride ions are isolated by applying pressure more than osmotic pressure on a semi-permeable membrane by the solids dissolved in wastewater. It is used for the desalination of seawater and brackish water. RO is a membrane method to eliminate molecules and ions from solutions. RO can be used to eliminate effectively all inorganic pollutants from water. Many researchers have worked in the past on RO technology to remove fluoride from the source water (Schneiter and Middlebrooks, 1983; Sehn, 2008). Uses of RO measures incorporate the treatment of wastewater from textile, paper and pulp industries, electroplating, food preparing industries and municipal wastewater (Slater *et al*., 1983; Cartwright, 1985). The demerit of this technique is its high cost. Lots of water gets wasted as brine in this method.

In the late 80's, Reverse osmosis process was broadly used in industries for fluoride elimination and wastewater treatment purposes. Reverse osmosis technique can be removed greater than 90% of fluoride from the initial fluoride range (Ndiaye *et al.*, 2005).

Diawara *et al.* applied the low pressure reverse osmosis technique for the elimination of salinity and fluoride from ground water. They observed that the low pressure reverse osmosis technique remove 94 to 99% fluoride from ground water (Diawara *et al.*, 2011).

Gedam *et al*. (2012) used Polyamide RO membrane for the elimination of fluoride from ground water of Chandrapur district. They observed that Polyamide RO membrane process 90 to 98% of fluoride was eliminate from ground water (Gedam *et al.*, 2012).

The merits and demerits of the Reverse osmosis are given below:

Merits

1. The method purifies the water in one stage.
2. This process eliminates the other unuseful substances.
3. Reverse osmosis process is least operational cost.
4. This technique can eliminate fluoride more than 90%.

Demerits

1. This technique is high cost.
2. Not fit for rural areas.

6. Coagulation/precipitation

Alum and lime are utilized as coagulants. The lime is added to metal/fluoride polluted water in the first step which prompts fluoride precipitates as insoluble CaF_2 or metal as CaM_2 (M is any heavy metal) and pH of the treated water becomes 11-12. Presently, alum is included and insoluble $Al(OH)_2$ is delivered. In this process, lime, alum, and bleaching powder are added to the water contaminated with fluoride, then followed by fast blending. It leads to co-precipitation of fluoride and the formation of insoluble aluminum hydroxide flocs, the residue at the base. This process is also applicable to heavy metal elimination from wastewater (Nawlakhe, 1974). Nalgonda method is one of the famous strategies generally used for fluoride removal from water in certain nations like India, Senegal, Kenya, and Tanzania. Nalgonda technique developed by NEERI is coagulation – precipitation process includes an expansion of lime and bleaching powder took after by quick mixing, flocculation and sedimentation. Nalgonda practice is mostly used for defluoridation at community level (Padmashri, 2001).

The merits and demerits of the Coagulation/precipitation are given below:

Merits

1. It is commonly utilized method.
2. Technique is easy in operation.

Demerits

1. This process release large amount of Sludge.

2. This process required large amount of chemical dosages.
3. This process required expert and educated talented labor.

7. Phytoremediation

It is the utilization of specific plants to purify the polluted water, soil, and sediment. It utilizes living green plants for pollutant removal from polluted water, air, soil, and sediments. Specially selected or designed plants are utilized in this process. Plants are given doses of a metal solution and their roots and stems accumulate metal ions in them and purify the water. But this is a time taking process for remediation of pollutants and regeneration of plants for further use (Kushwaha *et al*., 2015).

However, the above methods are used for fluoride and metal removal but there are various limitations. These methods are expensive, technically complicated and there is also a release of toxic material and improper heavy metal removal (Abdel *et al.,* 2003). Adsorption overcomes the disadvantages of conventional methods. In search of innovative and cheap methods for the elimination of contaminants from wastewater showed that adsorption is considered as the most cost-effective method. Adsorption can be used to remove the fluoride and in this study, the adsorption procedure has been used for fluoride elimination.

8. Adsorption

Adsorption process is one of the superior processes for the Fluoride elimination from contaminated water. Adsorption practice has been broadly used in industrial processes for purification and separation purposes. Adsorption is a process where gas or fluid collects on the solid surface (adsorbent), forming an atomic film on the adsorbate. Adsorption is practicable over other conventional methods as this is currently considered to be very suitable for removing or minimizing pollutants from wastewater. Among all methods, adsorption can be considered to be applicable for the treatment of wastewater due to its simple operation and low cost (Yadanaparthi *et al.,* 2009; Kwon *et al.,* 2010) high efficiency, no generation of sludge, less energy requirement, recovery of the adsorbent (Kratochvil and Volesky, 1998).

Types of adsorption

Adsorption practice divided in two parts:

1. Physical Adsorption: It is due to weak van der Waals forces of attraction b/w the solid and the adsorbed substance. Physical adsorption occurs when the intermolecular attractive forces are greater between the molecules of adsorbent and adsorbate than those between the molecules of the adsorbate itself. This process may be reversible.

2. Chemical Adsorption: It is due to the chemical attraction between the solid and the adsorbed surface. It is also called activated adsorption. This process is always irreversible. It is significantly used in catalysis. It can be an exothermic or endothermic process. It involves large activation energy which is the elementary step in chemisorption (Activated adsorption).

Mechanism of the adsorption process

An ion in solution would see not a natural particle but a surface studded with both positive and negative sites. Under the proper circumstances, some of these solution ions will adhere to the surface and be considered "adsorbed". It is inconceivable that such a process could populate the surface of the crystal with more than a unimolecular layer of the adsorbate. In point of fact, less than a unimolecular layer is adsorbed on the surface because the adsorption mechanism is selective and withdraws only positive or negative ions from the solution. Once ions are adsorbed on the surface, the crystal carries an excess of either positive or negative charges and the surface attracts ions of opposite charge to maintain a sphere of electrical neutrality.

Adsorption occurs in three basic steps.

1. Transfer of adsorbate molecule from the bulk solution to the outer surface of the adsorbent. The concentration gradient acts as the main force.
2. Intraparticle diffusion of the adsorbate which depends upon the size of the pore.
3. Reaction of the adsorbate molecules with the adsorbent, involving the bond formation in case of chemisorption. Reaction kinetics predicts the rate of the adsorption practices (Leyva *et al.* 1997).

Various attempts are made to use waste materials in the form of adsorbents, particularly waste-derived siliceous materials, plant waste, agricultural waste, and industrial by-products. These can be found in abundant amounts and used as an adsorbent. An adsorbent is said to be "low-cost" if it is present in abundant quantity, need less processing, or could be waste material or a byproduct from another process.

Natural and low-cost adsorbents

Smittakorn *et al.* (2010) used bone charcoal for the scrapping of fluoride. The commercially available boiled bone was burnt in a simple household furnace. The batch practices were employed to study the competence of the absorbent to compare Thai and Indian bone char. Both adsorption isotherms, Freundlich, and Langmuir isotherms were fitted well. Results demonstrated that 80% of the fluoride was eliminated in both cases.

Errico *et al.* (2010) examined the accessibility of low-priced sorbents for the elimination of fluoride effectively from polluted water. The barks of *Azadirachtaindica* and *Acacia nilotica* were utilized for the adsorption of fluoride. The highest percentage of fluoride elimination was obtained at pH 6, contact time of 60 minutes with 5 mg/l fluoride solution.

Harikumar *et al.* (2012) used Vetiveriazizanioides, an herbal plant of Kerala for removal of fluoride. The adsorbent modified with phosphoric acid showed high adsorption than the raw plant. The batch study was conducted under different parameters like impact of pH and impact of adsorbent dose. Highest adsorption was obtained at pH 6.0. The elimination percentage of fluoride increased with increasing time and sorbent dose at a given initial fluoride range. The characterization of adsorbents was done by SEM and XRD used for elimination of fluoride. Kinetic and isotherms were plotted to observe the suitability of models on the adsorption data.

Kumar *et al.* (2017) evaluated the elimination efficiency of fluoride by rice husk, and sawdust in batch procedure. The adsorption capability of fluoride was obtained by optimizing different parameters, viz. impact of pH, dose, impact of contact time, and impact of initial fluoride range. It was observed that powdered rice husk is a better adsorbent in defluoridation technique. The fluoride removal efficiency observed for powdered rice husk was in the range of 85-90% within 7 hour at all optimized parameters. The study was also carried at pH 7 and observed no difference in the adsorption of fluoride at pH 4 and pH 7. The study revealed that the adsorbent can be utilized for the elimination of fluoride.

Tefera *et al.* (2020) investigated the adsorption efficiency of activated carbon made from avocado seeds (ACAS) for the scrapping of fluoride from groundwater as well as an aqueous solution. The batch study was carried out by optimizing various parameters. The adsorption equilibrium was attained within 1 hour under the pH 6. The maximum adsorption efficiency was found to be 86%. The pseudo 2nd order was well suitable to the adsorption data with $R^2 = 0.99$. The result showed the applicability of activated carbon for the elimination of fluoride from domestic purposes.

Conclusion

In this paper, we have reviewed various techniques to remove fluoride from ground water. It was found the conventional methods are not efficient to completely remove fluoride from ground water and these conventional methods are higher in cost. Further it was found that adsorption process is effective, eco friendly and low cost for the elimination of fluoride. So the authors advise the peoples where fluoride related problems exist they use adsorption process. It was found that various researchers used many type of low cost adsorbents for the removal of fluoride. In generally, waste material was used by researchers for the elimination of fluoride.

References

Abdel-Halim, S. H., Shehata, A. M. A. and El-Shahat, M. F. 2003. Removal of lead ions from industrial waste water by different types of natural materials. *Water Research*. 37(7): 1678-1683.

Adhikary, S.K., Tipnis, U.K., Harkare, W.P. and Govindan, K.P. 1989. Defluoridation during desalination of brackish water by electrodialysis. *Desalination.* 71(3): 301-312.

Annouar, S., Mountadar, M., Soufiane, A., Elmidaoui, A. and Sahli, M.M. 2004. Defluoridation of underground water by adsorption on the chitosan and by electrodialysis. *Desalination.* 165 : 437.

Cartwright, P. 1985. Membranes separations technology for industrial effluent treatment-a review. *Desalination*. 56: 17-35.

Diawara, C. K., Diop, S. N., Diallo, M. A. and Farcy, M. A. 2011. Determination performance of nanofiltration (NF) and low pressure reverse osmosis (LPRM) membranes in the removal of fluorine and salinity from brakish drinking water. *Journal of Water Resource and Protection*. 3 : 912-917.

Dysart, A. 2008. Investigation of defluoridation options for rural and remote communities. *CRC for Water Quality and Treatment*.

Ergun, E., Tor, A., Cengeloglu, Y. and Kocak, I. 2008. Electrodialytic removal of fluoride from water: Effects of process parameters and accompanying anions. *Sepa-*

ration and Purification Technology. 64(2) : 147-153.

Fawell, J., Bailey, K., Chilton, J., Dahi, E. and Magara, Y. 2006. *Fluoride in Drinking-eater*. IWA publishing.

Gedam, V. V., Patil, J. L., Kagne, S., Sirsam, R. S. and Labhasetwar, P. 2012. Performance evaluation of polyamide reverse osmosis membrane for removal of contaminants in ground water collected from Chandrapur district. *Journal of Membrane Science & Technology.* 2(3): 1–5.

Goel, P. K. 2006. *Water Pollution: Causes, Effects and Control.* New Age International.

Ho, L.N., Ishihaa, T., Ueshima, S., Nishiguchi, H. and Takita, Y. 2004. Removal of fluoride from water through ion exchange by mesoporous Ti-oxohydroxide. *Journal of Colloid and Interface Science.* 272 : 399-403.

Kabay, N., Arar, O., Samatya, S., Yuksel, U. and Yuksel, M. 2008. Separation of fluoride from aqueous solution by electrodialysis: Effect of process parameters and other ionic species. *Journal of Hazardous Materials.* 153 (1-2) : 107-113.

Kratochvil, D. and Volesky, B. 1998. Advances in the biosorption of heavy metals. *Trends in Biotechnology*. 16(7): 291-300.

Kushwaha, A., Rani, R., Kumar, S. and Gautam, A. 2015. Heavy metal detoxification and tolerance mechanisms in plants: implications for phytoremediation. *Environmental Reviews*. 24(1): 39-51.

Kwon, J. S., Yun, S. T., Lee, J. H., Kim, S. O. and Jo, H. Y. 2010. Removal of divalent heavy metals (Cd, Cu, Pb, and Zn) and arsenic (III) from aqueous solutions using scoria: kinetics and equilibria of sorption. *Journal of Hazardous Materials*. 174(1-3): 307-313.

Leyva-Ramos, R., Rangel-Mendez, J. R., Mendoza-Barron, J., Fuentes-Rubio, L. and Guerrero-Coronado, R. M. 1997. Adsorption of cadmium (II) from aqueous solution onto activated carbon. *Water Science and Technology*. 35(7): 205-211.

Maheshwari, R. C. 2006. Fluoride in drinking water and its removal. *Journal of Hazardous Materials*. 137(1) : 456-463.

Meenakshi, S. and Viswanathan, N. 2007. Identification of selective ion-exchange resin for fluoride sorption. *Journal of Colloid and Interface Science.* 308(2): 438-450.

Nawlakhe, W., Kulkarni, D., Pathak, B. and Bulusu, K. 1974. *Indian Journal of Environmental Health*, *16*.

Ndiaye, P. I., Moulln, P., Dominguez, L., Millet, J. C. and Charbit, F. 2005. Removal of fluoride from electronic industrial effluent by RO membrane separation. *Desalination.* 173 : 25-32.

Padmashri, J.P. 2001. Effectiveness of Low Cost Domestic Defluoridation. *International Workshop on Fluoridation Water Strategies, Management and Investigation.* Bhopal, pp. 27–35.

Schneiter, R.W. and Middlebrooks, E.J. 1983. Arsenic and fluoride removal from groundwater by reverse osmosis. *Environment International.* 9(4): 289-291.

Sehn, P. 2008. Fluoride removal with extra low energy reverse osmosis membranes: three years of large scale field experience in Finland. *Desalination.* 223 1-3: 73-84.

Sharma, B. K. 2014. *Environmental chemistry*. Krishna Prakashan Media.

Slater, C. S., Ahlert, R. C. and Uchrin, C. G. 1983. Applications of reverse osmosis to complex industrial wastewater treatment. *Desalination*. 48(2): 171-187.

USEPA, 1990. Ground Water, Volume I: *Ground Water and contamination*. US Environmental Protection Agency. Pub.No. USEPA/625/6-90/016a.

Yadanaparthi, S. K. R., Graybill, D. and von Wandruszka, R. 2009. Adsorbents for the removal of arsenic, cadmium, and lead from contaminated waters. *Journal of Hazardous Materials*. 171(1-3): 1-15.