

# A REVIEW ON REMOVAL OF FLUORIDE IN WATER

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**Abstract-** Water is the main component for the survival of human being. The major sources of water are rivers, lakes, ponds, tanks, and surface runoffs. Three fourth surface of the Earth is covered with water. For maintaining the fragile ecosystem, the physiochemical parameters of the water bodies plays a very important role. These parameters are disturbed due to the contaminants entering into the water bodies. Among the contaminants of water, Fluoride also causes a major contamination in drinking water which is due to natural and anthropogenic activities that causes a serious threat to human as well as animal health. So there is a need for the removal of fluoride from the drinking water. Current paper deals with a study of removal methods of Fluoride from the water like coagulation and precipitation, reverse osmosis, nanofiltration, electrodialysis, ion exchange, electrocoagulation and adsorption.

**Keywords:** Fluoride, Precipitation, Ion-exchange, Adsorption, electrocoagulation

## 1. INTRODUCTION:

Water is the most important component as it forms the basic medium for origin of life [1]. The water chemical composition mainly depends on the utilization for domestic, industrial, and agricultural purposes. 0.6% of the total water resources is covered with the ground water which is the suitable for drinking in rural and urban areas in India. But in the current days ground water is getting polluted by the urbanization and industrialisation. The major pollutants are hydrocarbons, heavy metals like nickel, fluorides, nitrates etc. which are effecting the human health.

Fluoride as a pollutant present in groundwater creates a major problem in drinking water supply. It exists either as inorganic fluorides or organic fluoride compounds [2]. Depending on the concentration of the fluoride in drinking water, it is either beneficial or detrimental to the human health [2, 3]. Fluoride is advantageous for bone and teeth mineralization, maintenance of fertility, hematopoiesis, and enzymes activation, such as adenylate cyclase [4]. It is a known fact that a less amount of fluoride intake decreases the vulnerability to dental caries in human beings [5]. A few decades ago, usage of fluorinated toothpaste for prevention of dental caries was obsession, but soon it became outdated due to increasing reports of ill effects on oral health such as the occurrence of perioral dermatitis [6]. According to WHO, the maximum acceptable concentration of fluoride is 1.5 mg/l [7]. While India's permissible limit of fluoride in drinking water is 1mg/l [8].

## 2. SOURCES:

Fluorite, apatite, rock phosphate and topaz igneous and sedimentary rocks are the most common natural fluorine bearing minerals that constitutes source of fluoride in drinking water [9]. Milk is usually responsible for the exposure of fluoride in small quantity. Fluoride is consumed due to ingestion of tea which is reported in a range of 0.04 mg to 2.7 mg per person per day [10]. Occurrence of alkaline soil around the fluoride contaminated water sources is the outstanding feature of the fluoride affected areas [11]. The main sources of fluoride can be broadly divided into two categories:

- 1) Natural sources :
  - Forage grasses and grains
  - Water
  - Volcanic activities
- 2) Anthropogenic sources
  - Mineral Mixture and Other Feed Supplements
  - Airborne Fluoride
  - Industrial Effluents
  - Agrochemicals and Household Products

### 3. HEALTH EFFECTS:

Several investigators had reviewed that, during the last 5-6 years the life-long impact and accumulation of fluorides causes human skeletal and teeth damage and also the changes in DNA-structure, paralysis of volition, cancer, etc. [12]. Susheela reported the effect of fluoride contamination on human health like aches and pain in the joints, viz. neck, back, hip, shoulder and knee without visible signs of accumulation; non-ulcer dyspepsia, viz. nausea, vomiting, pain in the stomach, bloated feeling/ gas formation in the stomach, constipation followed by diarrhea, etc.[13]. Czarnowski et.al. explained that increase in fluoride intake, have an impact on the bone density, urine and hair of the human being. [14].

**Table: 1** Permissible limit of fluoride of drinking water [15]

Name of the Organization	Desirable Limits
Bureau of Indian Standards	0.6-1.2
Indian Council of Medical Research	1.0
The Committee on Public Health Engineering Manual and Code Practice, Government of India.	1.0
World Health Organization (International Standards for Drinking Water)	1.5

The fluoride intake will effect both human health as well as animals:

#### 3.1 HUMAN HEALTH:

##### 3.1.1 Dental Fluorosis:

In dental fluorosis, enamel of the teeth loses its luster due to large amount of fluoride intake during permanent dentition, and it mostly affects children. The mild form of dental fluorosis is recognised by chalky white teeth, whereas yellowish brown pigmentation in the middle of the teeth and severe pitting of the teeth. 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.

##### 3.1.2 Skeletal Fluorosis:

Skeletal fluorosis affects both children and adults. It does not manifest until the disease attains an advanced stage. In the early stages of skeletal fluorosis, patients complain of arthritic symptoms. Fluoride gets deposited in joints of shoulder bones, neck and pelvic, and knees and makes it difficult to move, walk, and bend. In later stages, skeletal fluorosis is marked by restriction of spine movements and, hence, can be easily diagnosed. The advanced stage is osteoporosis.

##### 3.1.3 Nonskeletal Fluorosis/Other Problems:

Besides skeletal and dental fluorosis, excessive consumption of fluoride may lead to muscle fiber degeneration, low hemoglobin levels, deformities in RBCs (red blood corpuscles), excessive thirst, headache, skin rashes, nervousness, neurological manifestations (it affects brain tissue similar to the pathological changes found in humans with Alzheimer's disease), depression, gastrointestinal problems, urinary tract disorders, nausea, abdominal pain, tingling sensation in fingers and toes, reduced immunity, repeated miscarriages or still births, male sterility, etc. It is also responsible for alterations in the functional mechanisms of liver, kidney, digestive system, respiratory system, excretory system.

#### 3.2 ANIMAL HEALTH:

Almost all terrestrial and aquatic animals are susceptible to high doses of fluoride, although the tolerance level varies from one species to another. For terrestrial animals, important sources of excess fluoride intake include drinking water, soil, or vegetation naturally containing excess soluble fluoride compounds or contaminated with fluoride compounds emitted by volcanic eruptions or industrial activities.

### 3.2.1 Invertebrates:

Many invertebrates are highly susceptible to fluoride toxicity. Honeybees and silkworm larvae are highly susceptible to fluoride toxicity; the silk industry in several countries has been badly affected by industrial fluoride pollution [16,17]. Aquatic invertebrates and vertebrates including fish are also susceptible to fluoride toxicity. In general, freshwater or softwater-dwelling aquatic animals have lower fluoride tolerance than marine or hardwater-dwelling animals [18].

### 3.2.2 Vertebrates:

Among terrestrial vertebrates, herbivores are more susceptible than carnivores and other animals occupying an upper position in the food pyramid. Domestic and wild herbivores are more exposed to environmental contaminants as they are nonselective eaters and can consume contaminated feed, forage, and water.

It is thus required to bring the concentration of fluoride to required level. So here are some article reviews of the various techniques available for the removal of fluoride from water.

## 4. METHODS FOR DEFLUORIDATION OF WATER

Surendra roy et.al. [19] said that the fluoride contaminated groundwater used for drinking purposes should be determined examined and accordingly a suitable method can be chosen for its treatment.

Sl.no	Removal Method	Process	Advantages	Disadvantages	Name of the Author	Medium used	Reference numbers
1	Coagulation and Precipitation	Involves the addition of chemicals and the formation of fluoride precipitates	1. Commonly used 2. It is more practical. 3. Easy to understand	1. Low treatment efficiency upto 70% 2. Requirement of large dosage of chemicals for treatment. 3. Requirement of skilled manpower	Meenakshi et.al., Lawler,D.F. et.al., Larsen,M.J. et.al., Qafas,Z.et.al., Dahi,E et.al., Aldaco et.al.	Aluminium sulfate and lime (NEERI METHOD),salts of Calcium, aluminium and iron, bone char combined with sodium dihydrogen phosphate and calcium chloride, granular calcite.	20-25
2	Reverse Osmosis	It is a physical process in which the anions are removed by applying pressure on the feed water to direct it through the semi permeable membrane.	1.Membrane can be completely recovered after every arrangement of examination. 2.This can remove 90% of fluoride regardless of initial concentration	1.Non attainable for rural regions. 2. Very expensive. 3.Skilled labor required. 4.Need pH improvement.	Ndiaye et.al. Behanu et.al Gedam et.al. Diawara et.al.	1. RO membrane of Ethiopian Rift Region, 2.Polyamide RO Membrane, 3.Low Pressure RO	26-29
3	Nano Filtration	It removes the larger dissolved solids when compared with RO.	1. High productivity. 2. No Chemicals needed. 3.used for wide range of pH.	1. Highly expensive technique. 2. Prone to fouling, scaling or membrane degradation.	Tahaikt et.al. Pontie et.al. Bejaoui et.al.	1.NF90 2.NF400.	30-32
4	Electro-dialysis	Removal of ionic components	1. Flexible 2.low chemical	1. Only separation of Ionic	Adhikary et.al. Amor et.al. Annour et.al.	used this method in the combination of chitosan with	33-39

		from aqueous solutions through ion exchange membranes under the driving force of an electric current	request. 3.High water recovery.	Components. 2. Specific power consumption for Pumping. 3.Necessity of concentrate treatment.	Sahli et.al. Kabay et.al. Ergun et.al. Lahmid et.al.	the help of CMX-ACS membranes, others used the combination of electro dialysis and anion exchanger.	
5	Ion Exchange	Fluoride can be removed from water supplies with a strongly fundamental anion-exchange resin containing quaternary ammonium functional groups.	1.Removes fluoride upto 90-95 %. 2.Retains the taste and color of water intact	1. Presence of sulfate, phosphate, bicarbonate, etc. results in ionic competition. 2. Relatively higher cost. 3. Treated water sometimes has a low pH and high levels of chlorides.	Mohan Rao et.al. Haron et.al. Castel et.al. Zhou et.al.	yttrium loaded poly(hydroxamic acid) resin,lanthanum-impregnate cross linked gelatin	40-43
6	Electro-coagulation	Technique for applying direct current to sacrificial electrodes that are submerged in an aqueous solution.	1.obliges basic equipment 2.simple to handle 3.less support cost 4.treated water is consumable, colorless and odourless	1.electrodes should be consistently supplanted 2.utilizes high electricity 3. Loss of productivity due to the formation of oxide film on the cathode.	Yang et.al. Feng Shen et.al. Drouiche et.al. Un et al. Bennajah et al.	Aluminium electrodes, Iron cylindrical reactor as anode,	44-47
6	Adsorption	Adsorption is the bond of molecules species from bulk solution for a surface of a solid by physical or chemical forces.	1. Ease of operation. 2.Adsorption procedure in worthwhile 3. High productivity for fluoride removal and can remove up to 90% fluoride. 4. Cost effective. 5. Produce high quality water. 6. Regeneration is conceivable.	1. Process is dependent on pH. 2. Regeneration is required. 3. Disposal of fluoride-laden material.	Kariyanna et.al. J.P. Barbier et.al., Muthukumaran et.al., Rongshu et.al., Y.Min et.al., Y. Wang et.al., Nava et.al., Padmavathy et.al. Theragaonkar et.al. Gandhi et.al. Mohapatra et.al. Amit Bhatnagar et.al. Prins Satish et.al.	Activated alumina, activated carbon coated with silica gel, calcite, activated saw dust, activated coconut shell powder, activated fly ash, groundnut shell, coffee husk, rice husk, magnesia, serpentine, bone charcoal, orange peel, chalk powder	48-60

## 5. CONCLUSION:

A large number of factors and geological conditions influence the correlations between different pairs of physio-chemical parameters of water samples directly or indirectly. Some parameters are directly measured by their respective measuring equipments, some are determined by titrimetric methods and some elements like fluorides are to be treated by various

methods. As there is a need for the treatment of fluoride present in water, which causes lot of problems. The method for treatment of fluoride can be chosen as per the advantages and limitations, among which adsorption is the best process for the removal of fluoride from water according to the study.

## REFERENCES:

1. Manoj Kumar, Avinash puri-'A Review of permissible limits of drinking water'- Indian Journal of Occupational and Environmental Medicine - April 2012 - Volume 16 - Issue 1.
2. Sneha Jagpat et.al. - 'Fluoride in Drinking Water and Defluoridation of water'- Chemical Reviews, 2012, 112, 2454-2466.
3. Muturu C., Onyango, M.S. et.al. - 'Fluoride removal performance of Phosphoric acid treated lime: breakthrough analysis and point-of-use system performance. Water SA, 38 (2), 279-286.
4. Kirck KL (1991) Biochemistry of the elemental halogens and inorganic halides. Plenum, New York; pp 19-68.
5. Treasure ET, Dever JG (1992) The prevalence of caries in 5 year old children living in fluorinated and non fluorinated communities in New Zealand NZ Dent J 88:9-13
6. Mellete JR, Aeling JL, Nuss DD (1983) Perioral dermatitis J Assoc Military Dermatol 9:3-8.
7. WHO (World Health Organisation), 2006, Guidelines for Drinking Water Quality: Incorporating First Addendum to Third Edition. World Health Organisation, Geneva., 375 p.
8. Misra, A.K. and Mishra, A., 2007, Study of quaternary aquifers in Ganga Plain India: Focus on groundwater salinity, fluoride and fluorosis. J. Hazardous Mater., 144, 438-448.
9. Teotia, S.P.S., Teotia, M. and Singh R.K., 1981, Hydro-geochemical aspects of endemic skeletal fluorosis in India- An epidemiologic study., Fluoride, 14 (2), 69-74.
10. Murray J.J., (Ed.) 1986, Appropriate Use of Fluorides for Human Health., World Health Organisation, Geneva.
11. Paya, P. and Datta, S.A., 2010, Fluoride contamination in groundwater of Patan District, Gujarat, India., International Journal of Engineering Studies, 2(2), 171-177.
12. Johnston, R. and Heijnen, H., 2002, Safe Water technology for arsenic removal., Report World Health Organisation.
13. Susheela, A.K., 1999, Fluorosis management programme in India., Curr. Sci., 77(10), 1250-1255.
14. Czarnowski, W., Krechniak, J., Urbanska, B., Stolarska, K., Taraszewska-Czarnowska, M. and Murasko-Klaude, A., 1999, The Impact of Waterborne Fluoride on Bone density, Fluoride, 32 (2), 91-95.
15. Payel Roy, Ritesh Kumar and Goutham Kumar Roy, Fluoride Pollution Abatement, Research gate.
16. Bourbon P (1967) Analytical problems posed by pollution by fluorine compounds J Air Pollut Control Assoc 17:661-663.
17. Weinstein LH, Davison A (2004) Fluorides in the environment: effects of plants and animals. CABI Publishing, Cambridge.
18. Camargo JA (2003) Fluoride toxicity to aquatic organism: a review Chemosphere 50: 251-264.
19. Surendra Roy, Gurucharan Dass, 2013, Fluoride Contamination in Drinking water, Resources and Environment, 3(3), 53-58.
20. Meenakshi, R.C.; Maheshwari J. Hazard. Mater. 2006, B137, 456.
21. Lawler, D.F.; Williams, D.H. Water Res. 1984, 11, 25.
22. Larsen, M.J.; Pearce, E.I.F. Caries Res. 2002, 36, 341.
23. Qafas, Z.; Kacemi, K.E.; Ennaassia, E.; Edelahi, M.C. Sci. Lett. 2002, 3, 1.
24. E. Dahi, Contact Precipitation for defluoridation of water, 22<sup>nd</sup> WEDC Conference New Delhi, India, 1996, pp. 266-268.
25. R. Aldaco, A. Garea, and A. Irabein, Modelling of particle growth: Application to water treatment in a fluidized bed reactor, Chemical Engineering Journal, 134, 2007, pp. 66-71.
26. P.I. Ndiaye, P. Moulln, L. Dominguez, J.C. Millet, and F. Charbit, Removal of Fluoride from electronic industrial effluent by RO membrane separation, Desalination 173, 2005, pp. 25-32.
27. B. Aseefa, Defluoridation of Ethiopian rift valley region water using reverse osmosis membranes, Journals of EEA, 23, 2006, pp. 1-6.
28. V.V. Gedam, J.L. Patil, S. Kagne, R.S. Sirsam and P. Labhassetwar, Performance evaluation of Polyamide reverse osmosis membrane for removal of contaminants in ground water collected from Chandrapur district, Journal of Membrane Science and Technology, 2(3), 2012, pp. 1-5.
29. C.K. Diawara, S.N. Diop, M.A. Diallo, and M.A. Farcy, Determination Performance of nanofiltration and low pressure reverse osmosis (LPRM) membranes in the removal of fluorine and salinity from brackish drinking water, Journal of Water Resource and Protection, 3, 2011, pp. 912-917.
30. M. Tahaikt, R.E. Habbani, A.A. Haddou, I. Achary, Z. Amor, M. Taky, A. Alami, A. Boughriba, M. Hafsi and A. Elmidaoui, Fluoride removal from groundwater by nanofiltration, Desalination, 212, 2007, pp. 46-53.

31. M.Pontie, H. Dach, and J. Leparc, Nanofiltration as a sustainable water defluoridation operation dedicated to large scale pilot plants for the future, 13<sup>th</sup> International World Water Resource Association (IWRA) World Water Congress, Montpellier, France, 1-4 September 2008, pp.1-6.
32. I.Bejaoui, A. Mnif, and B. Hamrouni, Performance of Reverse Osmosis and Nanofiltration in the Removal of Fluoride from Model Water and Metal packaging Industrial Effluent, *Separation Science and Technology*, 49, 2014, pp. 1135-1145.
33. S.K. Adhikary, U.K. Tipnis, W.P. Harkare, and K.P.Govindan, "Defluoridation during desalination of brakish water by electro dialysis", *Desalination*, 71(3), 1989, pp.301-312.
34. Z. Amor, S. Malki, M. Taky, B. Bariou, N.Mameri, and A. Elimidaoui, "Optimization of fluoride removal from brakish water by electro dialysis", *Desalination*, 120(3), 1988, pp. 263-271.
35. S. Annouar, M. Mountadar, A. Soufiane, A. Elmidaoui, and M. A. Menkouchi Sahil, "Defluoridation of underground water by adsorption on the chitosan and by electro dialysis", *Desalination*, 165, 2004, 437.
36. M. A. M. Sahli, S. Annouar, M. Tahaikt, M. Mountadar, A. Soufiane, and A. Elimidaoui, "Fluoride removal for underground brakish water by adsorption on the natural chitosan and by electro dialysis", *Desalination*, 212 (1-3), 2007, pp. 37-45.
37. N. Kabay, O. Arar, S. Samatya, U. Yuksel, and M. Yuksel, "Separation of fluoride from aqueous solution by electro dialysis: Effect of process parameters and other ionic species", *Journal of Hazardous Materials*, 153 (1-2), 2008, pp. 107-113.
38. E. Ergun, A. Tor, Y. Cengeloglu, and I. Kocak, "Electrodialytic removal of fluoride from water: Effects of process parameters and accompanying anions", *Separation and Purification Technology*, 64 (2), 2008, pp. 147-153.
39. S. Lahnid, M. Tahaikt, K. Elaroui, I. Idrissi, M. Hafsi, I. Laaziz, Z. Amor, F. Tiyal, and A. Elmidaoui, "Economic evaluation of fluoride removal by electro dialysis", *Desalination*, 230 (1-3), 2008, pp. 213-219.
40. Mohan Rao, N.V.R; Bhaskaran, C.S. J. *Fluorine Chem.* 1988, 41, 17.
41. Haron, M.J.; Wan Yunus, W.M.Z.; Wasay, S.A. *Int. J. Environ.* 1995, 48, 245.
42. Castel, C.; Schweizer, M.; Simonnot, M.O.; Sardin, M. *Chem. Eng. Sci.* 2000, 55, 3341.
43. Zhou, Y.; Yu, C.; Shan, Y.; *Sep. Purif. Technol.* 2005, 36, 89.
44. F. Shen, X. Chen, P. Gao, and G. Chen, "Electrochemical removal of fluoride ions from industrial wastewater", *Chemical Engineering Science*, 58, 2003, pp. 987-993.
45. D. Ghosh, C.R. Medhi, and M.K. Purkait, "Treatment of fluoride containing drinking water by electrocoagulation using monopolar and bipolar electrode connections", 73 (9), 2008, pp. 1393-1400.
46. U.T. Un, A. S. Koparal, and U. B. Ogutveren, "Electrochemical process for the treatment of drinking water", Thirteenth International Water Technology Conference, IWTC 13, Hurghada, Egypt, 2009, pp. 129-137.
47. M. Bennajah, M. Maalmi, Y. Darmane, and M.E. Touhami, "Defluoridation of drinking water by electrocoagulation/electroflotation –kinetic study", *Journal of Urban and Environmental Engineering*, 4 (1), 2010, pp. 37-45.
48. H. Kariyanna, "Geological and geochemical environment and causes of fluorosis—possible treatment—a review", in *Proceedings Seminar on Role of Earth Sciences in Environment*, Bombay, 1987, 113–122.
49. J.P. Barbier, and P. Mazounie, "Methods of reducing high fluoride content in drinking water", *Water Supply* 2, 1984, SS 8/1-4.
50. K. Muthukumaran, and N. Balasubramanian, T.V. Ramakrishna, "Removal of fluoride by chemically activated carbon", *Indian Journal of Environmental Protection*, 15 (7), 1995, pp. 514–517.
51. W. Rongshu, H. Li, P. Na, and W. Ying, "Study of a new adsorbent for fluoride removal from waters", *Water Quality Research Journal of Cananda* 30 (1), 1995, pp. 81–88.
52. Y. Min, T. Hashimoto, N. Hoshi, and H. Myoga, "Fluoride removal in a fixed bed packed with granular calcite", *Water Research*, 33 (16), 1999, pp. 3395–3402.
53. Y. Wang, and E.J. Reardon, "Activation and regeneration of a soil sorbent for defluoridation of drinking water", *Applied Geochemistry*, 16, 2001, pp. 531–539.
54. C.D. Nava, M.S. Rios, and M.T. Olguin, "Sorption of fluoride ions from aqueous solutions and well drinking water by thermally heated hydrocalcite", *Separation and Purification Technology*, 38 (1), 2003, pp. 31–147.
55. S. Padmavathy, J. Amali, R.E. Raja, N. Prabavathi, and B. Kavitha, "A study of fluoride level in potable water of Salem district and an attempt for defluoridation with lignite", *Indian Journal of Environmental Protection*, 23 (11), 2003, pp. 1244–1247.
56. V.P. Thergaonkar, and W.G. Nawalakhe, "Activated magnesita for fluoride removal", *Indian Journal of Environmental Health*, 16, 1971, pp. 241–243.
57. N. Gandhi, D. Sirisha, K.B. Chandra Shekar and Smita Asthana, Removal of fluoride from water and waste water by using low cost adsorbents, *International Journal of Chem Tech Research*, 4, 2012, pp. 1646-1653.
58. M. Mohapatra, S. Anand, B.K. Mishra, Dion E. Giles, P.Singh, 'Review of Fluoride Removal from Drinking Water, *Journal of Environmental Management*, 91 (2009) 67-77.

59. Amit Bhatnagar, Eva Kumar, Mika Sillanpaa, Fluoride removal from water by adsorption- A review, Chemical Engineering Journal, 171, 2011, pp. 811-840.
60. Prins Sathish Jain, S.B. Benaka Prasad, A.V. Raghu, A short review: Removal of Fluoride ions from ground water by using various techniques, International Journal of research- Grandhalaayah, 5, 2017, pp. 98-104.