

9. Nanotechnology: Green Option for Defluoridation of Drinking Water

Gagandeep Kour

Department of Environmental Sciences
Central University of Jammu,
RahyaSuchani, Bagla, Samba, J&K.

Richa Kothari

Department of Environmental Sciences
Central University of Jammu,
RahyaSuchani, Bagla, Samba, J&K.

Sunil Dhar

Department of Environmental Sciences
Central University of Jammu,
RahyaSuchani, Bagla, Samba, J&K.

Deepak Pathania

Department of Chemistry,
Sardar Vallabhbhai Patel Cluster University,
Mandi, Himachal Pradesh, India.

Abstract:

Among the widely occurring contaminants, fluoride is one of the anionic contaminants which is present in excess amounts in water and the sources of contamination of water body by fluoride can be anthropogenic as well as natural process of weathering and directly or indirectly posing a serious threat to the living organisms consuming the fluoride contaminated water. This assures a need of efficient technology which can help in the elimination of fluoride from the drinking water. Literature confirms, nanotechnology-based approaches are capable to develop efficient system to effectively solve water related problems owing to its high efficiency. The new and advanced nanoadsorbents can serve as novel, effective and low-cost tool for the removal of fluoride. Therefore, present study highlights some of the advanced, cost effective techniques of nanotechnology for the adsorption process, their types of nanoadsorbents. The application, advantages as well the limitations associated with the use of nanoadsorbents is also highlighted in the present study. Enhancing the benefits of nanotechnology and overcoming the limitations of nanoadsorbents will help in remediation of fluoride from water in an eco-friendly way.

Index Terms: Defluoridation, Drinking water, Fluoride, Nanoadsorbents, Nanotechnology

9.1 Introduction:

Fluorine is the 13th most abundant element present on the earth's crust constituting 0.08% of the earth's crust, is considered as one of the most reactive chemical elements and exists in the natural environment in the form fluoride having F⁻ ions [1]. Fluoride is one of the constituents in water as is considered as an essential element in optimum range for humans as well as animals for strong teeth and bone density. However, excess of fluoride can lead to deleterious health effects both to humans as well as to animals [1, 2, and 3]. The possession of negative charge makes fluoride most electro negative element and has the tendency to attract positively charged ions like calcium (Ca²⁺) present in teeth and bones of human beings [4]. Hence there is an urgent need of Defluoridation of drinking water for safe drinking. A large number of conventional methods are available for Defluoridation of water such as Chemical additive method (Nalgonda process), adsorption process, and ion exchange method, membrane separation processes [2, 5, and 6].

Several studies have been carried regarding the effectiveness of these conventional techniques and the results have positioned adsorption technique as the most reliable because of its ability to remove up to 90% of fluoride and cost effectiveness [4, 6]. The performance of the adsorption process is further improved by applying the field of nanotechnology. Researchers across the globe have developed some adsorbent materials at nanoscale dimensions which can effectively remove fluoride from water as compared to their conventional contour parts because of their unique and novel properties [7]. Therefore, the present study highlights the utilization of nanoadsorbents for the removal of fluoride from drinking water for safe drinking.

9.2 Fluoride in Water and Its Recommended Range:

Fluoride in water can be of natural as well as anthropogenic origin. Anthropogenic activities like use of phosphatic fertilizers, industrial effluents from glass, ceramic, toothpaste, electroplating industries are held responsible for increasing concentration of fluoride in water [8]. Natural sources of fluoride contamination include rock weathering, volcanism and geothermal activities [1, 2].

Rocks containing minerals such as sellaite, villianmite, cryolite, topaz, biotite, muscovite, apatite, mica, clays contribute natural sources of fluoride [9]. High fluoride concentration in groundwater is also associated with neutral to alkaline pH (7.6 to 8.9), low calcium (Ca) and high concentrations of sodium (Na) and bicarbonate (HCO₃) [2]. World health organization (WHO) suggests optimum level of fluoride must be within 0.6 to 1.5 mg/L in drinking water for human consumption [3] and must be between 0.6 to 1.2 mg/L as prescribed by Bureau of Indian Standards [10]. The maximum permissible limit can be extended to 1.5 mg/L. Fluoride concentration above or below this limit can have severe health implications [11]. Therefore, it becomes necessary to eliminate excess of fluoride form drinking water and bring it to the safe range.

9.3 Role of Nanotechnology in Fluoride Removal:

During the past couple of years, researchers have prepared nanosize materials for their use in Defluoridation of water. Among the numerous applications of nanotechnology, novel and advanced nanoadsorbents have been paid much attention for the fluoride removal.

These nanoscale adsorbents offer very high adsorption capacity, have active adsorption sites, as well as increases the chemical activity because of their larger surface area as compared to their conventional counterparts, improved mechanical strength, high surface binding energy, absence of internal diffusion resistance, and low temperature modification [12,13]. All these qualities foster the use of nanoadsorbents as potential candidates for reclamation of drinking water. A wide variety of nanoadsorbents are now available which can be employed for the Defluoridation of water.

9.4 Nanoadsorbents for Defluoridation:

The different types of nanoadsorbents employed for the fluoride removal can be summed up as follows:

9.4.1 Nanoscale Metal Oxide:

Nanoscale metals and their oxides have been used as potential adsorbents for the removal of fluoride from water. Literature confirms the use of iron oxide-hydroxide, nanoscale zero valent iron, nano magnesium oxide, nano sized γ -alumina for fluoride removal from water [14, 15, and 16] and these have shown outstanding results. Iron oxide-hydroxide nanoparticles have shown maximum adsorption capacity for fluoride for as high as 16.70 mg/g at room temperature. pH of the medium plays a significant role in the sorption of fluoride ions onto iron oxide-hydroxide nanoparticles. Fluoride removal mechanism by iron oxide-hydroxide nanoparticles follows both adsorption as well as ion-exchange process which is mainly due to physical adsorption [16]. Nano sized γ -alumina is considered as an efficient candidate for fluoride removal from water with very good adsorption capacity in the pH range of 3 to 10 [4, 17]. Fluoride removal by nano magnesium oxide is not affected by shifts in pH but is mainly influenced by OH⁻ ions [14].

9.4.2 Magnetic Nanoparticles:

A large number of magnetic nanoparticles have been used for Defluoridation of water because of possession of larger surface area, high specificity and reactivity. Super paramagnetic nanoparticles prevent particle aggregation and ensures colloidal stability [9]. Different types of magnetic nanoparticles have been synthesized and made to remove fluoride from the drinking water depending upon adsorption capacities, pH, dosage, contact time etc [18]. Several synthesized magnetic nanoparticles include Ce-Ti@Fe₃O₄, Fe₃O₄@Al(OH)₃, Fe₃O₄ magnetic nanoparticles modified with Zirconia (ZrO₂), Fe₃O₄ coated with Fe-Ti bimetallic oxide, iron oxide magnetic nanoparticles anchored on graphene oxide etc [18,19, 20]. Iron oxide magnetic nanoparticles anchored on graphene oxide exhibits super paramagnetism, good selectivity for fluoride, have high adsorption capacity and can be applied for the defluoridation process [19].

9.4.3 Carbon Nanotubes:

Carbon nanotubes (CNTs) are allotropes of carbon which are used in nanotechnology because of their valuable characteristics, capability of being functionalized by other chemicals. CNTs are basically graphene structures rolled in the form of cylinder. CNTs exists in two forms: Single walled carbon nanotubes (SWCNTs) and multi-walled nanotubes (MWCNTs).

Because of these unique properties, CNTs are considered as potential and effective candidates for fluoride removal from water. Adsorbents made of both SWCNTs and MWCNTs have been used for the defluoridation process as reported in literature [9].

9.5 Advantages:

There is a huge advantage associated with the use of the above mentioned nanoadsorbents in the removal of excess of fluoride from water. The advantage is in terms of their removal efficiencies and the dose of the nanoadsorbents as shown in Table-9.1.

Table 9.1 Nanoadsorbents with their fluoride removal efficiencies

Nanoadsorbents	Fluoride removal efficiency	References
Nanoscale zero valent (nZVI) at pH 4 and a dosage of 0.6 g/L	Increases the fluoride removal rate to 84% in 35 minutes	[15]
Nano sized γ -alumina	Very high fluoride adsorption capacity of 32 mg/g as compared to commercially available γ -alumina with an adsorption capacity of 14 mg/g	[4, 17]
Nano-MgO with a dosage of 0.6 g/L	Capable to bring maximum (90%) fluoride removal from water	[14]

9.6 Limitations Associated With Nanotechnology:

The limitations associated with the use of nanotechnology is the toxicity issues associated with it. The toxicities associated with nanoparticles is attributed to its small size, larger surface area to volume ratio.

Their smaller size makes their easy entry into the living systems where they may translocate from one site to another through bloodstream thereby affecting the vital body organs like brain, nervous system, liver, heart, kidneys, and bone marrow thereby affecting their normal functioning.

The widely recognised nanoparticles for their toxicity are carbon nanotubes, nano-metal oxides like titanium dioxide, zinc oxide, etc. The nanoparticles have been reported responsible for the production reactive oxygen species (ROS) and free radicals which may cause damage to proteins, membranes and DNA.

Defluoridation of water is required for healthy and safe drinking as the excess intake of fluoride leads to severe health implications.

For this purpose, novel nanotechnology approaches have been used particularly the use of nanoadsorbents such as carbon nanotubes, nanoscale metal oxides and magnetic nanoparticles for efficient fluoride removal and these have shown significant positive results.

However, the limitations associated with their use is the toxicity issues which need to be acknowledged and should be overcome by carrying out extensive research in this field.

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9.8 References:

1. Akuno M. H., Nocella G., Milia E. P. and Gutierrez L., "Factors influencing the relationship between fluoride in drinking water and dental fluorosis: a ten-year systematic review and meta-analysis". *J Water Health*. Vol.17, No.6, pp 845-862, 2019.
2. Madhukar M., Murthy B. S. and Udayashankara T. H., "A Review on Conventional and Alternative Methods for Defluoridation of Water". *J Water Pollut Purif Res*. Vol.1, No.2, pp 1-12, 2014.
3. World Health Organization (WHO). 2011 Guidelines for Drinking Water Quality, 4th edition. WHO, Geneva.
4. Chinnakoti P., Chunduri A. L., Vankayala R. K., Patnaik S. and Kamiseti, V., "Enhanced fluoride adsorption by nano crystalline γ -alumina: adsorption kinetics, isotherm modeling and thermodynamic studies". *Appl Water Sci*. Vol.7, No.5, pp 2413-2423, 2017.
5. Sivarajasekar N., Paramasivan T., Muthusaravanan S., Muthukumar P. and Sivamani S., "Defluoridation of water using adsorbents-a concise review". *J Environ Biotechnol Res*. Vol.6, No.1, pp186-198, 2017.
6. Waghmare S. S. and Arfin T., "Fluoride removal from water by various techniques". *Int J Innov Sci Eng Technol*. Vol.2, No.9, pp 560-571, 2015.
7. Ali I, "New generation adsorbents for water treatment". *Chem. Rev*. Vol.112, No.10, pp 5073-5091, 2012.
8. Nigussie W., Zewge F. and Chandravanshi B. S., "Removal of excess fluoride from water using waste residue from alum manufacturing process". *J Hazard Mater*. Vol.147, No.3, pp 954-963, 2007.
9. Premathilaka R. W. and Liyanagedera N. D., "Fluoride in Drinking Water and Nano technological Approaches for Eliminating Excess Fluoride". *J Nanotechnol*. Vol. 2019, 2019.
10. Indian Standard Drinking Water- Specifications, Second Revision, Bureau of Indian Standards. IS: 10500:2012
11. Virk H. S., "Fluoride Contamination of Ground Waters of Two Punjab Districts and Its Implications". *OmniScience: A Multidisciplinary J*. Vol.8, No.2, pp 25-31, 2018.
12. Anjum M., Miandad R., Waqas M., Gehany F. and Barakat, M. A., "Remediation of wastewater using various nano-materials". *Arab J Chem*. Vol.12, No.8, pp 4897-4919, 2019.
13. Mehta K., Sata P., Saraswat A. and Mehta D., "Nanomaterials in water purification", *International Journal of Advance Engineering and Research Development*, Conference of

Nanotechnology & Applications In Civil Engineering, Vol 5, Special Issue 3, February, 2018.

14. Devi R. R., Umlong I. M., Raul P. K., Das B., Banerjee S. and Singh, L., “Defluoridation of water using nano-magnesium oxide”. *J Exp Nanosci.* Vol.9, No.5, pp 512-524, 2014.
15. Jahin H. S., “Fluoride removal from water using nanoscale zero-valent iron (NZVI)”. *Int Water Technol J.* Vol.4, pp 173-182, 2014.
16. Raul P. K., Devi R. R., Umlong I. M., Banerjee S., Singh L. and Purkait M., “Removal of fluoride from water using iron oxide-hydroxide nanoparticles”. *J NanosciNanotechnol.* Vol.12, No.5, pp 3922-3930, 2012.
17. Kumar E., Bhatnagar A., Kumar U. and Sillanpää M., “Defluoridation from aqueous solutions by nano-alumina: characterization and sorption studies”. *J Hazard Mater.* Vol.186, No.2-3, pp 1042-1049, 2011.
18. Sharma M., Kalita P. and Garg A., “Magnetic nanoparticles as an effective adsorbent for removal of fluoride—a review”. *MOJ Eco Environ Sci.* Vol.3, No.3, 207-210, and 2018.
19. Liu L., Cui Z., Ma Q., Cui W. and Zhang X., “One-step synthesis of magnetic iron–aluminum oxide/graphene oxide nanoparticles as a selective adsorbent for fluoride removal from aqueous solution”. *RSC advances.* Vol.6, No.13, pp 10783-10791, 2016.
20. Markeb A. A., Alonso A., Sánchez A and Font X., “Adsorption process of fluoride from drinking water with magnetic core-shell Ce-Ti@ Fe₃O₄ and Ce-Ti oxide nanoparticles”. *Sci Total Environ.* Vol.598, pp 949-958, 2017.