

Magnetic nanoparticles as an effective adsorbent for removal of fluoride—a review

Abstract

Fluoride concentration more than 1.5mg/L in drinking water can create various health issues and can lead to various human diseases. Adsorption is considered as one of the best technique for fluoride removal. Poor adsorption capacities, long contact time, high dosage, extremely low or high pH are the major drawbacks of various adsorption processes. In recent years several surface modified magnetic nanoparticles paves the way for effective removal of fluoride from water. The review fundamentally assesses the potential use of different surface modified magnetic nanoparticles (MNPs) for the effective removal of fluoride from contaminated water. High fluoride adsorption capacity of 91.04 mg/g at pH value of normal water is seen in case of Ce-Ti@Fe₃O₄ magnetic nanoparticle whereas the adsorption capacity of Zr based MNP is as high as 158 mg/g at very low water pH. Interestingly, Fe₃O₄ encapsulated Zr (IV)-poly (acrylamide) magnetic nanomaterials exhibit very high fluoride adsorption capacity of 124.5 mg/g in normal water. Though the magnetic assistance makes the whole separation process easy in using magnetic material adsorbent, there are still challenges like reusability, toxicity regarding the material selection, environmental impact etc.

Keywords: fluoride, magnetic nanoparticles, water treatment, adsorption, defluoridation

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Introduction

The clean and affordable water is one of the basic needs of every human on this planet. The population is increasing day by day and hence the per capita water availability is decreasing. Rapid industrialization has also polluted the water. Use of chemical fertilizers to enhance the agriculture productivity in addition to using pesticides, herbicides in crop management are also among one of the major causes of water pollution. The spread of contaminants in to surface water and groundwater has become a serious issue. There are various contaminants in water polluting the water bodies such as organic, inorganic, heavy metals, microbial and radioactive species which may in different forms viz. suspended, dissolved, or dispersed materials. Fluoride is among one of the major water pollutants and responsible for various diseases. The fluoride content less than 1.5 mg/L has beneficial effect but exposure to high concentration can cause serious health hazards.¹ The permissible limit of fluoride is 1.5mg/L (WHO)² in case of potable water. Defluoridation is the only option to overcome the problem of fluoride in drinking water. There are many processes for the defluoridation such as adsorption and ion exchange, coagulation and precipitation, membrane separation processes.² Adsorption is considered as the one of the best technique for the removal of fluoride from drinking water, however it depends upon the adsorbent i.e. its adsorption capacity, contact time, dosage, change in pH value when added to water etc. Recent advancements in nanotechnology have opened the way for efficient treatment of water. There are various nanoparticle based products such as carbon nanotubes, nanoscale metal oxides, nanofibers, etc. used for water purification.³ The magnetic nanoparticles offer an advantage of surface modification for targeting a particular contaminant for adsorption as well as magnetic separation which make the whole process easy (Figure 1). The use of magnetic nanoparticles (magnetite Fe₃O₄) for separation of water

pollutants has already been established in ground water remediation, in particular for the removal of arsenic.⁴ However, the use of magnetic nanoparticles and their surface functionalized composites have not been much studied in fluoride removal. There are different methods for the synthesis of magnetic nanoparticles such as co-precipitation, hydrothermal, solvochemical, micro-emulsion, sonochemical etc. Co-precipitation method is one of the simplest techniques to obtain magnetic nanoparticles. In this method a stoichiometric ratio of Fe²⁺ and Fe³⁺ is used as an iron source, which under suitable alkaline medium gives Fe₃O₄ magnetic nanoparticles. In this method of synthesis, the size, shape, composition of the synthesized nanoparticles depends upon the salt used, the stoichiometric ratio of Fe²⁺ and Fe³⁺, temperature, type of stabilizing agent, and pH value of the reaction media.^{5,6} In this method of synthesis, the reaction temperature is generally 20–90°C.⁷ Hydrothermal method is generally used for the synthesis of single crystals of minerals in hot water under high pressure in an autoclave.⁸ It is different from the co-precipitation method because in this method in place of a stoichiometric mixture, one ferrous precursor is used. In this route of synthesis, the reaction temperature is normally 100–320°C.⁹ Solvochemical method of synthesis is similar to hydrothermal synthesis, but an organic solvent is used as a dispersion media instead of water. Using solvochemical synthesis the morphology of the particles can be controlled to a large extent. Along with the advantage of morphology control, hydrophobic particles can also be yielded.¹⁰ Micro emulsion method of synthesis can be used to prepare nanoparticles from two types of immiscible solvents in the presence of a surfactant. In this method different shapes of nanoparticles can be obtained. Micro emulsion can be used to obtain the uniform size, morphology, good disparity. Zhang et. al reported that using solvothermal analysis at pH = 8.5, a mixture of spherical particles and needle like rods can be obtained on the other hand at pH=10.5, spherical nanoparticles can be obtained.¹¹

Sonochemical method of synthesis uses the ultrasonic activation in the internal liquid to generate transient high temperature, high partial pressure also accompanied by micro-effects, such as shock waves, that can promote oxidation, reduction, decomposition and hydrolysis. In this method of synthesis, the size of the particle, shape, and magnetic behavior is dependent upon the ultrasonic frequency, sonicating duration, reaction temperature, etc.¹² Herein, various types of magnetic nanomaterials in fluoride removal are addressed and their fluoride adsorption capacities are compared.

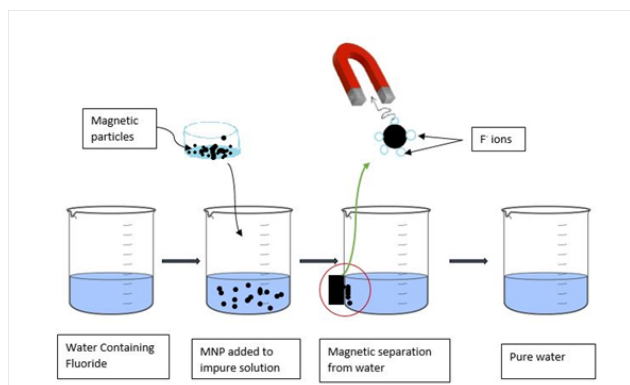
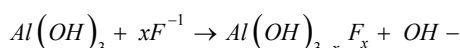


Figure 1 Schematic illustration of the defluoridation using MNPs.

Discussion

Magnetic nanoparticles for fluoride removal

Magnetic nanoparticles have large surface area; high reactivity, specificity, and self-assembly make them different from common adsorbents. A number of magnetic nanoparticles were synthesized for fluoride removal. Markeb et al.,¹³ synthesized Ce-Ti@Fe₃O₄ nanoparticles for fluoride removal. They found the maximum adsorption capacity of 91.04 mg/g at pH 7 and also showed a fast adsorption rate. They also observed that it can be used for 5 cycles without significant loss of adsorption capacity. Similarly, Zhao et al.,¹⁴ synthesized Fe₃O₄@Al(OH)₃ nanoparticles which combines the advantages of magnetic separation and aluminum oxide has a high affinity towards fluoride.



Riahi et al.,¹⁵ synthesized Fe₃O₄ magnetic nanoparticles modified with zirconia (ZrO₂) using co-precipitation method and calculated the adsorption capacity using Langmuir equation and it was found to be 158.6 mg/g at pH 2.5. Zhang et al.,¹⁶ synthesized Fe₃O₄ magnetic nanoparticles coated with Fe-Ti bimetallic oxide by co-precipitation method and found that saturation adsorption capacity of 57.22mg/g. They also found that adsorption was fast and equilibrium reached in 2 minutes. They further used this bimetallic magnetic composite nano adsorbent (Fe₃O₄@Fe-Ti) in a fluidized bed system for fluoride removal.¹⁷ Asgari et al.,¹⁸ synthesized Fe₃O₄ magnetic nanoparticles and modified the surface with 3-aminopropyltriethoxysilane and a Ga (III) porphyrin complex, Ga (TCPP) Cl₂ [TCPP: tetrakis (4-carboxyphenyl) porphyrin]. They tested the sample for fluoride adsorption and found that fluoride with an initial concentration of 10 mg/L was reduced to 0.3mg/L in contact time of 30 minutes. They also tested the reusability and they found that removal efficiency of fluoride in 5 cycles reduced from 97.2% to 87%.

Liu et al.,¹⁹ synthesized iron aluminum oxide magnetic nanoparticles anchored on graphene oxide (IAO/GO). They found that IAO/GO exhibits super paramagnetism, good selectivity for fluoride, high adsorption capacity and good acid alkali stability. They found the maximum sorption capacity from Langmuir model was 64.72mg/g. They also concluded that the IAO/GO can be applied for defluoridation of natural water environments because of its good selectivity for fluoride removal when co-anions exist, good removal efficiency, and low residual iron and aluminum concentration after defluoridation. They explained that electrostatic interactions, ion exchange and inner-sphere complexations were the main factors of adsorption mechanisms. Azari et al.,²⁰ synthesized iron-silver magnetic binary oxide nanoparticles using co-precipitation method for removal of fluoride from aqueous solution. They found the adsorption capacity of 22.88 mg/g and the maximum adsorption was observed at pH 3 and the equilibrium was reached within 20 minutes. Yang et al.,²¹ synthesized magnetic alumina aerogel for the removal of fluoride from water. In their process, magnetic alumina hydrogel adsorbent was fabricated by amending alumina aerogel with Fe₃O₄. They found the adsorption capacity of 32.1 mg/g at pH 5.0. They also tested it for fluoride removal from well water. They reported that the as prepared magnetic alumina aerogel was an effective and easily prepared adsorbent and was easily separable after adsorption.

Chang et al.,²² prepared Mg-Al layered double hydroxides magnetic composites for removal of fluoride from aqueous solution using ultrasound assisted co-precipitation method. The prepared composite showed the high adsorption capacity of fluoride i.e. is 47.7mg/g. They also showed that ultrasound irradiation assistance increases the specific surface area and reduces the size of the nanocomposite. Srivastava et al.,²³ synthesized the magnetic nickel/polypyrrole nanostructures and found that it exhibits excellent adsorption capacity for fluoride and arsenic. They found the adsorption capacity for fluoride to be 67.71mg/g. Bandpiet al.,²⁴ synthesized chitosan impregnated Fe₃O₄ nanoparticles using chemical co-precipitation method. The maximum fluoride uptake of the linear polysaccharide coated magnetic nanocomposite (Fe₃O₄-chitosan) was 9.43mg/g. They also suggested that Fe₃O₄-chitosan can be easily reused for at least five successive cycles while maintaining the high adsorption capacity. Gao et al.,²⁵ synthesized Mg-Al-layered double hydroxides (Mg-Al-LDH) nanoflake impregnated magnetic alginate beads and evaluated defluoridation performance. They showed that the Mg-Al-LDH magnetic nanocomposites have high adsorption capacity and the bio-based (alginate) sorbents offers advantages of biodegradability, hydrophilic properties etc. They also tested for fluoride removal from real groundwater samples and they reported the feasibility of fluoride removal from contaminated groundwater. Wen et al.,²⁶ synthesized three component nanomagnetite adsorbent (γ-Fe₃O₄-graphite-La) for fluoride adsorption. They found the maximum adsorption capacity of 77.12mg/g at 25°C and pH=7±0.1. Bhaumiket al.,²⁷ synthesized polypyrrole/Fe₃O₄ magnetic nanocomposites similar to the Ni/polypyrrole nanocomposite for fluoride removal and found the adsorption capacity for fluoride within the range of 17.63–22.31 mg/g at pH 6.5. They reported that the magnetic adsorbent retained the original adsorption capacity after one complete adsorption-desorption cycle and was reusable in fluoride removal from water. Kumari et al.,²⁸ worked over the development of a cost-effective, portable, environment and user-friendly defluoridation technique. They developed the Fe₃O₄ nanoparticles impregnated on to the polyurethane foam (Fe₃O₄@PUF) and made into tea infusion bags.

They obtained the defluoridation capacity of $\text{Fe}_3\text{O}_4@\text{PUF}$ to be 34.48mg/g for fluoride.

Poursaberi et al.,²⁹ synthesized 3-aminopropyltriethoxysilane (APTES) coated magnetic nanoparticles functionalized with a zirconium (IV) porphyrin complex, Zr (TCPP) Cl_2 [TCPP: tetrakis (4-carboxyphenyl) porphyrin]. They found the fluoride adsorption capacity of $92 \pm 1.7\%$ in contact time of 20 minutes at pH 5.5. Thakur et al.,³⁰ synthesized super paramagnetic Zirconium (IV)-polyacrylamide/ Fe_3O_4 magnetic composites and found a very high fluoride adsorption capacity of 124.5mg/g from natural water. Kumar et. al.,³¹ synthesized bimetal doped micro and nano adsorbent for removal of fluoride and found high fluoride adsorption capacity of 100 mg/g. Chai et al.,³² developed sulfate-doped $\text{Fe}_3\text{O}_4/\text{Al}_2\text{O}_3$ magnetic nanoparticles for the removal of fluoride from drinking water. He found the adsorption capacity of the nannoadsorbent to be 70mg/g at pH 7. Interestingly he found that the performance of nannoadsorbent was good at a wide range of pH 4–10. Ma et al.,³³ synthesized and studied the characteristics of equilibrium, adsorption of fluoride on magnetic-chitosan particle and he found the adsorption to be 20.93–23.98mg/g. Wan et al.,³⁴ synthesized $\gamma\text{-AlOOH}@CS$ (pseudoboehmite and chitosan shell) magnetic nanoparticles for the removal of fluoride from drinking water. They observed that 80% of the adsorption took place within initial 20 minutes and equilibrium was reached in 60 minutes. They also found the maximum adsorption capacity of 67.5mg/g at 20°C and pH = 7 ± 0.1. Dong et al.,³⁵ developed a lanthanum loaded magnetic cationic hydrogel for the adsorption of fluoride from drinking water. They found the adsorption capacity reached to 93% of the ultimate adsorption capacity in the initial 10 minutes. They also found the maximum adsorption capacity of 136.78mg/g. Chang et al.,³⁶ synthesized super paramagnetic zirconia material for the adsorption of fluoride. They found that as the pH decreases the fluoride adsorption capacity of the material increases. They found the adsorption capacity of 14.7mg/g at pH 4. Mohan et al.,³⁷ synthesized magnetic and nonmagnetic corn stoverbiochar for the adsorption of fluoride and they found that the maximum adsorption takes place at pH 2.0. They performed the adsorption study at 25°, 35°, and 45° and found the maximum adsorption of 5.17mg/g at 35°C. Zhang et al.,³⁸ synthesized the $\text{Fe}_3\text{O}_4@\text{Ag-La}$ magnetic nanoparticles using electro-extrusion method for fluoride removal. They found the maximum adsorption capacity of 45.320mg/g at pH 4. They also found that other ions such as Cl^- , SO_4^{2-} , HCO_3^- and PO_4^{3-} has almost no effect on fluoride adsorption.

Conclusion

In this review, different type of magnetic nanoparticles for the removal of fluoride has been discussed which is depending upon their adsorption capacities, contact time, dosage, pH etc. Ce-Ti@ Fe_3O_4 nanoparticles were reported to the maximum adsorption capacity for fluoride removal at pH value of 7. With a little surface modification, the targeted contaminant can be effectively removed with these MNPs. Magnetic nanoparticles are already being used for the removal of heavy metal from wastewater. The review also showed that coating with some green organic material can also be used for adsorption of contaminants. Therefore, it can be concluded that magnetic nanoparticles have a huge potential for water treatment processes.

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Conflict of interest

The author declares there is no conflict of interest.

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