

A review on adsorption efficiency of widely adopted adsorbents used in Defluoridation of aqueous media

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ABSTRACT

The review article provides an insight on various adsorbents and their efficiency in fluoride removal from drinking and waste water. The capacity of fluoride removal of adsorbent is dependent on pH, contact time, temperature, surface area of adsorbent and initial concentration of fluoride solution etc. In comparison to the traditional natural methods, the synthetic and nanostructure-based adsorbents, exhibited higher performance and efficiency of defluorination which provides a sustainable approach to safe drinking water quality. The present paper deals with some widely adopted natural adsorbent, synthetic and nanostructure-based adsorbents. The natural adsorbent includes, thermally treated lateritic soil, modified natural magnetite ore (Fe_3O_4) with aluminum and lanthanum ions, lateritic soils, Titanium hydroxide, limestone (LS) and aluminium hydroxide, sedimentation with calcium and aluminium. The Synthetic adsorbent includes, Surface-functionalized polyurethane foam (SPUF); Schwertmannite; Carbonaceous material from pyrolysis of sewage sludge; Chitosan. And the effective adsorbent nano scale structure includes, nanoscale aluminium oxide hydroxide (AlOOH), Magnetic iron oxide/aluminium hydroxide composite, sulfatedoped $\text{Fe}_3\text{O}_4/\text{Al}_2\text{O}_3$ nanoparticles, nano-scale aluminium oxide hydroxide (nano-AlOOH), Graphene Nanoparticles adsorbent, $\text{Al}_2\text{O}_3/\text{Bio-TiO}_2$ nano composite (ABN), Green synthesized $\text{Fe}_3\text{O}_4/\text{Al}_2\text{O}_3$ nanoparticles with coated polyurethane foams etc. The activated alumina is most conventional fluoride adsorbing material. However, activated alumina performs well in acidic environment with complex regeneration issue. Although other traditional adsorbents remove fluoride from water but they have lower efficiency, which restrict their application. In case of synthetic and nano structured based adsorbents, due to increased surface area, nontoxic nature, limited solubility in water and high adsorption efficiency, these methods are widely accepted and proven environmentally suitable.

Key words : *Defluorination, Adsorption techniques, Natural and modified adsorbent, Nanostructure-based adsorbent.*

Introduction

All water sources have a natural source of fluoride which has a significant role in prevention of tooth decay. Evidence is mounting that, there is wide spread in use of fluoride- containing toothpaste which also fills up the requirement of fluoride for health. WHO recommended the permissible limit of fluoride 0.5 mg to 1 mg/l which is beneficial for the production and maintenance of healthy bones and

teeth, while excessive intake of fluoride causes dental or skeletal fluorosis which is a chronic disease manifested by mottling of teeth in mild cases, softening of bones and neurological damage in severe cases (Wang and Reardon, 2001). Many regions have water containing more than 1.5 mg/l of fluoride due to its natural presence in the earth's crust, or discharge by agricultural and industrial activities, such as steel, aluminium, glass, electroplating. Surface water seldom has fluoride concentration more than

0.3%. Ground water sources such as dug well, shallow and deep hand pumps, especially tube well, may contain excess fluoride where minerals like Cryolites, Biotites and Fluoroapatite are present. The disposal of industrial waste leads to the contamination of river with fluoride along with other toxic materials. River water near industries/mines like bauxite, graphite, aluminium, phosphate and fertilizer does contain some fluoride.

Defluoridation is a process to reduce or removal of high concentration of fluoride to optimal level. The available methods can be broadly classified into five categories, namely adsorption, coagulation/precipitation, ion exchange, membrane-based method (nanofiltration, ultra-filtration, reverse osmosis, electro dialysis and Donnan dialysis) and electrolytic techniques (Tomar *et al.*, 2013). Adsorption techniques have been quite popular due to their simplicity, cost effectiveness, and availability of wide range of adsorbent materials (Bhatnagar *et al.*, 2011). When water is passed through the bed (containing defluoridating agent) this material retains the fluoride. The adsorbent gets saturated after a period of operation and requires regeneration. Most of developing countries use adsorption since it involves the use of low-cost materials (Suneetha *et al.*, 2015; Waghmare *et al.*, 2015). Therefore, adsorption becomes the most promising technique for fluoride removal through infiltration systems that prevent the release of fluoride to receiving water bodies.

This review paper deals with some widely adopted various categories of adsorbents used and parameters affecting the whole process. Adsorbents studied by researchers are enlisted with their adsorption capacity, optimum pH, temperature, equilibrium isotherm, kinetics, interfering ions, thermodynamic studies and regeneration procedure adapted.

The natural adsorbent includes, thermally treated lateritic soil, modified natural magnetite ore (Fe_3O_4) with aluminium and lanthanum ions, lateritic soils, titanium hydroxide, limestone (LS) and aluminium hydroxide, sedimentation with calcium and aluminium.

The Synthetic adsorbent includes Surface-functionalized polyurethane foam (SPUF); Schwertmannite; Carbonaceous material from pyrolysis of sewage sludge; Chitin, chitosan and lanthanum (modified chitosan).

And the effective adsorbent nano scale structure includes, nanoscale aluminium oxide hydroxide

(AlOOH), Magnetic iron oxide/aluminium hydroxide composite, sulfate doped $\text{Fe}_3\text{O}_4/\text{Al}_2\text{O}_3$ nanoparticles, nano-scale aluminium oxide hydroxide (nano-AlOOH), Graphene Nanoparticles adsorbent, $\text{Al}_2\text{O}_3/\text{Bio-TiO}_2$ nanocomposite (ABN), Green synthesized $\text{Fe}_3\text{O}_4/\text{Al}_2\text{O}_3$ nanoparticles with coated polyurethane foams.

Adsorptive Method

Natural Adsorbent

Adsorption on thermally treated lateritic soils

According to Kefyalew Gomoro *et al.* (2012), the capacity of thermally treated lateritic soil is within the range of 22 to 47 mmol/kg. The maximum capacity of 47 mmol/kg was obtained for RGS fired at 500 °C. The result indicates a strong correlation between fluoride removal capacity and gibbsite content of the soil. The study infers gibbsite as an active component in lateritic soil which strongly influence the fluoride removal capability. Research reveals that the dissolution of gibbsite is facilitated by the adsorption of fluoride onto gibbsite. This may result in the formation of aluminium fluoro complexes in water. The kinetic study of fluoride indicates two mechanisms with different rate constants: an initial rapid adsorption of fluoride on surface of the adsorbent followed by slower diffusion of the fluoride into the interior of the adsorbent. RGS with maximum iron oxide and aluminium oxide content was found to exhibit the highest removal capacity.

Schwertmannite as adsorbent

According to Eskandarpour *et al.* (2008) and Goswami and Purkait (2013), Schwertmannite (an iron oxide hydroxide) adsorbent is stable in low pH and has high magnetic properties. Schwertmannite at pH 3.58 with an adsorbent dose of 3 g/l effectively remove fluoride. Kinetic study revealed that fluoride adsorption process was controlled by pseudo-second-order rate equation. The equilibrium data was fitted with Langmuir and Freundlich isotherm models. The Langmuir isotherm model was fitted well to this system with an adsorption capacity of 11.3 mg/g of adsorbent. Schwertmannite has strong affinity for chromate and arsenate anions.

Low-cost local sorbents

Research was made by Beraki *et al.* (2014) for preliminary assessment of low-cost local sorbent mate-

rials for water defluoridation. Fluoride sorbent local materials named crushed burnt clay pot, household ash, Keren and adigerghish soil were studied in a batch defluoridation. The effect of amount of adsorbent, pH, contact time, particle size and fluoride concentration were examined. The crushed burnt clay pot has average fluoride removal capacity about 0.26 mg/g fluoride. Others ranged from 0.08-0.1 mg/g for the same mass of 7 g and thus crushed burnt clay pot was selected for defluoridation.

Mixed rare earth oxides

Langmuir isotherm model and isosteric heat calculation showed that adsorption process followed a heterogeneous model (Mohapatra *et al.*, 2004). Fluorides can also be adsorbed onto mixed rare earth oxides rapidly and effectively (Raichur and Jyoti 2001). Optimum (> 90%) adsorption occurred within first 5-10 min at pH 6.5. Adsorbed fluoride can also be desorbed by using an alkali solution of pH 12. Other natural materials that remove fluoride from water are kaolinite, natural phosphate rock and alumina.

Active alumina as adsorbent

Tang *et al.* (2009) studied fluoride adsorption onto active alumina using batch methods and at equilibrium contact time of 10 h. The ionic strength did not show any impact on fluoride adsorption during the entire experiment with pH range between 5.0 to 10.5. Bicarbonate acts as a strongest interfering agent for As and fluoride removal adsorptive process. During adsorption of fluoride on activated alumina, co-anions reduced fluoride adsorption in the order of: $\text{HPO}_4^{2-} > \text{HCO}_3^- > \text{SO}_4^{2-} > \text{Cl}^-$. (Mishra *et al.*, 2010)

Sedimentation with calcium and aluminum salts

One of the commonly applied methods for defluorination in industrial waste water treatment is the sedimentation with calcium and aluminium, which can reduce the fluoride concentration to about 2 mg/l. (Huang *et al.*, 1999) This process generates huge amount of sludge containing fluoride and mandate the sludge treatment and disposal with increased expenses (Aldaco and Irabien, 2005).

Limestone (LS) and Aluminium hydroxide impregnated limestone

Adsorption of fluoride on limestone (LS) and aluminium hydroxide impregnated limestone (AILS) was investigated using a batch adsorption technique

(Jain and Jayaram, 2009) (Nath and Dutta, 2010) experimented on crushed limestone of diameter 3-4 mm to precipitate fluoride as CaF_2 in addition to adsorption of fluoride on limestone. The study has been carried out in batches by varying the acid concentration and contact time.

Natural biological adsorbent: *Ipomoea aquatica* plant

For defluoridation, different parts of plant (*Ipomoea aquatica* L) like root, stem, leaves can be used after phyto treatment, as natural adsorbent which removes 1.015 $\mu\text{g/g}$, 0.0085 $\mu\text{g/gm}$ and 0.0054 $\mu\text{g/g}$ of fluoride respectively. The removal percentage becomes all most constant after (Four to ten) days. It means the removal approach is very slow. Activated carbon derived from Royal Gulmohor fruit shell can also be used for fluoride abatement. Moringa seeds as coagulant can be used for defluorination up to some extent (Jahn, 1988).

Modified and Synthesized adsorbent

Modified natural magnetite ore (Fe_3O_4) with aluminum and lanthanum ions

According to García-Sánchez *et al.* (2016), modified natural magnetite ore (Fe_3O_4) with aluminum and lanthanum ions increases the fluoride removal efficiency from aqueous solutions. Batch tests showed the adsorption efficiency of 90% and 96% for the aluminum and lanthanum modified materials, respectively. But its adsorption capacity is 1.5 mg/g with contact time of 24 hours.

Magnetic iron oxide/aluminum hydroxide composite

The presence of phosphate and bicarbonate (100-500 mg/l) decreases the fluoride removal efficiency approximately 35 to 39%, respectively. While the presence of sulphate, chloride and nitrate (100-500 mg/l) slightly decreases the removal efficiency to 82.3%, 88% and 87.8%. On adsorption capacity, the divalent and trivalent anions have more effect than monovalent anions (Eyobel Mulugeta *et al.*, 2015). Also, in the presence of bicarbonate the removal efficiency decreases due to significance increase in concentration of pH and competitive nature of HCO_3^- on to adsorption site (Srimurali and Karthikeyan, 2008)

Surface-functionalized polyurethane foam (SPUF)

According to Subhashini *et al.* (2012) The SPUF

shows exceptionally high potential and quick adsorption of Fluoride (maximum 7.8 mg to 21mg) from drinking water. The adsorption capacity of SPUF significantly influenced by pH of the solution. The advantage of the adsorbent is, it can be easily recharged by altering the pH of the solution using NaOH or Ca (OH)₂. A maximum adsorption of 97% at 10 mg of SPUF can be marked. No further increase of adsorption percent be marked by increasing adsorbent dose. (Krupadam *et al.*, 2010) Water Science & Technology- WST 62.4, 759)

Chitosan as adsorbent

As investigation made by Nagraj and Kumar (2018), biopolymer chitosan in its powder and solution form can be technically economical for efficient removal of fluoride. Chitin is a polysaccharide adsorbent, found in varieties of organism including fungus and bacteria, but commercially extracted from shellfish processing waste. The adsorbent chitosan is a polymer of 2-glucosamine and N-acetylglucosamine derived from chitin, by deacetylation reaction in hot alkali. With increase in adsorbent doses, contact time and mixing speed the fluoride concentration decreases in synthetic water. For defluorination the optimal condition was found to be of 2.5 g of chitosan in powder form at 60 rpm mixing speed. In solution form 15 ml of 0.1 g chitosan solution proved to be the optimum dosage, where exceptionally good efficiency of fluoride removal achieved, that is 65-70%. The experimental data of adsorption fit well with Freundlich adsorption isotherm. Chitosan in powder and solution form proved to be very effective in defluorination.

Titanium hydroxide derived adsorbents

Investigation made by Wajima *et al.* () for adsorption of fluoride by a gel like adsorbent, Titanium hydroxide. The adsorbent was prepared by using a Titanium Oxy sulfate TiOSO₄ XH₂O. The mechanism of adsorption involves ion exchange between Fe ion of the solution and hydroxyl ion of adsorbent. The adsorbent slurry concentration varies between 0.78 g/l and 15.6 g/l. Using the adsorbent in aqueous solution, the fluoride concentration increased initially. The fluoride ion concentration largely depends on pH and contact time. The optimum pH range is 3-4. Within 30 minutes the fluoride ion concentration reached the equilibrium value 4.0 mmol/g. As the surface area of adsorbent is 96.8 m²/g, hence more amount of fluoride ions is

adsorbed. The study revealed; the concentration of fluoride reduced from 1.9 mg/l to 0.5 mg/l in waste water. The titanium hydroxide adsorbent has high selectivity for adsorption of fluoride ion in compare to others in waste water.

Amorphous Fe/Al/Ca based adsorbent

According to Yogendra Singh Solankia *et al.* (2019) the amorphous Fe/Al/Ca based adsorbent was developed for defluorination of drinking water. Research carried out with conformation test using Box-Behnken methodology and achieved 91.2% fluoride removal at an optimum condition of 7 mg/l, pH 7.0, initial fluoride concentration with 3g/l dosage and 3h of contact time with estimated co-efficient of determination (R²) value of 0.98. A high potential of defluorination with maximum adsorption capacity of 6.47 mg g⁻¹ and a rate constant of 0.063 ml/min/mg was observed from Thomas model. 50% of adsorbent bed exhausted in 157.3 h at constant flow rate of 1.08 ml min⁻¹ was estimated from Yoon Nelson model. Synthetic adsorbent can able to remove fluoride up to 88% with an adsorbent dose of 1.5 mg l⁻¹.

Carbonaceous material from pyrolysis of sewage sludge

Marquez-Mendoza *et al.* (2012), describes the pseudo second order model of fluoride kinetic sorption process by carbonaceous material from pyrolysis of sewage sludge. The rate limiting step may be chemisorption involving valence forces through sharing or electron exchange between sorbent and sorbate. Fluoride can partially be desorbed from the CM by bicarbonate ions solutions. Moreover, partial regeneration of CM was observed using a solution of HCl (pH =1). The carbonaceous material from pyrolysis of sewage sludge is an economical possibility for defluorination of water.

Graphene oxide/Eggshell adsorbent

Mohamad *et al.* (2020) investigated the defluorination of drinking water with application of synthesized Graphene oxide/Egg shell (GO/ES) adsorbent. The experiment was carried out at 25 °C, with an initial F⁻ concentration of 25 mg/l, 0.05 g of GO/ES adsorbent dosage and 120 minutes of contact time. At this condition the maximum 56 mg/l, adsorption capacity of Fluoride was obtained. The adsorption isotherm study show that the experimental data were best fitted with Langmuir isotherm.

This indicates The Fluoride adsorption is following monolayer adsorption on a homogeneous surface of GO/ES, with a R^2 value of 0.9983.

Nano-structure based Adsorbent

Sulfatedoped $\text{Fe}_3\text{O}_4/\text{Al}_2\text{O}_3$ nanoparticles

Chai *et al.* (2013) reported a novel adsorbent of sulfatedoped $\text{Fe}_3\text{O}_4/\text{Al}_2\text{O}_3$ nanoparticles with magnetic separability for fluoride removal from drinking water. Its adsorption capacity is 70.4 mg/g with an equilibrium time of 8 h and the fluoride removal efficiency reached up to 90%.

Nano-scale aluminum oxide hydroxide (nano-AIOOH)

According to (Fentahun Adeno *et al.*, 2014) and (Wang *et al.*, 2009), nano-AIOOH is an efficient defluorinating material. Aluminium nitrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, 95%) and ammonium bicarbonate (NH_4HCO_3 , 98%) were used as starting materials. The absolute density of nano-AIOOH was found to be 2.18 g cm^{-3} . The lower density indicates more pore spaces making nano AIOOH an effective defluorinating agent. At pH below 8, fluoride adsorption might take place by ion exchange reaction, i.e., by replacement of hydroxide ion (OH) by fluoride ion (F). According to Wang, its fluoride removal efficiency is higher than 90% with an adsorption capacity of 3.26 mg/g and 6 hours equilibrium time. Its fluoride removal efficiency is comparable but its adsorption capacity is lower and equilibrium time is longer. But Fentahun Adeno *et al.* (2014) describes the nano-scale aluminium oxide hydroxide (nano-AIOOH) with adsorption capacity 20.75 mg/g and equilibrium time of 1 hour. It has higher adsorption capacity and shorter equilibrium time. The adsorption mechanism indicates the fluoride removal by nano-AIOOH is chemisorption process.

$\gamma\text{-Fe}_2\text{O}_3$ nanoparticle

An investigation on fluoride adsorption on $\gamma\text{-Fe}_2\text{O}_3$ nanoparticle has been made by Jayarathna *et al.* (2015). Within 15 minutes a rapid adsorption occurred by removing $95 \pm 3\%$ and reached equilibrium thereafter. The removal of fluoride capacity is 3.65 mg/g. The fluoride removal efficiency of $\gamma\text{-Fe}_2\text{O}_3$ nanoparticle is higher and faster.

Graphene and graphene oxide Nanoparticle's adsorbent

Mahin Mohammadnia *et al.* (2020), describes the removal of fluoride by the application of graphene and graphene oxide nanoparticle from the aqueous solution. For both the adsorbents, the maximum adsorption capacities observed during the first 15 minutes at pH 3 and an initial fluoride concentration of 10 mg/l. This method fitted well with Freundlich and Langmuir isotherms respectively. The result showed, graphene nanoparticles have higher adsorption capacity of fluoride than graphene oxide nanoparticles. The increasing temperature also led to reduce the adsorption capacity, indicating exothermic adsorption reaction.

$\text{Al}_2\text{O}_3/\text{Bio-TiO}_2$ nano composite adsorbent

According to the investigation carried out by Suriyaraj *et al.* (2015) for defluorination of drinking water, $\text{Al}_2\text{O}_3/\text{Bio-TiO}_2$ nanocomposite (ABN) and $\text{Al}_2\text{O}_3/\text{Bio-TiO}_2$ nanocomposite were impregnated into electrospun (TPU) nanofiber membrane (ABN/TPU-NFM) has been developed. The adsorption capacity of the adsorbent reported as 1.9 mg/g which is relatively low, expensive, uneasy and unsuitable for rural areas.

Green synthesized $\text{Fe}_3\text{O}_4/\text{Al}_2\text{O}_3$ nanoparticles coated polyurethane foams

Sonu Kumari and Suphiya Khan (2017) made research on development of cost effective, portable, environment and user-friendly defluorination technique. They prepared a green and cost-effective method that utilizes Fe_3O_4 and Al_2O_3 nanoparticles (NPs) which are synthesized from *Simmondsia chinensis* (jojoba) defatted meal extract by a green synthesis route. For F removal from tea, easy to use tea-bag like pouches containing Al_2O_3 NPs impregnated with polyurethane foam (PUF), $6 \times 6 \text{ cm}^2$ PUF and tea bag filter paper were prepared. For F adsorption, the Al-PUF bag was dipped in 100ml of prepared tea for 5min. Similar tea-bag like pouches were also prepared using Fe_3O_4 NPs impregnated PUFs and the tea bag filter paper, further utilized for F remediation. The Al_2O_3 NPs-PUF showed high defluorination capacity of 43.47 mg/g, whereas the Fe_3O_4 NPs-PUF showed the defluorination capacity of 34.48 mg/g. The synthesized Al_2O_3 -PUF infusion bags removed the F, that was under the permissible limit of 1.5 mg L^{-1} . Different properties of adsorbent were characterized using a combination of FESEM, EDX, XRD and FTIR techniques respectively. The

NPs-PUF per pouch costs approximately US \$0.05, which make the technology more affordable for rural communities.

Other trialed methods

Except the above methods there are certain methods which also have investigated for defluorination purpose. The techniques include, ion exchange, Donnan dialysis and integrated physiochemical and biological adsorption of active alumina, fly ash, membrane (including reverse osmosis and nano-filtration) and carbon nanotube (Lounici *et al.*, 1997; 2004; David and Herbet, 1998; Kettunen *et al.*, 2000; Li *et al.*, 2001; 2003; Garmes *et al.*, 2002; Ruiz *et al.*, 2003; Hu *et al.*, 2005; Subhashini *et al.*, 2005). Physically and chemically activated carbon can be successfully used for removal of fluoride from water. Selective ion exchange resin for fluoride sorption has been identified.

The low-cost adsorbents investigated for the defluorination purpose also include: hydroxy apatite, calcite, fluorspar and quartz (Fan *et al.*, 2003), fly ash Chaturvedi *et al.*, 1990), silica gel (Wang *et al.*, 1995), activated bone char (Bhargav *et al.*, 1992), spent catalyst and red mud (Cengelogke *et al.*, 2002). Other industrial waste materials, bauxite, kaolinite and various types of clays are some of the naturally occurring materials that have been used as adsorbent for fluoride removal (Kloos and Redda Tekle Haimanot, 1999; Beneberu Shimelis *et al.*, 2006; Srimurali and Karthikeyan, 2008; Deshmukh *et al.*, 2009; Jayarathna *et al.*, 2015). Most widely investigated magnetic materials are iron, cobalt and nickel compounds and alloys (Khan, 2015).

Among the various methods, it has been accepted that the ion exchange, reverse osmosis, electro-dialysis and membrane processes are effective and can remove the fluoride to a suitable level. But they are expensive and require frequent regeneration of ion exchange beds or cleaning of the scaling and fouling on the membrane (Aldaco and Irabien, 2005). Surface of oxide minerals, being positively charged, has capability of abating fluoride from water. Refractory grade bauxite showed best result towards fluoride adsorption among refractory grade bauxite, feed bauxite, manganese ore and hydrated oxides of manganese ores (WAD).

Other tested nanomaterials include hematite, magnetite, ferrihydrite, goethite, hematite-alpha, hydroxyapatite (HAP), brucite, and four titanium dioxides (TiO₂-A [anatase], TiO₂-B [rutile], TiO₂-C

[rutile], and TiO₂-D [anatase]). Among 11 (hydro)oxide nanomaterials tested in this study, ferrihydrite, HAP, and brucite showed two to five times higher removal of fluoride than other nanomaterials from synthetic fluoride solutions.

The process of selection of suitable and efficient adsorbent of fluoride is quite problematic. The findings elucidate that increasing surface area could potentially enhance removal capacity. Thus, nanoscale (hydro)oxides were selected to evaluate fluoride removal from water due to their physicochemical properties and high surface area as well as natural presence in natural environment. Among the various methods, it has been accepted that the ion exchange, electro-dialysis and membrane processes are effective and can remove the fluoride to a suitable level. But they are expensive and require frequent regeneration of ion exchange beds or cleaning of the scaling and fouling on the membrane (Aldaco and Irabien, 2005).

Conclusion

The study reveals that the adsorption efficiency of nano structure-based adsorbent is more in comparison to others for defluorination of drinking as well as industrial waste water. Due to increased surface area, nontoxic nature, limited solubility in water and high adsorption efficiency the modified and synthesized nano-scale adsorbents are proven effective for defluorination. In addition, further studies examining the regeneration capacity of each nanomaterial for practical application and reuse should be conducted. Future work is needed to better understand fluoride removal on a pilot scale level using the nanomaterials, especially pertaining to drinking and industrial waste remediation.

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