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Defluoridation of contaminated water by using low cost adsorbents: A review

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Abstract

This paper depicts the fluoride occurring in the groundwater in many parts of the world is harmful for human health. The fluoride level must be maintained at certain limits. According to World Health Organization the permissible limit of fluoride concentration in drinking water is 1.5mg/L. The excess fluoride present in groundwater causes skeletal fluorosis, dental fluorosis, non-skeletal problems. This review paper presents the past work on defluoridation by using adsorption techniques. The adsorption procedure is broadly utilized in many countries like India, Sri Lanka, and China, Turkey etc. It is relative simple and cost effective method. The adsorption process using bio-adsorbents that is abundant, easily available have been investigated. The main purpose of this paper is to provide new ideas about the removal of fluoride in aqueous and synthetic solutions by adsorption technique that has been given by various researchers in the field of fluoride removal.

Keywords: Adsorption, drinking water, fluoride, low cost adsorbents

Introduction

Fluoride is a commonly occurring element in minerals, geochemical deposits, and usual water systems and enters food chains through either drinking water or eating plants and cereals (Ravikumar *et al.,* 2015) [21]. The ground water containing high levels of fluoride is used for drinking purpose, this usage of fluoride contaminated water over a period of time causes health problems, such as fluorisis i.e., deformations of skeletal, non-skeletal, dental and also other hazardous effects (Rao *et al*., 2009) [20]. The removal of fluoride from water is one of the most important issues due to its ill- effects on human health and environment. According to World Health Organization the maximum permissible limit of fluoride concentration in drinking water is 1.5 mg /L (Mondal *et al.,* 2012, Malakootian *et al.,* 2011) [16, 13]. In India, the problem is common in places such as Andhra Pradesh, Tamilnadu, Karnataka, Kerala, Rajasthan, Gujarat, Uttar Pradesh, Punjab, Orissa and Jammu and Kashmir (Alagumuthu *et al*., 2010) [2]. Fluoride is found in both surface waters and ground water because some fluoride compounds present in the earth's upper crust are readily soluble in water. The average earth's crust abundance is 300 mg kg^{-1} spread in a wide variety of minerals such as fluorspar, rock phosphate, cryolite, apatite, mica, hornblende, and others (Chakrabarty and Sharma, 2012) [5]. The discharge of industrial wastewater, such as semiconductor industries, aluminum industries, and glass manufacturing industries, also contributes fluoride in water pollution, especially in groundwater (Battula *et al.,* 2014) [4]. The International Society for Fluoride Research (ISFR) has reported studies implicating fluoride in the rising rates of Down's syndrome, chronic fatigue syndrome and sleep disorder (Jamode *et al.,* 2004) [11]. The occurrence of high fluoride concentrations in ground water is a problem faced by many countries, notably Sri Lanka, and China, the Rift Valley countries in East Africa, Turkey, and parts of South Africa (Tembhurkar and Dongre, 2006) [28]. Methods of addition of alum, lime and bleaching powder followed by rapid mixing, flocculation and filtration, called Nalagonda technique, has been adopted in several Indian States (Gupta *et al.,* 2014) [10]. Several fluoride containing compounds have industrial applications, are extensively used in industries such as semiconductors, fertilizers, and electrolysis of alumina, and contribute to fluoride pollution (Palishajee *et al*., 2013) [18]. High fluoride concentrations in ground water, up to 30 mg/L occur in some parts of the world (Togarepi *et al*., 2012) [29]. India is among 23 nations in the world, where the fluoride contaminated groundwater is creating the health problems (Deshmukh *et al*., 2009) [8]. The fluoride level in the ground water used for drinking purposes in Thar and Aravali regions of Rajasthan, has been found as 12-90 ppm and 1.44-28.1 ppm respectively (Choudhary *et al*., 2014) [6]. Adsorption techniques have been quite popular in recent years due to their simplicity, as well as the availability of wide range of adsorbents (Goswami *et al*., 2015) [9]. Effects of various operating parameters that may affect the adsorption process are also assessed (Poudyal and Babel, 2015) [19]. Within last few years, the plant based bioremediation approach to improve the quality of water has become an area of intense study. Bioremediation is recognized as a cost-effective and environmental friendly option for cleanup of contaminated water (Veeraputhiran and Alagumuthu, 2011) [30].

2. Health Effects of Fluoride Containing Water

Dental fluorosis

Dental fluorosis, also called "mottled enamel", occurs when the fluoride level in drinking water is marginally above 1.0 mg/l. A relationship between fluoride concentration in potable water and mottled enamel was first established in 1931. Typical manifestations of dental fluorosis are loss of shining and development of horizontal yellow streaks on teeth. Since this is caused by high fluoride in or adjacent to developing enamel, dental fluorosis develops in children born and brought up in endemic areas of fluorosis. Once formed, the changes in the enamel are permanent. When the above manifestations are seen in an adult, they clearly indicate that the person has been exposed to high fluoride levels during her or his childhood. (Manjunath *et al.,* 2014) [15].

Skeletal fluorosis

It is primarily associated with the consumption of drinking-water containing elevated levels of fluoride but exposure to additional sources of fluoride such as high fluoride coal is also potentially very important (Husain *et al.*, 2015). Crippling skeletal fluorosis, which is associated with the higher levels of exposure, can result from osteosclerosis, ligamentous and tendinous calcification and extreme bone deformity. Skeletal fluorosis is tingling sensation in legs and feet followed by pain and stiffness of the back (Nemade *et al.*, 2002) [17].

3. Removal of Fluoride Using Low Cost Adsorbents:

3.1 Fluoride Remediation by Adsorption

Adsorption is considered one of the most efficient technologies for fluoride removal in drinking water when compared to other technologies for fluoride removal based on initial cost, flexibility and simplicity of design, and ease of operation and maintenance. The efficiency of this technique mainly depends on adsorbents (Stoica Ligia *et al.,* 2012) [26].

Adsorption depends on ions (adsorbate) in fluid diffusing to the surface of a solid (adsorbent), where they bond with the solid surface or are held there by weak intermolecular forces. Adsorption of fluoride on to solid absorbant usually occurs through three phases:

1. diffusion or transport of fluoride ions to the external surface of the adsorbent from bulk solution across the boundary layer surrounding the adsorbent particle, called external mass transfer;
2. Adsorption of fluoride ions on to particle surfaces;
3. The adsorbed fluoride ions probably exchange with the structural elements inside adsorbent particles depending on the chemistry of solids, or the adsorbed fluoride ions are transferred to the internal surfaces for porous materials (intra particle diffusion) (Stanić Mirna Habuda *et al.*, 2014) [25].

Several adsorbent materials have been tried in the past to find out an efficient and economical defluoridating agent. Some of those adsorbents are activated coconut shell carbon and activated fly ash, groundnut shell, coffee husk, Phyllanthus emblica, bark of babool, pine apple peel powder, orange peel powder, grind neem and pipal leaves, groundnut shells, etc. Adsorption methods are adopted for removal of fluoride and these methods are suitable when fluoride is present in low concentration (Sharma Sharad *et al.*, 2014) [24].

3.2 Advantage of low-cost adsorbents over conventional adsorbents

1. The efficiencies of removal of fluoride ions of various nonconventional adsorbents vary between 50 and 90% depending upon the characteristics and particle size of adsorbent(s). A combination of adsorbents can also be used effectively in defluoridation treatment.
2. Nonconventional adsorbents are relatively cheaper compared to conventional ones and are easily available resulting in savings in cost.
3. Nonconventional adsorbents require simple alkali or/and acid treatment for the removal of lignin before their application and to increase efficiency.
4. Since the cost of these adsorbents is relatively low they can be used once and discarded.
5. Nonconventional adsorbents require less maintenance and supervision. Separation is possible to segregate the nonconventional adsorbents from the effluents before their disposal.
6. These nonconventional adsorbents can be disposed of easily and safely. Used adsorbents can be reused as a filler material in low-lying areas and hence their disposal does not pose any serious problem. (Jamode *et al.*, 2004) [11].

3.3 Advantage of adsorption process

1. **Cheap:** The cost of adsorbent is low since they are often made from locally, abundantly and easily available materials.
2. **Metal Selective:** The metal adsorbing performance of different types of bio-mass can be more or less selective on different metals.
3. **Regenerative:** Sorbent material can be possible to reuse after regeneration.
4. **No Sludge Generation:** Unlike the problems in other techniques (ex: precipitation), there is no issue of sludge generation in adsorption process.
5. **Metal Recovery:** If adsorbate is a metal ion, it is possible to recover the metal ion after being desorbed from the adsorbent materials.
6. **Competitive Performance:** Performance of adsorption process in terms of efficiency and cost is comparable with the other methods available (Mann and Mandal, 2014) [27]

3.4 Factors Affecting Adsorption

- **Effect of Contact Time:** The adsorption of metal ion by adsorbent also depends on the interactions of functional groups between the solution and the surface of adsorbent. Adsorptions can be assumed to be complete when equilibrium is achieved between the solute of solution and the adsorbent. However, specific time is needed to maintain the equilibrium interactions to ensure that the adsorption process is complete (Abas *et al.,* 2013) [1].
- **Effect of pH:** Adsorption of metal ions from the wastewater is mainly influenced by the pH of the solution. pH can influence the surface charge of the adsorbent, the degree of ionization also the species of adsorbate. In a particular pH range, most metal sorption is enhanced with pH, increasing to a certain value followed by a reduction when further pH increases. The dependence of the metal uptake on pH can be associated with both the surface functional groups on the biomass' cell walls and also the metal chemistry of the solution (Abas *et al.,* 2013) [1].
- **Effect of Initial Concentration:** Initial concentration of metal ions can alter the metal removal efficiency through a combination of factors such as the availability of specific surface functional groups and the ability of surface functional groups to bind metal ions. Initial concentration of solution can provide an important driving force to overcome the mass transfer resistance of metal between the aqueous and solid phases (Abas *et al.,* 2013) [1].
- **Effect of Temperature:** Temperature plays a double role in the fluoride sorption process. Temperature can impact the physical binding processes of fluoride to a sorbant. However, temperature also canhave a direct impact on the physical properties of a sorbant, if thermally treated prior to exposure, so that sorption capacities can be significantly altered. Most sorption studies are conducted at room temperature in laboratory settings. As temperature increased, sorption was shown to be less favored most

likely due to increased deprotonation or hydroxylation of the surface causing more negatively charges sorbant surfaces. This is an important observation to note when attempting to apply defluoridation methods on site in hot climates, for sorption capacities attained under room temperature conditions may be higher than in the field as a result of increased temperatures (Sreenivasa K *et al.,* 2015) [12].

- **Surface area of adsorbent:** Larger sizes imply a greater adsorption capacity (Wikipedia).
- **Particle size of adsorbent:** Smaller particle sizes reduce internal diffusional and mass transfer limitation to the penetration of the adsorbate inside the adsorbent (i.e., equilibrium is more easily achieved and nearly full adsorption capability can be attained). However, wastewater drop across columns packed with powdered material is too high for use of this material in packed beds. Addition of powdered adsorbent must be followed by their removal (Wikipedia).

3.5 Limitations of adsorption process:

1. The process is highly dependent on pH and works best
2. only in a narrow pH range (5–6)
3. High concentration of total dissolved salts (TDS) can result in fouling of the alumina bed.
4. Presence of sulfate, phosphate or carbonate results in ionic competition.
5. The process has low adsorption capacity, poor integrity and needs pretreatment.
6. Disposal of fluoride laden sludge and concentrated regenerant is also a problem. (Razbe *et al.*, 2013) [22].

4. Use of Low Cost Adsorbents in Past

Table 1 shows that the removal of fluoride by using different adsorbents and its optimal parameters. Some low cost adsorbent used in this table which indicates that adsorbents were outstanding removal capabilities for fluoride in ground water. Parameters which were shown in table 1 such as adsorbent dose, pH, contact time, percentage removal of fluoride determined by using several low cost adsorbent. Maximum adsorption occurs in between 2-8 pH. It is clear that maximum up take capacity takes place by low cost adsorbents used in adsorption process and it gives better removal efficiency of fluoride.

Table 1: Removal of fluoride by using different adsorbents and its optimal parameters

Name of adsorbents	pH	Dosages	Contact time	Removal percentage	References
Clay material	2.0	5 to 10 g/l	3 hr	40 to 50 %	Ravikumar and Nazeebkhan (2015)
Activated dolichos lablab carbon	7.40-8.24	3 g/L	30 to 75 min	83.6 %	Rao *et al.*, (2010)
Cynodon dactylon activated carbon	Neutral	1.25 g	105 min	83.77 %	Alagumuthu *et al.*, (2010)
Granular activated carbon(GAC) & Sewage sludge(SS)	Neutral	GAC-4g/l SS-3g/l	180 min	GAC-78%,SS-88%	Poudyal& Sandhya (2015)
Tea ash	6.0	0.8 g/l	60 min	51.3 to 97.6 %	Mondal *et al.*, (2012)
Pumic	7.0	20 g/l	180 min	74.64 %	Malakootian *et al.*, (2011)
Neem stem charcoal	5.0	0.1 to 0.6 g	180 min	94 %	Chakrabarty & Sharma (2012)
Bleaching powder	between 6.0 to 10.0	73 g/l	8 hr -9 hr	from 28 % to 90.60 %	Palishahjee *et al.*, (2013)
Sand	6.0	12 g	3 hr	10.3 mg/g	Togarepi *et al.*, (2012)
Saw dust	8.0	0.15 g	30 min	80%	Choudhary *et al.*, (2014)
Phyllanthus emblica	Neutral	0.75 g	75 min	82.1 %	V. Veeraputhiran & G. Alagumuthu, (2011)
Neem, Pipal,Khair	2-10	10 g/l	180 min	90 %	Jamode *et al.*, (2004)
Electrocoaglation	Neutral		20 min	87 %	Battula *et al.*, (2014)
Activated charcoal	2.0	2 g	120 min	94 %	Tembhurkar & Dongre, (2006)
Neem leaves	2	10 g/l	60 min	90 %	Goswami *et al.*, (2015)
Bark of babool	8	5 mg/l	8 hr	77.04%	Mamilwar *et al.*, (2012)
Bagasse Dust (BD), Bagasse Fly ash (BF), Aluminum treated Bagasse Flyash (ABF)	6.0	1-20 g/l	5 hr	BD-36.8%, BF-42.6%, ABF-59.0%, BP-67.9% SP-84.4%	Gupta *et al.*, (2014)
SiO2	6.0	0.5 g/l	20 min	99.4 %	Balark *et al.*, (2015)
Clay-Hydroxyapatite	6.0	1.25 g/l	30 min	99.5	Dangi *et al.*, (2015)
Bottom ash	6.0	70 mg	105 min	83.2%	Ramesh *et al.*, (2012)
Ferric poly mineral	3.32	0.2 g	30 min	90%	Wambu *et al.*, (2012)
Saw dust	7.0	2 g	120 min	70 %	Mann and Mandal, (2014)
Rice Husk	2-10	10 g/l	120 min	75 %	Deshmukh *et al.*, (2009)

5. Conclusion

This review paper provides an overview of various low cost adsorbents in place of expensive commercial adsorbents used for the effective removal of fluoride from water. The efficiency of different adsorbents is depending on parameters such as pH, adsorbent dose, surface area, contact time, temperature and initial fluoride concentration. The removal capacity increases by increasing dose of the adsorbent and decreasing size of the adsorbent. The WHO standards prescribe 1.5 ppm as maximum level of fluoride in drinking water. The future research should be concentrated on development of effective and economic defluoridation adsorbents with proper domestic or community units for developing countries in terms of cost and feasibility for the removal of fluoride.

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