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Review article

A review of emerging adsorbents and current demand for defluoridation of water: Bright future in water sustainability

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ABSTRACT

Fluoride contamination of groundwater is a serious problem in several countries of the world because of the intake of excessive fluoride caused by the drinking of the contaminated groundwater. Geological and anthropogenic factors are responsible for the contamination of groundwater with fluoride. Excess amounts of fluoride in potable water may cause irreversible demineralisation of bone and tooth tissues, a condition called fluorosis, and long-term damage to the brain, liver, thyroid, and kidney. There has long been a need for fluoride removal from potable water to make it safe for human use. From among several defluoridation technologies, adsorption is the technology most commonly used due to its cost-effectiveness, ease of operation, and simple physical process. In this paper, the adsorption capacities and fluoride removal efficiencies of different types of adsorbents are compiled from relevant published data available in the literature and represented graphically. The most promising adsorbents tested so far from each category of adsorbents are also highlighted. There is still a need to discover the actual feasibility of usage of adsorbents in the field on a commercial scale and to define the reusability of adsorbents to reduce cost and the waste produced from the adsorption process. The present paper reviews the currently available methods and emerging approaches for defluoridation of water.

1. Introduction

Fluoride is a widely distributed monoatomic anion of fluorine characterised by a small radius (0.133 nm). It has a marked tendency to behave as a ligand and also to form a great number of different organic and inorganic compounds in air, soil, rock, and water. The sources of fluorine in water and soil are mostly geogenic and include several rock forming minerals (García and Borgnino, 2015). Among these, cryolite may contain about 54 wt% F and fluorite, topaz, and fluorapatite may contain about 48 wt%, 11.5 wt%, and 3.8 wt% F, respectively. Some other minerals, such as biotite and muscovite, may contain about 1 wt% F (Limaleite et al., 2015). Some of these minerals, including cryolite, fluorite, and fluorapatite, are highly soluble in water and release fluoride ions into it. Fluoride usually competes with other anions such as sulphate, chloride, carbonate, and phosphate for surface sites (García and Borgnino, 2015). In addition, various industries such as pesticides, ceramics, refrigerants, aerosol propellants, Teflon™ cookware, and glassware industries increase the load of fluoride in water. Fertiliser, iron, and aluminium manufacturing industries release fluoride as an unwanted byproduct (Peckham and Awofeso, 2014). Fluoride is considered to be a micronutrient for humans because it prevents dental caries by decreasing the rate of demineralisation of dental enamel or reverses the progression of existing decay by promoting the rate of remineralisation (Margolis and Moreno, 1990; Martinez-Mier, 2012). The process of demineralisation occurs during dental plaque metabolism in which acids (produced from the reaction of bacteria, saliva, and food) interact with surface dental enamel and remove minerals from it (Thylstrup and Fejerskov, 1994). Fluoride is a beneficial constituent, but this is only the case when its concentration in potable water is within the permissible limit (Jiménez-Reyes and Solache-Ríos, 2010). There are different international standards for fluoride in drinking water. According to the EU Council (1998), WHO (2011), and BIS (2012), the maximum acceptable limit of fluoride in drinking water is 1.5 mg/L, but this limit is 4 mg/L according to the USEPA (2009). Excess intake of fluoride can cause various diseases, such as osteoporosis, brittle bones, arthritis, cancer, infertility, thyroid disorder, and Alzheimer's syndrome (Wambu et al., 2013; Vinati et al., 2015; Tiwari et al., 2017a). Skeletal deformities occur over long-time consumption of drinking water with > 8 mg/L fluoride during adolescence. Fluoride can cause weakening of bones, leading to an increase in hip and wrist fractures. Some reports have mentioned that chronic fluoride toxicity occurs in the form of osteo-dental fluorosis in both children and adults.

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Individuals with kidney disease are at higher risk of fluorosis at even normal permissible limits due to their decreased ability to excrete fluoride in urine (Ghosh et al., 2013). Fluoride toxicity does not only have adverse effects on human health; it also affects animals and plants. Excessive intake of fluoride by animals can have toxic effects in reproduction, growth, thyroid hormones, learning and memory abilities, blood, and feeding efficiency (Dolottseva, 2013). The toxic action of fluoride in aquatic organisms is as an enzymatic poison, inhibiting enzyme activity and ultimately interrupting metabolic processes such as glycolysis and synthesis of proteins (Ghosh et al., 2013). Plants uptake fluoride from contaminated soil because it is highly soluble in acidic soils. The absorbed fluoride is translocated to shoots, causing physiological, biochemical, and structural damage and even cell death, depending on the concentration in the cell sap (Gupta and Mondal, 2015).

Fluoride contamination of drinking water has been recognised as a major public health hazard in many parts of the world (Lavecchia et al., 2012), such as China (up to 21.5 mg/L) (Ayoob et al., 2008), India (0.12–24.17 mg/L) (Jha et al., 2013), Pakistan (1.13–7.85 mg/L) (Rafique et al., 2009), and Thailand (0.01–14.12 mg/L) (Chuah et al., 2016). Fluoride enters the human body primarily through the consumption of fluoride contaminated drinking water (Sujana et al., 2009), and once absorbed in the blood, rapidly distributes throughout the body. The greatest proportion of the fluoride (almost 60% in adults and 80–90% in infants) is retained in calcium-rich areas such as bones and teeth because fluoride has an affinity for calcium phosphate. The rest of the fluoride is excreted via urine (Barbier et al., 2010). The tea plant (*Camellia sinensis* L.) is a known accumulator of fluorine compounds, which are released upon forming infusions such as the common beverage, and it can be considered a potential vehicle for fluoride dosing (Chan et al., 2013). High concentrations in tea can be caused by high natural concentrations in tea plants or by the use of additives during growth or fermentation (Ghosh et al., 2013). The fertilisers used to promote the growth of green tea trees inevitably cause significant fluoride accumulation in tea leaves. Thus, tea drinking populations are at increased risk of dental and skeletal fluorosis (Chan et al., 2013).Therefore, its remediation is very important (Singh et al., 2014), and there is an urgent need to seek out an efficient and emphatic defluoridation technology to prevent the negative effects on human health. Among the fluoride removal technologies, the adsorption process is a significant method for removing excess fluoride from potable water. This process has been used extensively by many researchers and has shown remarkable results. This paper presents a brief overview of the technical applicability of various adsorbents for the removal of fluoride from potable water.

Although excellent review articles have been published, these articles provide a somewhat scattered treatment of the topic because some discuss the importance of adsorbents for fluoride removal, others describe the adsorption capacity and pH (Tomar and Kumar, 2013; Velazquez-Jimenez et al., 2015), and yet others summarise the concentration range (Tomar and Kumar, 2013; Jadhav et al., 2015). Many studies have also focused on applicable isotherms and kinetics (Mohapatra et al., 2009; Bhatnagar et al., 2011; Habuda-Stanic et al., 2014; Vinati et al., 2015). The present review is a compilation of all the aspects of defluoridation, including fluoride adsorption capacity, removal efficiency, optimum pH, adsorbent dose, contact time, initial fluoride concentration, temperature, applicable isotherms and kinetics model, presence of co-anions, and reusability of adsorbent, including the detailed mechanisms of the influencing factors that affect the whole/partial process of adsorption. Additionally, based on the published data, this review highlights the least and most promising adsorbents according to their efficiency from each respective category.

2. Technologies for fluoride removal

Various techniques such as coagulation/precipitation methods, membrane processes, ion-exchange processes, and adsorption processes are used to remove fluoride from aqueous solution. Each technique has its own advantages, limitations, and influencing factors and works efficiently under ideal conditions.

2.1. Precipitation/coagulation

Alum and lime are the most utilised coagulants for defluoridation by the precipitation method (Waghmare and Arfin, 2015). The Nalgonda technique is the best example of a coagulation/precipitation method. It involves the addition of aluminium salts, lime, and bleaching powder to fluoride-contaminated water followed by rapid mixing, flocculation, sedimentation, filtration, and disinfection (Renuka and Pushpanjali, 2013). With the addition of lime and alum, the disinfection process takes place in the following steps: (a) insoluble aluminium hydroxide flocs form, (b) sediment sinks to the bottom, and (c) bleaching powder and fluoride co-precipitate (Bhatnagar et al., 2011). Although this method is effective for defluoridation, it may not be able to lower the fluoride concentration to a desirable limit (1.5 mg/L) (Ayoob et al., 2008). The precipitation technique is rarely used because of its high chemical costs, formation of sludge with a high content of toxic aluminium fluoride complex, unpleasant water taste, and high residual aluminium concentration.

2.2. Membrane process

A semi-permeable membrane is used in membrane processes between the adjacent phases (Velazquez-Jimenez et al., 2015) to serve as a barrier for suspended solids, pesticides, organic pollutants, inorganic pollutants, and microorganisms (Suneetha et al., 2015). Reverse osmosis, nanofiltration, dialysis, and electrodialysis are examples of this technique.

2.2.1. Reverse osmosis

Reverse osmosis is a physical phenomenon in which hydraulic pressure beyond the osmotic pressure applied to the higher concentration side of a semi-permeable membrane results in a flow of the solvent toward the less concentrated side (Wimalawansa, 2013). The selection of the membrane to be used for water purification depends on the recovery, cost, salt rejection, temperature, pressure, and characteristics of the water to be treated (Velazquez-Jimenez et al., 2015). Several researchers have studied reverse osmosis technology for the purification of water (Sara et al., 2013; Pontie et al., 2013; Bejaoui et al., 2014).

2.2.2. Nanofiltration

Nanofiltration is a process that has properties between the reverse osmosis and ultrafiltration. The required pressures for nanofiltration are lower than those for reverse osmosis, which reduces the energy costs. The permeability of nanofiltration membranes is also superior to those of reverse osmosis. Nanofiltration is suitable for reducing the hardness of water because the membranes have high retention capacity for charged particles, especially bivalent ions. This technique appears to be the best method of all membrane processes for fluoride removal due to the high and specific membrane selectivity (Tahaikt et al., 2007).

Diawara et al. (2011) compared the efficiency of nanofiltration and low pressure reverse osmosis (LPRO) membranes for removal of fluoride and salinity from brackish drinking water. They observed that nanofiltration membranes are more efficient than LPRO membranes if the drinking water to be treated has fluoride and salinity concentrations slightly above the WHO permissible limits. In the opposite case, LPRO membranes are more effective than nanofiltration membranes. Hoinkis et al. (2011) studied the performance of two commercial nanofiltration membranes, i.e. NF 90 and NF 270, for the removal of fluoride from surface and groundwater. The results demonstrated that the NF 270 membrane was able to reduce fluoride to 1.5 mg/L from an initial concentration of 10 mg/L and that the NF 90 membrane was efficient