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A review on the sorptive elimination of fluoride from contaminated wastewater

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ABSTRACT

Biosorption is considered to be one of the favourable remediation techniques for fluoride removal from aqueous solutions. Other conventional techniques such as precipitation, reverse osmosis, ion exchange, nanofiltration etc, have several demerits such as huge initial costs, higher electricity consumption, generation of sludge, etc. The process of biosorption has become an economically feasible and environmentally benign alternative technique in the treatment of water and wastewater industries owing to the disadvantages associated with above-mentioned techniques. In this regard, numerous biosorbents have been developed for their successful implementation on defluoridation. Due to various technical barriers in the biosorption process which hinder its commercialization, there has been a steadily growing interest in this area of research. Of late more attention is being paid towards the development of cost-effective adsorbents using various agricultural wastes, plant biomass, bacteria, algae and fungi. This review paper highlights the use of various biosorbents, sorption isotherm, and kinetics. Literature review indicates the potentiality of such wastes as biosorbents for fluoride removal. Maximum fluoride removal of 91% was obtained by lanthanum-modified bone waste with a biosorption capacity of 8.96 mg/g which is reportedly the highest till date. However, it is important to determine whether these biosorbents could be used on the commercial scale which, in turn, might result in controlling pollution.

1. Introduction

Fluoride contamination in groundwater has been taking a heavy toll on human life with only about 2.5 billion people having access to safe and consumable water [1]. Fluorine exists as fluoride in nature and is the most reactive of all chemical elements. Several health hazards are associated when the fluoride concentration in water either exceeds or goes below the prescribed limit of 1.5 mg/L. The influence of fluoride on human health can be either advantageous or deleterious based on the concentration and dietary intake. Trace amounts in water are required for the prevention of cavity formation but when the concentration goes beyond the permissible limit, it causes crippling skeletal fluorosis [2]. WHO (World Health Organization), IS (Indian Standard), USEPA (U. S. Environment Protection Agency) and EU (European Union) have prescribed the acceptable limit of fluoride as 1.5 mg/L, 1.0 mg/L, 4 mg/L and 1.5 mg/L respectively [3,4]. Fluoride is extensively dispersed in the ecological environment which is released into groundwater due to the presence of fluoride-rich rocks [5]. Fluoride laden rocks composed of biotite, a fluorinated compound, increases the concentration beyond 4 mg/L in groundwater [6–8]. Apart from natural sources, various industrial operations like phosphate mining, zinc and aluminium smelters, etc. also contribute to an increase in fluoride concentration in groundwater [5]. Certain reports suggest that fluoride might hinder the synthesis of DNA [9]. Toxicity of fluoride might take place in several ways. For example, when the fluoride is consumed it acts on the intestinal mucosa which can form hydrofluoric acid in the stomach resulting in gastro-intestinal irritation [10]. The actions of several enzymes are also inhibited by fluoride which upsets the mechanisms of glycolysis, oxidative phosphorylation and coagulation [10]. Extremely high concentrations of fluoride are sometimes related to bladder cancer, predominantly among workers working in fluoride-induced conditions [5]. Therefore, considering the harmful effects of fluoride on human, an effectual and robust technique is the need of the hour to curb the problem associated with excessive fluoride in water.

Precipitation, reverse osmosis [11], ion exchange [12], Nalgonda technique (chemical precipitation) [12], electrodialysis [12], etc are some of the processes reported for defluoridation. In both cases of precipitation and reverse osmosis, two major drawbacks are associated viz., in absence of piped or continuous water supply, it is difficult to arrange the essential flow through the system and gradual exhaustion of the active agent is not easily detected [13]. Therefore, the Nalgonda technique was adopted to overcome these drawbacks. Advantages like

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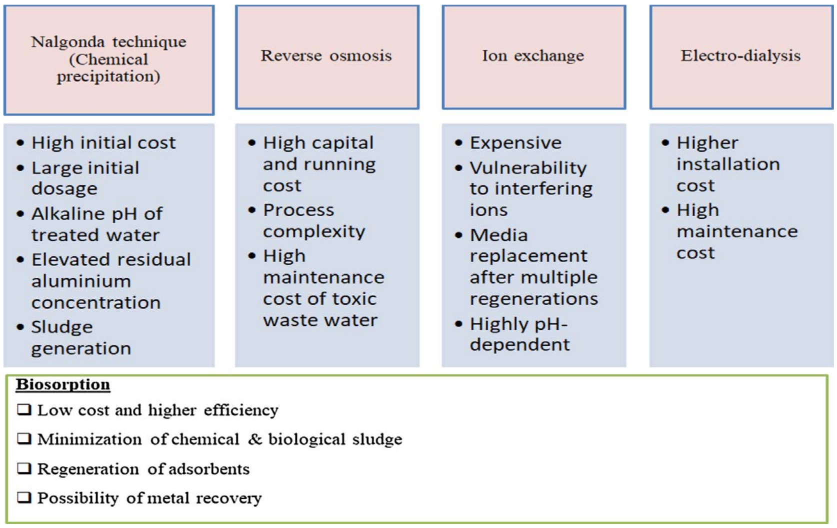

Fig. 1. Precedence of biosorption over other techniques of defluoridation.

non-requirement of media regeneration, easy availability of chemicals, no usage of caustic acids and alkalies, conversion of generated sludge into alum to be used elsewhere etc. Shortcomings of the process include desalination of the water if the concentration of total dissolved solids goes beyond 1500 mg/L, addition of huge amounts of alum for fluoride removal, cautious pH monitoring of the treated water etc [13]. This technique can be accepted only when the concentration of total dissolved solids is below 1500 mg/L, hardness of the water is maintained within 600 mg/L and the fluoride concentration in the contaminated water is within the range of 1.5–20 mg/L [14]. In ion-exchange, the method of regeneration of anion and cation exchange resins involve large amount of the regenerant. Generation of waste is higher as well. Moreover, the resins are quite complex, susceptible to contamination and expensive [14]. Electrodialysis is defined as an electro-membrane process designed to remove salt from brackish water. The major disadvantages of the system include higher water consumption, excessive energy consumption and higher capital costs [15]. Fig. 1 presents an overview of the advantages of biosorption over other techniques of fluoride removal.

Among the afore-mentioned methods, biosorption appears as a preferable choice owing its lower operational cost, lesser sludge generation, regeneration of spent sorbent, no additional nutrient requirement, local availability of raw materials, chances of metal recovery etc [16]. This review paper aims towards discussing on the biosorption mechanism, various equilibrium studies, kinetic models, thermodynamics and instrumental tools and techniques used in fluoride sorption. A summary of various biosorbents used for defluoridation as per literature review has also been discussed.

2. Biosorbent materials

Till date, various materials have been used as biosorbents towards defluoridation of contaminated water which can be broadly categorised into various subsections like bacteria, algae, fungi, agricultural wastes and products etc. Various types of microbial biomass such as algae, fungi and bacteria can serve as the foundation of a new, potent, fluoride-sequestering biosorbents. Biosorbents are known to exhibit higher uptake capacity for the contaminant of choice [17]. Metal binding is usually considered a two-step process wherein, interaction between the contaminant ion and the reactive chemical groups in the cell wall is a stoichiometric one and secondly, deposition of enhanced quantities of contaminant ions. Such metal ions come across the cell wall before getting accessibility to the cell cytoplasm and plasma membrane. The cell wall is composed of several polysaccharides and proteins which offer many binding sites for the contaminant ions [18]. In many cases, the contaminant bound onto the biosorbent can be eluted and the biomass can be regenerated to be used in multiple sorption-desorption cycles. Usually, the physical and mechanical characteristics of a biomass decides the number of cycles and re-usability of the biosorbent. Immobilization technique often helps in enhancing the particle size, particle strength and resistance to various chemicals and microbial degradation. Often, granular biosorbents are somewhat similar to ion-exchange resins in many aspects, including their practical applicability in metal remediation or recovery processes. However, the use of dead microbes is more preferable than live ones since it abolishes the periodical maintenance of live culture comprising supplying of nutrients, observing the maximum tolerable limit of the species, other microbial contamination etc. In many situations, better uptake capacities of the non-living biomass have been observed as compared to live ones. As such, selection of a particular biosorbent depends on its efficiency and feasibility to remove or recover the contaminant from wastewaters. Algae are considered as an inexpensive source of biomass due to their ubiquitous distribution. It is said that alginate in the cell wall is the key component in the biosorption process. Alginates comprise mannuronic and guluronic acid units in the algal cell wall which have carboxylic acid in their structures. This carboxylic acid is directly related to the metal binding capacity of algae. Cyanobacteria have certain advantages over other microorganisms due to their excess extracellular mucilage with better binding affinity, enhanced surface area and simple nutrient requirements [6]. Fluoride uptake by dried biomass of several algal species such as *Spirogyra* IO1 [19], *Spirogyra* IO2 [20], *Ulva fasciata* [21], *Nostoc* sp. BTA394 [6] etc. have been reported among which the live biomass of *Nostoc* species were pre-treated with calcium. As per reports [192], the carboxylic group binds with divalent cations like calcium and helps in stabilizing the internal structure of the alginates due to dimerization of the guluronic acid unit chains. This binding often aids in the formation of an alginate gel which, in turn, enhances the biosorptive capacity of the algal biomass. Concentrations and kinds of the contaminant are also important to be considered for opting the most suitable and viable biosorbent. Bacterial cell walls have peptidoglycans as their chief constituent which are composed of linear chains of disaccharide *N*-acetylglucosamine-1, 4-*N*-acetylmuramic acid with peptide chains. It is said that Gram-negative bacteria have thinner cell walls than that of Gram-positive bacteria and are usually not cross-linked heavily. Gram-negative bacteria have an outer layer of lipopolysaccharide, phospholipids and proteins [22]. Studies suggest that fluoride contamination in groundwater is often a result of microbial activities since they have the ability to dissolve the fluoride-containing minerals at a very rapid rate, thereby releasing fluoride ions into the water [23,8]. Due to insufficient information on the reaction kinetics of