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Fluoride removal from water

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ABSTRACT

According to published research, drinking water is a limited and valuable resource that must be protected from contamination. In addition, it must be used with caution and moderation. The abundance of fluoride-bearing rocks in the ground causes fluoride to leach and harm nearby water resources and soil, according to published research. Groundwater can contain concentrations of fluoride ions, up to 30 mg/L. Many of the severe and harmful effects in our data result from this excessive fluoride ion concentration. When fluoride ions are ingested at higher doses (20–80 mg/day) over a period of 10–20 years, they cause skeletal fluorosis and other disabilities. There is growing concern about the advance of fluoride remediation technology globally in the current environment. In this review study, we focused on the relationship between high fluoride ion concentrations and their products, their health effects, and methods for their removal.

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1. INTRODUCTION

The purity of water is scared and gets always contaminated by several pollutants. Fluorine is one of such contaminants that contaminate water all place around the universes. The primary wellsprings of disintegration of fluoride in the ground water are delicate rocks that contain fluoride. The industrial effluents from aluminum, phosphate, semiconductor, glass and ceramic, fertilizer, uranium, electroplating, toothpaste manufacturing units and coal plant adds fluoride to the ground water [1]. The other source of fluoride intake for human beings are water, air, food, cosmetic and medicine. The

permissible limit of fluoride was 1.5 mg/l and 1.0 mg/l for India as set by the World Health Organization (WHO). Apart from fluorosis, excess fluoride in water causes diseases like cancer, damage kidney-liver nervous systems, thyroids, respirator problems, Alzheimer, reduce pregnancy. The fluorosis were pervasive among the 200 million people groups from more than 30 nations over the globe [2]

Many methods have been developed for fluoride removal from water such as adsorption [3], ion exchange [4], membrane processes such as reverse osmosis and nano filtration [5], [6], electro dialysis [7], [8], and precipitation [9]. Among these methods, adsorption is a widely used method for defluoridation which depends on ions (adsorb ate) in fluid diffusing to the surface of a solid (adsorbent) when they are bound to the solid surface or are held there by weak intermolecular forces [10]. Adsorption is recognized as the most efficient, promising, and widely used fundamental approach in water and wastewater treatment processes [11]. Different adsorbents such as activated alumina [12], bleaching earth [13], iron oxide [14], activated titanium rich bauxite [15], activated carbon [16], red mud [17], and clay [18], [19] were tested to find out efficient and economically viable defluoridating ones. Among these adsorbents, clay and clay minerals are naturally abundant, renewable, and environmentally sustainable [20], [21]. In recent years, considerable amount of work has been done on activation of clay and clay minerals to improve the adsorption capacity and hence removal efficiency [22], [23] the present study described the overview of various way to reduce fluoride Proponents of adsorption technology argue that the technique is economical efficient and produces high quality water. The removal of fluoride by adsorption methods has been widely studied in recent years and interest is growing in the use of high-valency metals to functionalized sorbents [24]. Adsorption of fluoride on to solid absorbant usually occurs through three phases [25]:

- (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). 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 [26].

Adsorption studies pointed most important characteristics which determined adsorbent suitability for practical application: adsorption capacity, selectivity for fluoride ions, regenerability, compatibility, particle and pore size, and cost while fluoride removal efficiency always depends on raw water quality profile, i.e., initial fluoride concentration, pH, temperature, contact time and adsorbent dosage [27].

2. METHODOLOGY

2.1 Technologies for Fluoride Removal from Water Membrane Process

[28] Although various conventional techniques of water purification described earlier are being used at present to solve the problem of groundwater pollution, none of them is a user friendly and cost effective technique due to some or the other limitations and has either no or very long payback period Show in Figure 1. RO membrane was totally regenerated in every set of experiments. Nano-filtration makes use of a similar overall development as reverse diffusion. For nano-filtration, the membranes have slightly larger pores than those used for reverse diffusion and provide less resistance to passage each of solvent and of solutes. As a consequence, pressures needed are a lot of lower, energy needs are less, removal of solutes is far less complete, and flows are quicker. The property of nano-filtration relative to reverse diffusion may be a specific advantage, and experimental and theoretical analyses are being dedicated to getting a mechanism of substance retention to facilitate production and choice of targeted membranes in addition to optimization of conditions.

[29] Fluoride removal by means of ion exchange technology using anion exchange resins is difficult, since the order of selectivity for anionic species by anion-exchanger resins is as follows: Citrate > SO24 > oxalate > I> NO3 > CrO2 4> Br> SCM > Cl > formate > Acetate > Fconsequently The cation/chelating type resins were equally employed for sorption of fluoride. Research work on fluoride removal has been carried out using metal loaded cation exchangers such as silica gel and alumina gel or chelating resins where high valence metal such as irons (III), Lanthanum (III), Cerium (IV) and Zirconium (IV) have been loaded as The fluoride removal capacity of the resin IND may be controlled by an adsorption mechanism. The equilibrium data agree with both Freundlich and Langmuir isotherms.

[30] Gas concrete waste materials were used to remove fluoride from aqueous solutions. The influence of pH, temperature, agitation rate and gas concrete dosage on fluoride removal was investigated by conducting a series of batch adsorption experiments. In this study, fluoride removal in excess of 96% was obtained. It was thought that the removal of fluoride by gas concrete took place both adsorption and precipitation of Al3+ and Ca2+ salts (fluoride). As a result of this study, it was concluded that wastes of gas concrete were an efficient adsorbent for the removal of fluoride. The Fluoride removal up to 96% was obtained. It was found that the amount of fluoride adsorbed on gas concrete efficiently depends on pH, and weakly agitation rate and temperature.

Chemical Methods

[31] The objectives of this study are to assess the feasibility of using the cement paste as an alternative agent for fluoride removal and to investigate fluoride removal capacity of the cement paste. The cement paste was competitive to lime, common fluoride removal agent. Various Ca bearing hydrates such as portlandite, calcium silicate hydrate (CSH), and ettringite in the cement paste were identified to remove fluoride by precipitating CaF2 and/or adsorbing F– ions. In the batch slurry experiments using cement paste and lime simultaneously, 50–67% of lime can be substituted by cement paste to satisfy fluoride effluent limitation of 15 mg/L. Fluoride removal reactions in cement paste slurries were strongly affected by pH, and an optimal pH for the cement paste slurries exists between 7.0 and 11.5. From the result of the column experiment to observe the successive fluoride removal capacity of cement paste, the real hydrofluoric acid wastewater concentration of 1150 mg/L immediately reduced to the level of less than 15 mg/L. These results indicate that the cement paste generally has advantageous characteristics as an economical and viable substitute for lime to remove fluoride.

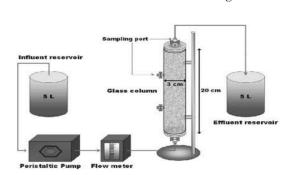


Figure 1. Schematic diagram of the column apparatus

Adsorption

[32] Adsorption of fluoride onto fired clay pots from Cameroon has been studied in detail. Fired clay is composed of different oxides. Kinetic studies reveal that equilibrium is attained within 10 min whatever the pH studied. The maximum adsorbed fluoride is 1.3 mg/g at a stirring speed of 120 rpm. Adsorption follows pseudo-second-order and both the surface adsorption and intra particle diffusion contribute to the rate determining step. Freundlich isotherm fits the adsorption data adequately. The

effect of ionic strength has a significant effect on fluoride adsorption. Being a useless and abundantly available material, fired clay pots can be used for industrial application for removing fluoride from water.

[33] Also investigated the possibility of fluoride removal from model water using aluminum oxide coated pumice. Initial fluoride concentrations were between 1.5 mg/L and 5.0 mg/L and adsorption time was approximately 1 h, while adsorbent dose was 10 mg/L. The equilibrium adsorption of fluoride by aluminum oxide coated pumice conformed reasonably to five isotherm models in the order: Generalized model > Langmuir type 2 > BET > Temkin > Dubinin-Radushkevich; with a maximum capacity of 7.87 mg/g. Efficient fluoride removal was obtained within the pH range of 6–9, which makes it possible to avoid pH adjustment of treated water which implies additional cost and operational difficulties during water treatment. Based on the results of kinetic adsorption experiments, authors emphasized that at a neutral pH = 7.0 which is a more suitable condition for groundwater treatment, fluoride adsorption by aluminum oxide coated pumice was faster in the initial period of contact. The effects of different parameters such as pH (6-9), initial fluoride concentration (1.5-13 mg/L), contact time (0.5–24 h) and co-existing ions (bicarbonate, sulfate, chloride, nitrate) on fluoride adsorption onto magnesium substituted HAP were studied [34]. The authors reported that maximum measured fluoride uptake of synthesized magnesium substituted HAP was 2.66 mg/g, emphasizing that, within 30 min, 25.68% of fluoride was removed, while equilibrium waseached in less than 24 h with 47.94% removal. The fluoride removal from aqueous solution using magnesium substituted HAP showed significant dependence of initial fluoride concentration, contact time and pH while the presence of co-existing anions does not affect the defluoridation capacity.

[35] In a batch defluoridation study, fluoride-sorbent local materials such as crushed burnt clay pot, home ash, Keren, and Adigerghish soil were examined. We looked at the effects of fluoride concentration, particle size, contact time, pH, and adsorbent quantity. The ideal pH for home ash was 4, whereas the ideal pH for crushed burnt clay pot, Keren, and Adigerghish soil was 7, which was influenced by the pH of the water. Nonetheless, the equilibrium time was 120 minutes, and the contact duration was comparable. In the case of the crushed burnt clay pot, particle size had no discernible impact; nevertheless, fine particles outperformed coarse particles in the other three materials. Crushed burnt clay pot has a higher capacity than the others, according to the study's assessments of fluoride adsorption. On average, it was able to remove 0.26 mg of fluoride per gram of medium. For the same mass of 7 g, others ranged between 0.08 and 0.1 mg/g; hence, crushed burnt clay pot was chosen for defluoridation.

[36] Zirconium-attapulgite adsorbent has been synthesized and used for fluoride adsorption. The fluoride adsorption capacity of the Zr attapulgite adsorbent was higher in comparison with attapulgite, which was due to the changes of the surface charge of the adsorbent and the generation of abundant hydroxyl ions. The Zr-attapulgite adsorbent exhibited good performance for fluoride removal over a wide pH range of 3.70–7.50. Adsorption of fluoride reached the equilibrium in 110 min for different initialfluoride concentration. The equilibrium data were better represented by the Langmuir isotherm than the Freundlich isotherm. The adsorption process followed the pseudo-second-order model for fluoride; fluoride adsorption was influenced by the phosphate, sulfate and bicarbonate ions, but not by chloride and nitrate ions. The results of desorption and reuse experiments indicated that the Zr-attapulgite adsorbent could be employed as a promising adsorbent for fluoride adsorption from drinking water.

Nanotechnology

Materials with smallest dimensions ranging from a few nanometers to less than 100 nanometers are known as nano materials. On the nanometre scale, the properties of materials are size dependent and materials with higher surface to volume ratios possess high catalytic activities. The unique properties of materials on the nano scale can be utilized to address some of the most pressing environmental problems such as water pollution, air pollution and oil spill remediation. The potential application of

nano materials in water purification systems as reported in literature over the years are reviewed below under the headings; adsorption, photo catalysis and microbial disinfection.

[37] investigated the possibility of fluoride removal using a nano-adsorbent bimetallic oxide adsorbent synthesized by co-precipitation of Fe (II) and Ti (IV) sulfate solution using ammonia titration at room temperature. The influences of the washing and drying methods, Fe/Ti molar ratio, and calcination temperature used in the preparation on the morphology, crystallization, surface structure and adsorption capacity were investigated. Experimental results show that a Fe-Ti bimetallic oxide adsorbent had a Langmuir adsorption capacity of 47.0 mg/g, which was much higher than the adsorption capacities reported for a pure Fe oxide or Ti oxide adsorbent. Authors explained this as being a synergistic interaction between Fe and Ti in Fe-O-Ti bonds on the adsorbent surface and hydroxyl groups which provided the active sites and formation of Fe O-Ti-F bonds and economical fluoride removal from drinking water.

[38] this study investigated the removal fluoride ions from aqueous solution using chemically (sulfuric acid) activated C. edulis stems under the batch adsorption mode. Four factors such as the adsorbent dose, contact time and pH of solution were used in factorial experimental design under adsorption study. Te maximum fluoride removal of 73% was recorded at the optimum condition of adsorbent dose of 1.5 g in 100 mL, contact time 60 min and pH 2, whereas the model based predicted value of the fluoride removal under the same experimental condition was 69%. Fluoride removal was positive and strongly influenced by the adsorbent dose whereas the adsorption pH was negatively and weakly impacted on the removal. Removal of fluoride was effectively achieved using chemically modified of C. edulis. The results showed significant fluoride removal under the specific study condition.

Biopolymer

[39]. Chitosan has a number of commercial and possible biomedical uses. And its deacetylated product chitosan has been widely used for metal adsorption from water and wastewater, but the application of these materials as an adsorbent to remove fluoride from drinking water has seldom been explored. Chitin is an interesting and abundant polysaccharide, found in a wide range of organisms including bacteria and fungi but commercially most commonly extracted from shellfish processing waste. It is generally considered the most abundant biopolymer in the ecosphere after cellulose, which it resembles structurally. Chitosan is a copolymer of 2-glucosamine and N-acetyl-2-glucosamine derived from chitin by deacetylation reaction in hot alkali. The chitosan is mainly obtained from crustacean shells of prawn, crab, shrimp or lobster and has the ability to coordinate metal ions because of its high concentration of amine functional groups .It is also a non-toxic biodegradable and biocompatible material. In spite of its abundant use the adsorption ability of chitosan has not been realized to a satisfying level because chitosan flake or powder swells and crumbles and hence often unsuitable for use in an adsorption column. Chitosan also has a tendency to agglomerate or form a gel in aqueous media although the amine and hydroxyl groups in chitosan are mainly responsible for adsorption these active binding sites are not readily available for sorption when it is in a gel or in its natural form. The adsorption capacity can be enhanced by spreading chitosan on physical support that can increase the accessibility of the adsorbate-binding sites. Many scientists have done work on the applicability of chitin, chitosan and 20% lanthanum incorporated chitosan (20% La-chitosan) as adsorbent removal of excess fluoride concentration from drinking water. This adsorbents show excellent removal of fluoride from water that is much better than bare chitosan and chitin.

[40]. Titanium hydroxide-derived adsorbents, synthesized in a titanium hydroxide gel form, showed high adsorption abilities for fluoride ions, and its good adsorption characteristics and selectivity were noted even in the presence of coexisting chloride, nitrate and sulfate ions. The adsorbent could remove fluoride ions below 0.8 mg/L from solution with an initial fluoride concentration of 50 mg/L.

operation

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Figure 2. Comparison between Several Technologies of Fluoride Removal [26]

3. CONCLUSION

This review has attempted to cover a wide range of adsorbents which have been used so far for the removal of fluoride from the water and wastewater. Various technologies are currently available to remove fluoride from water, but adsorption processes are generally considered attractive because of their effectiveness, convenience, ease of operation, simplicity of design and for economic and environmental reasons. Performance comparison of different adsorbents is difficult because of inconsistencies in the data, principally due to different experimental conditions (pH, temperature, ionic strength, particle size, initial fluoride concentration, presence of competing ions, etc.). The pH of water is a dominant factor influencing fluoride adsorption. Generally, fluoride adsorption increases from acidic to near neutral pH and then decreases with increase in pH. Another highly important factor influencing fluoride adsorption is the type and concentration of other ions present in treated water, i.e., the adsorbent's selectivity for fluoride ions since they can occupy adsorbents' active sites and thereby reduce theoretical adsorption capacity.

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