Review Article

Defluoridation of Water Using Natural Adsorbents

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Abstract

Fluoride is often called a two-edged sword. In the human system, this fluoride has a dual personality, a destructive effect (>1.5 ppm – dental and skeletal fluorosis), and a beneficial effect (up to1.0 ppm – caries prevention and health promotion). World Health Organization recommends that the fluoride content in drinking water should be in the range of 1.0–1.5 ppm. Fluoride concentrations beyond the standards cause dental and skeletal fluorosis. Among various methods used for defluoridation of water, adsorption method is relatively simple, economical, and appropriate for drinking water treatment, especially for small communities. In this review, a list of various adsorbents and their adsorption capacities for fluoride are overviewed with various affecting parameters.

Keywords: Adsorption, fluoride, low-cost adsorbent, water

Introduction

Fluoride-related health hazards are considered to be a major environmental problem.[1] In India, 25 million people in 19 states and union territories have already been affected, and another 66 million are at risk including 6 million children below the age of 14 years.[2]

Defluoridation is the process of removing excess, naturally occurring fluorides from drinking water to reduce the prevalence and severity of dental fluorosis. World Health Organization in 1963 has recommended that the optimum limit of fluoride in drinking water for the prevention of dental caries is 0.7–1.2 ppm. India, the work on defluoridation was taken up by NEERI at Nagpur, Maharashtra, India in 1961 where various methods for removal of fluoride from potable waters have been tried. Defluoridation methods can be broadly divided into three categories according to the main removal mechanism: (1) chemical additive methods, (2) contact precipitation, and (3) adsorption/ion exchange methods. Among all available methods, adsorption is considered to be simple, economical, and globally pursued technique.

Adsorption is typically used in wastewater treatment to remove toxic or recalcitrant organic pollutants (especially halogenated but also nonhalogenated), and to a lesser extent, inorganic contaminants, from the wastewater. Researchers in recent year argue that the adsorption technique is economically efficient and produces good quality water.

A typical adsorption process has four steps: (1) addition of feed solution and the adsorbent solid particles; (2) good mixing to enhance the transfer of solutes from the liquid phase to the surface area of the adsorbent solid particles; (3) separation of the adsorbent plus adsorbate (solute) from the bulk of solution; (4) removal of adsorbed solute from the surface of the solid adsorbent using a different solvent. This is called elution of solute and the solvent is called elution solvent; and (5) at steady-state adsorption conditions, there is a physical equilibrium between the concentration of solute in the liquid.

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.[3-8] Processed materials such as activated alumina, activated carbon, bone char, defluoron-2 (sulfonated coal), and synthetic materials such as ion exchange resins have been extensively evaluated

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for defluoridation of drinking water. Among these materials, bone char, activated alumina, and calcined clays have been successfully used in the field.[9-11]

Objective of Review

The aim of this paper reviews the development of waste materials adsorbents as non conventional alternative for fluoride removal.

Review of Natural Waste Adsorbents

Low-cost adsorbents

Different low-cost adsorbent materials are available for effective removal of fluoride from water. The naturally available adsorbents are horse gram powder, ragi powder, multani mitti, red mud, calcined clay, concrete, pineapple peel powder, chalk powder, orange peel powder, rice husk, *Moringa oleifera* extract (MOE), gooseberry, activated alumina-coated silica gel, activated sawdust, activated coconut shell carbon, coffee husk, bone charcoal, activated soil sorbent, etc., are some of the different materials investigated for adsorptive removal of fluoride from water.

Singh *et al*.[12] "studied the defluoridation of drinking water using brick powder as an adsorbent, freshly fired brick pieces are used for the removal of fluoride in domestic defluoridation units." The brick bed in the unit is layered on the top with charred coconut shells and pebbles. Water is passed through the unit in an up-flow mode. It is reported that efficiency depends on the quality of the freshly burnt bricks. The unit could be used for 2540 days, when withdrawal of defluoridated water per day was around 8 L and raw water fluoride concentration was 5 mg/L.

Dobaradaran *et al*.[13] studied fluoride removal from aqueous solution using shrimp shell waste by batch experiment. Investigator reported that, for an initial F concentration of 8 mg/L, the removal percentage of F increased with increasing adsorbent dose from 3.2 g/L to 64 g/L. The maximum removal of 80% was obtained at pH 11 with 15 min of contact time and adsorbate dose of 8 mg/L. The investigator reported that shrimp shell waste exhibited a high defluoridation capacity within few minutes of contact time as compared to other adsorbents.

McKee and Jhonston[14] studied the removal of fluorides from drinking water using activated carbon prepared from various raw materials (rice husk and wheat husk) exhibits good fluoride uptake capacity. However, the adsorption process is highly pH dependent and is effective at pH <3.0 and there is little removal at neutral pH of 7.0. A maximum of 83% removal could be accomplished by rice husk and attains almost an equilibrium condition in nearly 180 min (3 h). Removal of fluoride by rice husk decreased continuously as pH was increased from 2.0 to 12.0 as depicted decrease in the removal of fluoride in pH range of 2.0–10.0 was low, i.e., 12.8%, whereas removal of fluoride decreased significantly from pH 10.0 to 12.0. The amount of fluoride adsorbed increased with increase in dose and maximum 84% removal was accomplished at a dosage of 6 g/L.

Mohammad and Majumder[15] investigated feasibility of three low-cost biomass-based adsorbents, namely, banana peel, groundnut shell, and sweet lemon peel for industrial waste water defluoridation at neutral pH range. The banana peel, groundnut shell, and sweet lemon peel removed 94.34, 89.9, and 59.59% of fluoride, respectively. Contact time for banana peel, groundnut shell, and sweet lemon peel is 60.0, 75.0, and 40 min, respectively, at doses of 14, 12, and 16 g/L, respectively. Action of these adsorbents on fluoride was compared with commercially available adsorbents. It was found to be much better, high removal efficiency at higher concentration (20 mg/L) of fluoride in industrial waste water.

Vardhan and Karthikeyan[16] studied the removal of fluoride from water using low-cost materials by the use of bone charcoal or bone char (carbonized animal bone) is reported to be an effective means for the reduction of fluoride. Bone charcoal contains a carbon structure while supporting a porous hydroxyapatite matrix (a calcium phosphate hydroxide in crystalline form which is rich in surface ions which can be readily replaced by fluoride ion). Regeneration of this material can be accomplished by a 2% sodium hydroxide rinse and a backwashing cycle. Reduction of fluoride using bone charcoal is somewhat pH dependent; the challenge water should be below 6.5 pH to suppress any ion competition. Fluoride removal was 100% in initial 4 h in case of the two flow rates 10 ml/min and 5 ml/min. Effluent fluoride concentration dose to 1 mg/L in 8.3 h in case of the flow rate which was maintained at 10 ml/min, whereas for the effluent fluoride concentration to reach 1 mg/L, it took 15 h at a flow rate of 5 ml/min. Further to reach 100% exhaustion, it took 13 h and 40 h, respectively, for flow rates of 10 ml/min and 5 ml/min.

Gandhi *et al*.[17] conducted a study on adsorbents such as concrete, ragi seed powder, red soil, horse gram seed powder, orange peel powder, chalk powder, pineapple peel powder (PPP), and multani mitti. The experimental setup was bath studies. Result indicated fluoride removal efficiency of 86% for chalk powder and pineapple peel powder. Seventy-nine percentage and 75% for horse gram seed powder, respectively. Percentage removal for ragi seed and red mud was found to be 65% and 71%. Removal efficiency was recorded less for multani mitti and concrete which was 56% and 53%.

Vardhan and Karthikeyan[18] carried out investigations for removal of fluoride from water employing physicochemical processes of adsorption and coagulation employing abundantly available and low-cost materials such as rice husk, seed extracts of *M. oleifera* (drumstick), and chemicals such as manganese sulfate and manganese chloride. Rice husk of 6 g/L accomplished a removal of 83% of fluoride from a 5 mg/L of fluoride solution requiring an equilibrium time of 3 h. Equilibrium isothermal data fitted well into rearranged linearized Langmuir adsorption model. *M. oleifera* seed extracts, manganese sulfate, and manganese chloride accomplished removal percentages of 92, 94, and 91 of fluoride from a 5 mg/L test solution at a dosage of 1000 mg/L. A slightly acidic pH of 6.0 was found favorable for fluoride removal by manganese sulfate, manganese chloride, and MOE.

Bhaumik *et al*.[19] investigated eggshell powder as a medium of fluoride removal from aqueous solution. Fluoride adsorption was studied in a batch system. The researchers reported that the maximum adsorption occurred at pH 2.0–6.0. Experimental equilibrium data provided best fit with the Langmuir isotherm model, indicating monolayer sorption on a homogeneous surface (maximum monolayer sorption capacity was 1.09 mg/g at 303 K). The activation energy of the adsorption process (Ea) was found to be 45.98 kJ/mol using Arrhenius equation, indicating chemisorption nature of fluoride onto eggshell powder also. Thermodynamic analysis suggests that removal of fluoride from aqueous solution by eggshell powder was a spontaneous and exothermic process. The present findings suggest that such eggshell can be used as a waste adsorbent; it also can provide a simple, effective, and low-cost method for removing F-form contaminated water.

Patil Satish *et al*. (2013)[20] performed batch study to investigate the efficacy of treated natural adsorbents such as mangrove plant leaf powder (MPLP), almond tree bark powder (ATBP), PPP, Chiku leaf powder (CLP), toor plant leaf powder (TPLP), and coconut coir pith (CCP). Researchers reported the effect of pH, contact time, adsorbent dose, and initial metal ion concentration to remove fluoride ions from the aqueous solutions. Uptake of fluoride ions by adsorbents at equilibrium is found to be in the order of MPLP > CCP > TPLP > CLP > PPP > ATBP. The optimum contact time for all the adsorbents was 60 min with an adsorbent dose of 10 g/L for initial fluoride concentration of 5 ppm. The highest percentage removal was found at pH 2.

In Pandey *et al*.'s,[21] this work was based on search of Biomass *Tinospora cordifolia* as bioadsorbent for removal of fluoride from wastewater. The efficiency of the sorption process was investigated under batch different experimental parameters such as pH 7, standing time 120 min, and biomass doses 7.0 g with 5 mg/L concentration of fluoride. Neutral pH was identified as the optimum condition of the medium and 120 min was the best contact time for maximum fluoride adsorption. The experimental data were found good fitting to Langmuir and Freundlich isotherm models. The maximum removal efficiency of 70% was reported at pH 7.

Mondal *et al*.[22] conducted a comparative study for removal of fluoride using activated silica gel (ASiG) and activated rice husk ash (ARHA) as adsorbents through batch studies. The authors reported that both adsorbents were efficient for the uptake of fluoride at pH 2.0 and contact time 100 min. ASiG was found to be more efficient than ARHA with an initial fluoride concentration of 5 mg/L; percentage removal efficiency was 88.30 and 96.7 for ARHA and ASiG, respectively. The study on equilibrium sorption revealed that Langmuir isotherm model give best fit to experimental data.

In Veeraputhiran and Alagumuthu[23] studied "treatment of high fluoride drinking water using bioadsorbent." The *Phyllanthus emblica* sample (powdered seed), common name, Indian gooseberry material, was dried at 378–383 K for 24 h. It was washed with doubly distilled water to remove the free acid and dried at the same temperature for 3 h. Later, the dried adsorbent was thermally activated in muffle furnace at 1073 K (here we avoid acid treatment for charring). The resulting product was cooled to room temperature and sieved to the desired particle sizes. Finally, the product was stored in vacuum desiccators until required. The adsorption of fluoride increases with time and gradually attains equilibrium after 75 min. At neutral pH, the success rate of defluoridation was observed as 82.1% for the 3 ppm initial fluoride concentration at the optimal adsorbent value. Furthermore, the presence of bicarbonate ions interferes the defluoridating property of this adsorbent, but this interference is insignificant for other co-anions.

Ramesh *et al*.[24] studied "batch and column operations for the removal of fluoride from aqueous solution using bottom ash." A batch and column studies will be carried out for the removal of fluoride from aqueous solution using bottom ash as adsorbent. The bottom ash is a waste material obtained by thermal power generation plants after combusting solid fuels. It is an undesired collected material, which is transported and dumped near the surrounding land. The equilibrium time decreases with the temperature without much increase in fluoride ion uptake. The time to reach equilibrium was slightly affected by the temperature of fluoride solution. Maximum adsorption by the bottom ash was observed at pH 6.0.

Mamilwar *et al*.[25] have used thermally treated Babul bark powder in a muffle furnace at 700°C for 2 h for defluoridation of aqueous solution. The 5 g/L doses of adsorbent could remove 77.04% fluoride from aqueous solution bearing 5 mg/L fluoride concentration at pH of 8.0 with an equilibrium time of 8 h and 303 K. The experimental results in equilibrium were best fitted with Langmuir isotherm than Freundlich isotherm. Furthermore, the pseudo-second-order kinetic model was best fitted as compared to the pseudo-first order.

Alagumuthu *et al*.[26] have investigated the *Cynodon dactylon* (Bermuda grass)-based thermally activated carbon for defluoridation of water. The maximum removal of 83.77% of fluoride was obtained by 1.25 g dosage of adsorbent for 3 mg/L of fluoride concentration for 105 min of contact time at neutral pH. The adsorption process followed Redlich–Peterson as well as Langmuir isotherms. The average monolayer adsorption capacity (qm) obtained for *Cynodon dactylon* was 4.702 mg/g. The adsorption process was unconstrained and endothermic in nature. The presence of bicarbonate ions reduced the fluoride removal from 83.7% to 51.5% with an increase of bicarbonate concentration 0–300 mg. The regeneration of exhausted adsorbent was done by 2% sodium hydroxide to regenerate 67.4% of adsorbent.

Kamble[27] has investigated defluoridation capability of basil (*Ocimum sanctum*, *Lamiaceae*) or tulsi leaves, stem, and extract of fresh leaves from aqueous solution in batch process. The maximum removal of 94%, 75%, 78%, and 74% achieved from 5 ppm of fluoride solution by fresh basil leaves, fresh basil stem, dry leaves, and dry stem at a dose of 75 mg/100 ml, 100 mg/100 ml, 250 mg/100 ml, and 250 mg/100 ml at pH of 9.0, 6.0, 6.0, and 7.0 for a contact period of 20 min. This technique is cost effective and environmental friendly to treat the fluoride contaminated water at rural and urban regions as per Indian Standard for drinking.

Conclusion

This review paper provides an overview of various waste materials as adsorbents used for the effective removal of fluoride from water. Most of the adsorbents performance is depend on parameters such as pH, contact time, adsorbent dose, and temperature. The removal capacity increases by increasing dose of the adsorbent and decreasing size of the adsorbent. From the overview, it is observed that defluoridation might be feasible with waste materials as adsorbents, but there is a need for more studies to establish waste adsorbents as nonconventional potential source of defluoridation and also to make this technique more user-friendly. The modification of adsorbent with suitable chemicals or composite adsorbents was also remarked for the enhancement of efficiency of fluoride removal from water. It is hoped that it will encourage even more rapid and extensive developments for the treatment of fluoride from aqueous phase.

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Conflicts of interest

There are no conflicts of interest.

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