ECONOMICAL TECHNOLOGY OF FLUORIDE REMOVAL USING FISHBONE CHARCOAL COLUMNS AT DOMESTIC LEVEL

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SUMMARY: Columns containing 45 g fishbone charcoal were tested in laboratory column bed with a continuous feed of water containing 2.5-20 mg fluoride /L. The useful capacity of the medium was defined as the volume of treated water or the amount of fluoride removed before the breakthrough at concentrations of 1 mg/L. It was observed that influent water containing 5 mgF/L resulted in useful volumes of 9.5 to 3 L, depending on the loading utilised (about 0.3 –1.7 mL/min/g). For a loading of 0.3 mL/min/g between 3 and 19 L of water could be treated to concentrations less than 1.0 mg/L, depending on the initial fluoride concentration utilised (2.5 - 20 mg/L). Useful removal capacities between 0.3 and 1.4 mg/g were obtained, the highest capacity being observed for lowest flow rate and highest initial fluoride concentration. Total prising of the process including purchase of fishbone, transportation, charring etc. indicates that the method may be workable and economical at individual domestic levels in seashore areas where fishbone is largely available.

Key words: Fluoride removal; Fishbone charcoal; Defluoridation columns; Domestic level; Economical defluoridation technology.

INTRODUCTION

Fluoride in drinking water can cause beneficial or detrimental effects depending on its concentration and the total amount ingested. The beneficial effect of fluoride in small quantities (up to an amount of 1.0 mg/L) lies in its capability to increase tooth resistance against dental caries, which is thus prevented. Fluoride acts by improving the acid resistance of the enamel reacting with it to form fluorapatite, which is less soluble than hydroxyapatite. Higher concentration of fluoride can cause dental or skeletal fluorosis.[1] Fluorosis (a disease, often escaping detection) tends to discolour teeth (feeling of having cavities all around, so need filling) and the affected teeth can turn brittle and break. The disease can attack neck, spine, pelvic and shoulder joints and small joints of hands and feet. In some parts of the world water with fluoride content less than 20 to 30 mg/L is not available. The Indian drinking water supply standards recommend an acceptable fluoride concentration of 1.0 mg/L. A concentration of 1.5 mg/L is allowable for potable waters.[2] There is thus, a dire need to develop some economical technology applicable at domestic levels to reduce the fluoride concentration from very high concentrations to acceptable concentrations in drinking water. The various defluoridating materials mainly used include animal bone and bone charcoal, synthetic tricalcium phosphate, activated carbon, activated alumina, synthetic ion exchangers, alum, lime, etc. A comprehensive review of the defluoridation methods as studied by various researchers[1,3,4] has been presented elsewhere. Bone charcoal prepared from animal bones has been successfully used in many full-scale installations for defluoridation of drinking water in Southern California.[5]

It will be shown later in the `Materials and Methods' section that fishbone can be a cheap material in fish cultivation areas. Relatively little research has been done on the subject of fluoride removal capacity of fishbone charcoal through column studies. The design of fluoride removal processes is, in many cases, largely empirical and based on past experience.[6]

In a continuous flow, fixed-bed column operation, the efficiency and system cost depend on the removal capacity of the media, i.e., the amount of solute adsorbed per gram of the

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adsorbent. This capacity is a function of several factors such as flow rate, column bed depth, initial solute concentration, pH, temperature, and desired quality of the treated water. Effects of these parameters have been studied and presented elsewhere.[7] In this paper, an attempt has been made to evolve a fixed bed column of fishbone charcoal usable at domestic levels to economically treat waters containing very high fluoride concentrations.

MATERIALS AND METHODS

Fishbone charcoal was prepared by carbonising the cleaned and pulverised fishbone in an electric furnace in a closed retort at 1000°C for 2.0 hours. The cooled material was then sieved to get the required size having geometrical mean diameter of 0.549 mm (0.355 – 0.850 mm size range). This size is close to the one used in field application in Southern California.[5] The material was thoroughly washed with distilled water, oven dried at 103°C, desiccated, and stored in air-tight containers. The specific surface area and density of the material were determined to be 85 m^2/g (as per ISS[8]) and 1.8 g/cm^3 respectively. These properties, however, depend on the kind of bones and the scheme of charcoal preparation.

The fluoride test solutions of different initial fluoride concentrations (C_0) were prepared by adding appropriate amounts of anhydrous sodium fluoride to tap water. The tap water used to identify field conditions had a pH of 7.9-8.1; total dissolved solids of 170 mg/L; total hardness (as $CaCO_3$) of 112 mg/L; calcium (as Ca^{++}) of 44 mg/L; chlorides (as Cl^-) of 10 mg/L; sulphate (as SO_4^{--}) of 1.5 mg/L; alkalinity (in $CaCO_3$) of 75 mg/L; and fluoride (as F^-) of less than 0.10 mg/L. A possible interfering effects of competing ions including calcium (Ca^{++}) present in the stated tap water, on fluoride adsorption was investigated through batch adsorption tests from trial jar tests, and the interference was found to be negligible and insignificant.[7]

Fixed bed column studies were conducted with 2.5 cm diameter glass column filled with fishbone charcoal. Four sets of column studies were performed. In each set, for a given initial fluoride concentration (C_0 = 2.5, 5.0, 10.0, or 20.0 mg/L) the downward flow rates were varied and maintained at 15 mL/min (3.06 $mL/min/cm^2$), 30 mL/min (6.12 $mL/min/cm^2$), 50 mL/min (10.2 $mL/min/cm^2$), and 75 mL/min (15.3 $mL/min/cm^2$) corresponding to each of the various C values. Additional runs were also conducted with fishbone charcoal filled to a column bed depth (D) of 15 cm with (i) the initial fluoride concentration of the test solution, kept constant at 5 mg/L and the flow rates maintained at either 15 mL/min, 25 mL/min, 50 mL/min or 75 mL/min, and (ii) a constant flow of 15 mL/min maintained and the initial fluoride concentration of the test solution kept at 2.5 mg/L, 6.0 mg/L, 10.0 mg/L, or 20 mg/L.

The fishbone charcoal was filled in glass columns to the required depths in such a way that the bulk density of the filled adsorbent material was 0.61 g/cm^2. For example, a 15 cm column bed depth of fishbone charcoal weighed 45 g such that $(45/(\pi/4 \cdot 2.5^2 \cdot 15) = 0.61\ mg/cm^2\}$. The top of the column was connected to a constant head-maintaining tank, which was charged by an overhead tank containing the feed solution.

In each of these tests, the effluent concentration was monitored at different times and samples were analysed for fluoride concentration using the specific ion electrode (Orion Ion Analyser, Model 901).

The various runs were terminated when the effluent fluoride concentration at the bottom of the column beds exceeded 1 mg/L (the permissible concentration, designated as the break-through concentration). The volume of the effluent treated prior to the break-through concentration, was designated as the `useful (or effective) treated effluent volume.

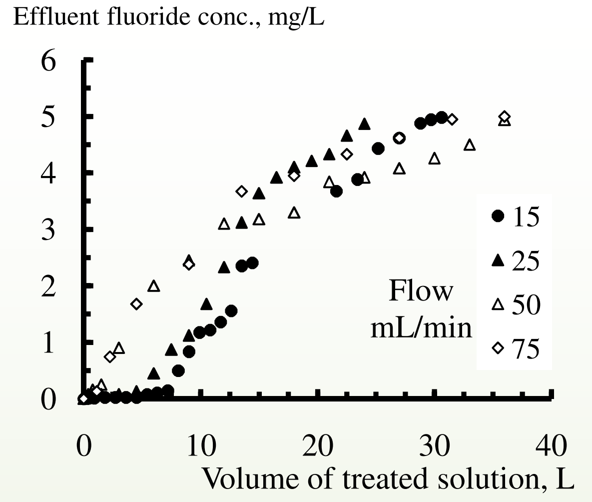

FIGURE 1. Break through curves corresponding to different flows with column bed depth D=15 cm, absorbent weight W=45 g, initial influent fluoride concentration C_0= 5 mg/L,and pH= 8.0 (tap water base).

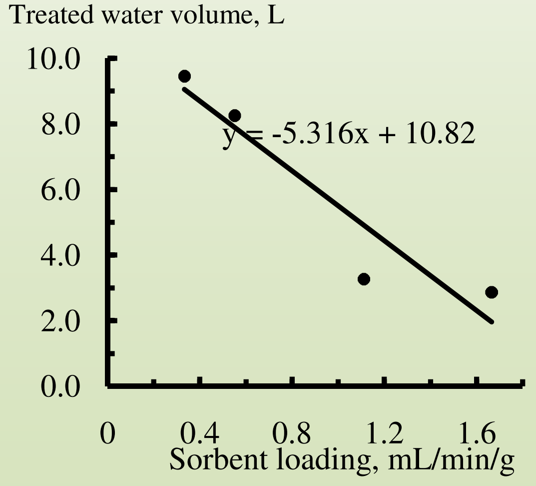

FIGURE 2. Variation of useful treated effluent volume (V) with influent flow rate per unit weight of adsorbent (Q_w) based on data of Figure 1.

RESULTS

The experimental observations are plotted in Figures 1 to 4.

The approximate cost of 167 kg of fishbone from Goa (India) seashore (including collection, transport, cleaning, manual pulverisation, etc.) was Rs. 167.00. The approximate cost of carbonisation is an electric furnace (36 kW for 2 hours, i.e., 72 units) including overheads and labour costs, was Rs. 216.00. About 40% material weight was lost during carbonisation. Thus, about 100 kg (167x0.6) of the fishbone charcoal cost Rs. 383.00 (167 216), i.e., approximately Rs. 4.00 (US $ 0.20) per kg cost of the fishbone charcoal.

DISCUSSION

Breakthrough vs. flow rate. The breakthrough curves for the initial fluoride concentration (C_0) of 5.00 mg/L corresponding to the various influent flow rates (Q = 15, 25, 50 and 75 mL/min) are depicted in Figure 1. The retention time or hydraulic residence time corresponding to the flow rates (Q) of 15, 25, 50 and 75 mL/min are 4.91, 2.95, 1.47 and 0.98 min, respectively.

The volume of treated effluent (V) at the different flow rates at the chosen effluent fluoride concentration at breakpoint, C_e of 1.0 mg/L is read as 9.45, 8.25, 3.27 and 2.87 L corresponding to the flow rates of 15, 25, 50 and 75 mL/min, respectively.

The variation of treated effluent volume (V) with respect to the flow rate per unit weight of adsorbent (Q_w) is shown in Figure 2. The volume of treated effluent decreases with an increase in flow rate per gram of the adsorbent. This is because, at higher flow rates, the decreased available retention time (or hydraulic residence time) of solution in the column may be inadequate. The optimum time of retention required for completing the sorption reaction between the solute and the media, which is likely to result in longer operation period until the breakthrough at C_e = 1.0 mg/L takes place, may require lower flow rates.

Mass balance calculations were done to determine the amount of fluoride removed (F) at different flow rates (Figure 1) till the breakthrough concentration point (C_e = 1.0 mg/L). The effluent concentration up to the breakthrough point varied from 0 to 1.0 mg/L as seen in Figure 1. During the breakthrough time, an average breakthrough effluent fluoride concentration ($C_{e\text{-}av}$) of 0.5 mg/L was assumed for the time interval in which C varied from 0 to 1.0 mg/L instead of using the procedure of integration of breakthrough curve or considering small time intervals. The amount of fluoride removed for flow rates of 15, 25, 50, and 75 mL/min is estimated to be 42.5 mg, 37.1 mg, 14.7 mg, and 12.8 mg, respectively. These correspond to removal capacities of approximately 1, 0.8, 0.4 and 0.3 mg/g respectively. The higher the flow rate the lesser the fluoride removal capacity, due to shorter available contact time (or hydraulic residence time).

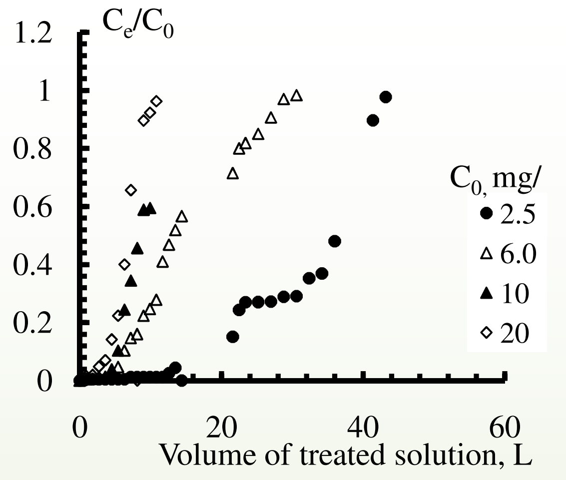

FIGURE 3. Breakthrough curves (C vs L) corresponding to different initial fluoride concentrations (C_0) with column bed depth (D) of 15 cm, absorbent weight (W) of 45 g, flow (Q) of 15 mL/min, and pH of 8.0 (tap water base).

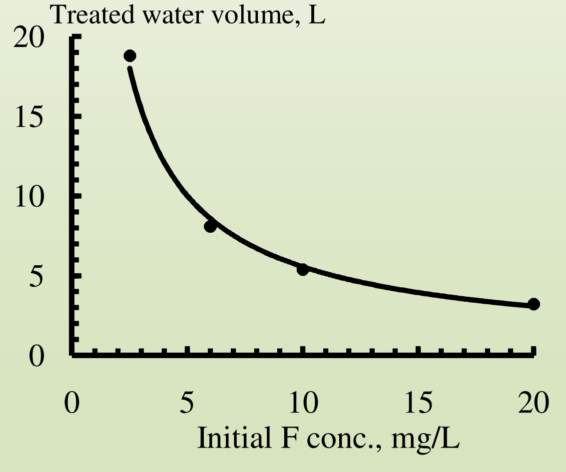

FIGURE 4. Variation of useful treated effluent volume (V) with initial fluoride concentrations (C_o) based on data of Figure 3.

Breakthrough vs. initial Conc.. Breakthrough curves at the different initial fluoride concentration (C_0) are shown in Figure 3. These curves are obtained corresponding to a constant flow rate of 15 mL/min. From Figure 3 the values of the useful volume (V) of the treated effluents corresponding to C_e = 1.00 mg/L were estimated as 18.8, 8.1, 5.4

and 3.24 L corresponding to C_0 values of 2.5, 6.0, 10.0 and 20.0 mg/L, respectively. The variation of volume of the treated effluent versus the initial fluoride concentration (C_0) is shown in Figure 4. At the chosen breakpoint concentration of C_e = 1.0 mg/L, the useful volume (V) of the treated effluent decreases with an increase in C_0 values. This is due to the fact that for a given flow rate and quantity of the adsorbent, the adsorption or exchange sites of the adsorbent are exhausted earlier when a higher initial fluoride concentration influent is encountered. Therefore, the operation period until the breakthrough point is less. Mass balance calculations were carried out, as before, to determine the amount of fluoride removed at different initial fluoride concentrations (Figure 3). The amount of removed fluoride (F) at C_0 of 2.5, 6.0, 10.0 and 20.0 mg/L was 28.2 mg, 44.6 mg, 51.30 mg, and 63.18 mg, respectively. These correspond to useful removal capacities of about 0.8, 1, 1.1 and 1.4 mg/g respectively. The breakthrough times are shorter for higher initial fluoride concentrations, but the amount of fluoride removed, and the useful removal capacity of the medium, increases with C_0. This is probably due to higher concentration gradients at higher C_0 values.

Practical applications. Fish bones can be considered to be a comparatively cheaper and effective material for the preparation of fishbone charcoal for defluoridation of drinking water as equally feasible for isolated communities of small sizes as well as at domestic level in the form of home filters.

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