Study on defluoridation of drinking water using zirconium ion impregnated activated charcoals

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Received 16 October 2006; revised received 18 May 2007; accepted 23 May 2007

Activated charcoals which are effective for fluoride removal, when impregnated with zirconium metal ions have an increase in their fluoride adsorption capacity by 3 to 5 times to that of plain activated charcoal. Continuous down flow adsorption mode at room temperature was adopted to defluoridate drinking water. Three columns were prepared by the impregnation of ZrOCl₂ in groundnut shell, coconut shell and coconut fiber activated charcoals. The column was run at a constant rate of 0.6-0.7 L/h with known fluoride influent water and a constant level of water was maintained. Treated water samples were analysed by the ion selective electrode method. In this study zirconium ion impregnated coconut fiber charcoal (ZICFC) showed maximum fluoride uptake and proved to be the most effective defluoridating agent followed by groundnut shell and coconut shell charcoals. ZICFC was effective for 21 liter lots of (8.0 mg F⁻ ion/L) test solution and 6 liter lots of (2.47 mg F⁻ ion/L) tap water, where the fluoride concentration in each of these liter lots is less than 1.5 mg/L.

Keywords: Activated charcoals, Continuous flow method, Defluoridation, Zirconium oxychloride

IPC Code(s): A23L2/00, G01N33/18

To encounter the fluoride menace, due to consumption of excess fluoride from drinking water leading to three types of fluorosis, namely- dental, skeletal and soft tissue fluorosis¹, various defluoridation techniques² have been employed to get the fluoride concentration within the recommendation standards of WHO (1.0 -1.5 mg/L) in potable waters. Three basic defluoridation processes namely adsorption, precipitation and membrane separation are in use, of which the precipitation methods involve the high probability of contamination of drinking water due to unwanted chemicals³,⁴. On the other hand membrane processes involve constant maintenance and heavy prices, which has made them less popular in India. Hence, adsorption on activated alumina⁵,⁶, coconut shell carbon⁷, chemically activated carbon⁸,⁹, natural zeolites¹⁰ and other low cost adsorbents¹¹,¹², involving water passage through a contact bed with subsequent fluoride removal is often the inexpensive method of choice to obtain safe drinking water.

Zirconium ion impregnated activated charcoal has been used for treating phosphate¹³, arsenic¹⁴, selenium, mercury¹⁶ and chromium (VI)¹⁷ from water samples. Based on the results available from the literature and from a previous study¹⁸, zirconium ion impregnated coconut shell charcoal proved to be the most effective defluoridating agent for treating effluents of lower fluoride concentrations from 2 - 10 mg/L followed by CaO and alum impregnated activated charcoals. The current study is being undertaken as an addition to the previous work¹⁸. The scope and objective of this defluoridation study is to determine the adsorption properties and in turn the defluoridation ability of various zirconium ion impregnated charcoals by the continuous down flow adsorption mode at room temperature.

**Experimental Procedure**

**Preparation of adsorbent**

About 100 g of the crushed raw material (groundnut shell, coconut shell or coconut fiber) was taken and kept for about 3 h in a low temperature muffle furnace at 300-400°C, at which all of the material was completely carbonized. The carbonized material was then taken out of the muffle furnace, cooled, powdered and kept in a beaker of 2 L capacity and 200 mL of concentrated sulphuric acid was gradually added to it, stirring the contents of the beaker continuously to ensure thorough mixing. The beaker was kept in a hot air oven at 100°C for 5 h. The activated charcoal was then cooled and left overnight and washed free of acid and dried at 110°C for 2 h, then sieved using 40 and 100 meshes.
Continuous down flow adsorption mode experiments

The defluoridation experiment was carried out in 5 cm diameter PVC columns of length 90 cms, run in continuous down flow method. Groundnut shell, coconut shell and coconut fiber activated charcoals (Table 1) were used to fill the three columns and these activated charcoals were prepared as per the procedure from groundnut shell, coconut shell and coconut fibers. As these raw materials are readily available in rural India from the agricultural sector, there is no expenditure involved in their procurement.

Two different columns were filled with 35 g of groundnut shell and coconut shell charcoals while in the third column, since the coconut fiber charcoal was very fine and passed through 100 mesh with the water percolation rate being very low, 35 g of it was homogeneously mixed with 525 g of sieved sand. Before mixing with the charcoal, the sand was thoroughly washed till the washings were colourless.

The carbon beds were percolated with 1% Na₂CO₃ solution till the effluent was alkaline. The columns were then washed free of alkali with 750 mL of water and 1% solution of zirconium oxychloride (300 mL) was percolated through each of the groundnut shell, coconut shell and coconut fiber carbon beds and the carbon beds were kept in contact with the 1% solution of zirconium oxychloride (200 mL) for 12 h. Thereafter, the three beds were washed free of excess zirconium ions with 750 mL distilled water and the effluents were confirmed for absence of zirconium ions using ammonia. OSHA standards for pulmonary exposure specify a threshold limit value of 5 mg zirconium per m³. As per the solubility product of zirconyl hydroxide \( K_{sp} = 6.3 \times 10^{-49} \), the solubility of it, is \( 26.7 \times 10^{-15} \) g/L. As solubility factor calculations could be at variance with experimental results, further a quantitative analysis was carried out to determine the concentration of Zr⁴⁺ in the effluents and in the treated water samples by using alizarin red S (ARS) as reagent to form ARS-Zr complex. This ARS is worthy of use as a reagent for spectrophotometric determination of Zr⁴⁺ at a wavelength of 520 nm, as it is sensitive towards small change of Zr⁴⁺ concentration and operates in the dynamic range of 5-35 mg/L at pH 2.5. All the tested samples had the Zr⁴⁺ ion concentration less than 5.0 mg/L. Hence quality assurance and quality control (QA/QC) checks assured that the amount of zirconium in the effluents is well below the safe limit.

A stock solution of 1000 mg F⁻ ion/L was prepared by dissolving 221 mg of NaF in distilled water and made up to the mark in a 100 mL volumetric flask. A 48 mL solution of this 1000 mg F⁻ ion/L was subsequently diluted to 6 L to obtain 8.0 mg F⁻ ion/L test solution. This 8.0 mg F⁻ ion/L standard solution (5 L) was percolated through the carbon bed with one- liter lots of the effluents being collected successively. Fluoride concentration in each of these lots was estimated by a potentiometric method using an Orion potentiometer, Model SA 720, with a fluoride ion selective electrode in combination with a single-junction Ag | AgCl reference electrode.

EDX spectrum of zirconium ion impregnated coconut fiber charcoal (ZICFC) was obtained with a Leica S-440I microscope fitted with an EDX spectrometer and Link ISIS detector. Further the pore size and surface area of ZICFC was evaluated using Quantachrome Autosorb-1 BET surface analyzer.

### Results and Discussion

ZICFC was found to be effective defluoridating agent followed by groundnut shell and coconut shell charcoals. Table 2 presents the residual fluoride in mg/L after adsorption from a standard solution of fluoride ion (8.0 mg F⁻ ion/L) by different zirconium ion impregnated activated charcoals in successive liter lots at a rate of 0.6 to 0.7 L/h by outflow control. The current flow rate was adopted, as the fluoride uptake efficiency of the impregnated activated charcoals increases with reduction in flow rate due to increased contact time which permits larger adsorbate / adsorbent interactions. A comparison with the previous study where a flow rate of 4.0 L/h resulted in reduced fluoride uptake, led to reduce the flow rate significantly. Further, the depth of the charcoal as in the case of ZICFC, with a bed height of 25 cms,
causes a significant reduction in flow rate with an increased contact time and in turn better defluoridation ability. The effect of zirconium impregnation in activated charcoal was studied by percolating the standard fluoride solution of 8.0 mg F\(^-\) ion/L through an unimpregnated activated charcoal to measure the difference with that of impregnated charcoal.

A preliminary analysis of the mean of the fluoride content of successive liter lots itself provides a measure to compare and determine the efficiency of fluoride uptake by the three different activated charcoals. A mean value of 0.02 for ZICFC, 1.53 for zirconium impregnated groundnut shell and 3.18 for zirconium impregnated coconut shell charcoals, are indicators to the defluoridation ability. Statistical analysis in the form of an independent samples t-test was conducted to test the null hypothesis of equal means. The data obtained shows that the mean residual fluoride content of ZICFC is significantly lower than that of zirconium impregnated groundnut and coconut shell charcoals respectively at a significance level of 5%. Hence the hypothesis is rejected and it is concluded that ZICFC is significantly better in its defluoridation ability.

Zirconium and its metal complexes have been conventionally used for the colourimetric determination of fluoride\(^2\) due to the high affinity of zirconium for fluoride ion. The high electronegativity\(^2\) of the fluoride ion enables it to form stable fluoro complexes with tetravalent metal ions like zirconium (IV).

From the current study it is clearly evident that the defluoridating ability of different activated charcoals impregnated with zirconium metal ions, depends on two factors: (i) the degree of adsorption of the zirconium ion on the particular activated charcoal (groundnut shell, coconut shell or coconut fiber) and (ii) on the adsorbent particle size.

### Physicochemical properties of adsorbents

Activated carbons are usually classified into two categories based on the acid-base behavior of the carbon. H- and L-type carbons are differentiated on the basis of pH of the carbon, with L-type carbons being more acidic in nature and H-type being more basic\(^2\). The carbons used in this study are of the L-type. The carbon surface of groundnut shell, coconut shell or coconut fiber activated charcoals have unsaturated C=C bonds, which on oxidation with concentrated sulphuric acid at 100°C enhances the amount of carbon-oxygen surface chemical structures by remarkably generating more oxygen-containing surface functional groups and yield large amounts of surface area available for metal uptake by improving its surface acidity and pore structure\(^2\). The adsorption sites in activated carbons can be divided into two major types: (i) hydrophobic surfaces comprising of the graphene layers and (ii) oxygen functional groups which are primarily hydrophilic.

In the case of these activated charcoals, the oxygen functional groups consisting of carboxylic, hydroxyl and carbonyl, present on their surface, may be involved in the physicochemical interactions with the metal ion. This suggests that surface modification of a carbon adsorbent with a strong oxidizing agent generates more adsorption sites on their solid surface for metal adsorption. This phenomenon has hence been exploited for removal of heavy metals (Ni, Cd, Pb and Zn) from wastewater using coconut shell carbon with high removal efficiency\(^2\).

Zirconyl chloride behaves as a Lewis acid in aqueous solution and is hydrolyzed\(^2\) according to the reaction

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\text{ZrOCl}_2 + H_2O \rightarrow \text{ZrOOH}^+ + H^+ + 2\text{Cl}^- 
\]

by forming HCl. This results in lowering the pH to 1.6, where the activated carbon has been reported to have high affinity for zirconium\(^1\). It was assumed that the physicochemical interactions that might occur during zirconium adsorption could be expressed in terms of ion exchange and/or hydrogen bonding mechanisms. In the ion exchange mechanism, the ZrOOH\(^+\) species may compete with H\(^+\) from –COOH and –OH functional groups and be adsorbed at the carbon surface of the activated charcoals, with the

| Table 2—Fluoride concentration (mg/L) after adsorption by zirconium impregnated activated charcoals |
|-----------------|-----------------|-----------------|-----------------|
| Liter-lot       | Groundnut shell | Coconut shell   | Coconut fiber   |
| 1               | 0.08            | 0.04            | 0.003           |
| 2               | 0.77            | 0.41            | 0.007           |
| 3               | 1.69            | 4.15            | 0.011           |
| 4               | 2.48            | 5.23            | 0.028           |
| 5               | 2.61            | 6.06            | 0.034           |
| Unimpregnated Charcoal* | 7.00 | 7.55 | 3.78 |

*Residual fluoride concentration after adsorption by unimpregnated charcoal for the first liter lot.
hydrogen bonding mechanism also being available for adsorption of ZrOOh¹, thus providing two main possibilities for the adsorption of ZrOOh¹ species.

Hence, adsorption of zirconium ions from solutions by solid phase can occur with formation of surface complex between the oxygen containing functional groups (-COOH, -OH, >C=O) and the metal. The hydrogen on carboxylic and hydroxy groups occurring on the surface of activated carbons appears to be more labile, possibly as a result of electron density diversion to the II-bond system of the graphite planes²⁵. Once these zirconium based Lewis acid sites are generated by chemisorption on the activated charcoals as a monolayer, they are responsible for the very strong adsorption of Lewis bases, such as the fluoride ion.

Energy dispersive X-ray (EDX) spectrometer and BET surface analyzer were used to study the physicochemical properties on zirconium ion impregnation in coconut fiber carbon (CFC). In EDX, the ZICFC sample was impinged with an electron beam of specific energy that knocked out the inner shell electrons. The outer electrons then filled the inner gap emitting X-rays that were characteristic of zirconium, confirming its presence (Fig. 1). The CFC used for zirconium ion impregnation was previously sulphonated¹⁹, which accounts for the intense sulphur signal in Fig. 1.

The surface area and total pore volume were also determined by nitrogen adsorption, for monolayer formation. Here, the sample taken in a glass holder was degassed at around 150°C to desorb any of the adsorbed gases on the sample. The nitrogen adsorption isotherms were measured at relative pressures from 0-1 and at -195.85°C adsorption temperature. The surface area was calculated from the BET plots (Fig. 2), as 163.2 m²/g. The pore volume of pore width in the range 5-10 Å for ZICFC is the maximum (Fig. 2 inset), which may be contributing to the surface area, as calculated by DFT Monte Carlo simulation based on the distribution of the surface area with respect to the different pore size, determined from the amount of nitrogen adsorbed. Hence, small particle size provides more active surface area, as the presence of large number of smaller particles provides the sorption system with a larger surface area available for fluoride ion removal and reduces the external mass transfer resistance¹³. ZICFC due to its large surface area showed maximum fluoride uptake and is remarkably effective for all of the five lots, as fluoride uptake was 99.96% for the first lot, 99.91% for the second, 99.86% for the third, 99.65% for the fourth, 99.58% for the fifth and 52.75% for the unimpregnated charcoal. As the focus was to see the efficacy of the process on fluoride removal, the defluoridation study with ZICFC was continued till saturation resulted. It was found that the defluoridation experiment carried out using ZICFC was effective for 21 liter lots of (8.0 mg F⁻ ion/L) test solution, where the fluoride concentration in each of these liter lots is less than 1.5 mg/L (Fig. 3). Further, in order to establish the amount of fluoride free, safe drinking water that can be obtained, a tap water sample having fluoride concentration equivalent to 2.47 mg/L was percolated through ZICFC at a rate of
0.7 L/h by outflow control. ZICFC was effective for 6 liter lots of tap water, containing fluoride less than 1.5 mg/L (Fig. 3). The reduced efficiency of ZICFC, which was effective for 21 liter lots of (8.0 mg F⁻ ion/L) test solution as against 6 liter lots of (2.47 mg F⁻ ion/L) tap water, is because of the presence of co-ions (anions and cations) in tap water that cause interference with fluoride ion uptake by principle of competition for the adsorption sites on zirconium ion impregnated activated carbon.

The fluoride adsorption capacity of ZICFC was also investigated by pursuing the batch equilibrium experiments, wherein the effect of various parameters such as pH, contact time and adsorbent dosage were studied. Maximum defluoridation of a fluoride rich water sample was achieved by maintaining the pH at 4, with 6 h stirring and 20 g /L adsorbent dosage as the optimum conditions.

Regeneration of the ZICFC is accomplished by elution with 0.02 M NaOH solution. These low-cost adsorbents can be disposed off easily and safely; they can be reused as filler material in low-lying areas (landfills) or in manufacture of bricks.

Conclusion
Of the various zirconium ion impregnated (groundnut shell, coconut shell and coconut fiber) charcoals used in this study, ZICFC proved to be the most effective defluoridating agent for treating effluents of lower fluoride concentrations from 2 - 10 mg/L.

Acknowledgement
The authors are grateful to the Chancellor, Bhagawan Sri Sathya Sai Baba, Sri Sathya Sai University, for His constant inspiration.

References
19 Seeopathiraou D, Indian J Environ Hlth, 64 (1964) 11.