Cashewnut sheath carbon: A new sorbent for defluoridation of water

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Received 26 August 2001; revised received 25 October 2002; accepted 8 January 2003

Cashewnut sheath, an agricultural waste discarded largely in India is identified for the preparation of an effective sorbent for fluoride removal. Experiments were conducted for the sorption of fluoride from aqueous solution using activated carbon from cashewnut sheath (CSC) in two phases, namely, batch studies and column studies. The influence of pH, adsorbent dose, particle size and contact time was investigated in batch studies. The adsorption process follows Freundlich adsorption isotherm. Continuous flow experiments in fixed bed columns packed with activated carbon were carried out in order to assess the feasibility of this for field applications. The carbon bed after exhaustion was regenerated with 0.1 N hydrochloric acid. The influence of initial concentration of fluoride ion, flow rate, particle size and concentration of the regenerant on the performance of the column was studied. Comparative study was conducted with commercially available carbon impregnated with 2% aluminium sulphate solution. The results revealed that CSC is found to be active and efficient for fluoride removal.

The social and physiological impact on children with unsightly discoloration of the teeth due to mottling is well-documented\textsuperscript{1}. It is well-known that fluoride in drinking water below 1.0 mg/L reduces the prevalence of dental caries by 50-60\%. The chronic and toxic effects of excessive intake of fluoride are usually observed as skeletal abnormalities or damage\textsuperscript{2}. The effects range from stiffness and rheumatism to a permanent crippling skeletal rigidity\textsuperscript{3}. According to World Health Organisation (WHO) the maximum acceptable concentration\textsuperscript{4} in drinking water is 1.5 mg/L\textsuperscript{4}. Hence there is a need for defluoridation of drinking water in order to prevent the occurrence of fluorosis.

Defluoridation has long been practiced in water supply and a variety of methods for fluoride removal are already known\textsuperscript{5,6}. The removal methods include chemical precipitation\textsuperscript{1}, adsorption on activated alumina\textsuperscript{8}, ion exchange\textsuperscript{9}, electrodialysis and reverse osmosis. The high cost of activated carbon has stimulated interest in examining the feasibility of using cheaper raw materials. Many reports have appeared on the development of activated carbon from cheaper and readily available materials from various sources\textsuperscript{10-13}. In recent years some low cost materials such as tree bark\textsuperscript{13}, fish bone charcoal\textsuperscript{14}, almond shells\textsuperscript{15}, olive stones\textsuperscript{16}, oil palm shells\textsuperscript{17}, coconut shell\textsuperscript{18}, etc. have been used for the preparation of activated carbon. In the search for new and low cost agricultural wastes as source material for activated carbon, attempts have been made to prepare activated carbon from cashewnut sheath (CSC) by chloride process\textsuperscript{14}. Extensive characterisation studies have been performed to assess the suitability of the activated carbon. The defluoridation studies were conducted in batch as well as column type continuous flow methods.

**Experimental Procedure**

**Preparation and characterisation of activated carbon**

Activated carbon from cashewnut sheath (Amacardiun occidentale L) was prepared by chloride process. Initially, the raw material was washed thoroughly with water to remove earthy matter and dried at 110°C. The material was broken into small pieces and soaked in 10% calcium chloride solution for 24 h. The soaked material was dried at 110°C and then subjected to pyrolysis followed by thermal activation at 850-900°C for 30 min. After activation the carbon was washed with 10% hydrochloric acid to remove residual inorganic impurities and washed with water.
repeatedly and finally dried at 110°C. The carbon was ground and sieved to particle size in the range of 300-800 micron for further characterisation.

The characterisation of activated carbon was carried out by adopting the standard procedures\(^{19,21}\). The moisture content of the carbon was determined by heating a known weight of the sample in an air oven maintained at 110°C for about 4 h. The residue was ignited in a muffle furnace at 1000°C for about 3 h to determine the ash content. Iron content in the ash was determined by atomic absorption spectrophotometer (Perkin-Elmer 2380). A known quantity of carbon was digested with freshly boiled water and the pH was measured with Orion pH electrode. Decolourising power of the carbon was determined using methylene blue solution. The amount of carbon required for 90% removal of phenol was taken as the phenol number. Surface area measurement was carried out using Micromeritics pulse chemisorb 2700 equipment. The characteristics of the CSC are presented in Table 1.

**Batch study**

Batch type adsorption experiments were conducted with 100 mL of aqueous solution containing 10 mg/L fluoride, adjusted to different pH values. The solution was taken in leak proof reaction bottles. The solutions were equilibrated for 24 h in a mechanical shaker at 27±1°C. After the equilibration period, the carbon was filtered and fluoride in the filtrate was estimated using pH/ISE meter (Model 710A, Orion Research Inc., USA). Experiments were performed to understand the effect of contact time, particle size and carbon dosage. Desorption studies were conducted using dilute hydrochloric acid. The removal efficiency of CSC was compared with aluminium sulphate impregnated commercial activated carbon.

**Continuous flow column experiment**

Generally, continuous flow adsorption process imparts advantages over batch operation. Unless the selectivity of a particular ion to be removed is very large, batch operations lead to an inefficient utilisation of the adsorption capacity of the sorbent owing to the decrease of solute concentration as adsorption continues. In continuous operation, the adsorbent is permanently in contact with solution of same concentration. Glass column of 25 mm diameter and 600 mm length was connected to a reservoir of 5 L capacity containing fluoride solution, and a peristaltic pump was connected at the bottom of the column to control the flow rate. The column was operated continuously and water height was maintained constant throughout the operation to maintain the flow accurately. A known quantity of carbon was weighed, sieved, washed with distilled water to remove carbon fines and then packed closely in the column by tapping to minimise air voids in the carbon bed.

**Results and Discussion**

The close examination of the results of characterisation study shows that the CSC possesses less bulk density than commercial activated carbon, CAC. The high moisture content is due to the porous surface of the carbon. However, no attempt was made to determine the porosity of the carbons. Surface area of CSC is more than CAC. The surface area values of the two varieties of CSC differ in particle size which clearly indicates that fine particles with greater surface area are more suitable for adsorption process. A preliminary screening study was performed to assess the suitability of CSC for the removal of fluoride from aqueous solution.

**Effect of pH**

In order to optimise the pH for efficient fluoride removal, batch experiments were conducted with 100 mL of 10 mg/L of fluoride containing known quantity of CSC and aluminium sulphate impregnated CAC in the pH range of 2-13 and the results are presented in Fig. 1. It is evident that percentage removal of fluoride is higher and remains constant in a wide pH range of 3-10 and above pH 10 it rapidly decreases.

<table>
<thead>
<tr>
<th>Sl No.</th>
<th>Control test</th>
<th>CSC</th>
<th>CAC</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Bulk density (g/cc)</td>
<td>0.45</td>
<td>0.68</td>
</tr>
<tr>
<td>2</td>
<td>Moisture content (%)</td>
<td>11.75</td>
<td>12.57</td>
</tr>
<tr>
<td>3</td>
<td>Ash content (%)</td>
<td>6.09</td>
<td>2.91</td>
</tr>
<tr>
<td>4</td>
<td>Fixed carbon content (%)</td>
<td>93.91</td>
<td>97.09</td>
</tr>
<tr>
<td>5</td>
<td>Matter soluble in water (%)</td>
<td>2.76</td>
<td>1.55</td>
</tr>
<tr>
<td>6</td>
<td>Matter soluble in acid (%)</td>
<td>5.00</td>
<td>4.58</td>
</tr>
<tr>
<td>7</td>
<td>pH</td>
<td>3.6</td>
<td>9.2</td>
</tr>
<tr>
<td>8</td>
<td>Decolourising power (mg/g)</td>
<td>49.5</td>
<td>73.5</td>
</tr>
<tr>
<td>9</td>
<td>Phenol number (mg)</td>
<td>6.33</td>
<td>5.15</td>
</tr>
<tr>
<td>10</td>
<td>Ion exchange capacity (meq/g)</td>
<td>0.007</td>
<td>Nil</td>
</tr>
<tr>
<td>11</td>
<td>Surface area (m²/g)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Grade I (294-710 µ)</td>
<td>303.81</td>
<td>296</td>
<td></td>
</tr>
<tr>
<td>Grade II (70-294 µ)</td>
<td>600.0</td>
<td>—</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>Iron content (%)</td>
<td>Nil</td>
<td>Nil</td>
</tr>
</tbody>
</table>
60% removal is reached at pH 2 and shows zero efficiency at pH 13. Hence pH of the solution was maintained at 6.9 for further studies. In the case of CAC, the maximum removal efficiency of 55% was observed in a pH range 5-8. Thus the CSC is efficient in the removal of fluoride over a wide range of pH values.

**Effect of carbon dose and particle size**

The results of variation in the removal of fluoride for different doses (0.1 to 2 g) of the two types of CSC and CAC at a contact period of 24 h are given in Fig. 2. An increase in the fluoride removal is observed as the dose of the adsorbent increases and also the overall percentage removal is more for the finer adsorbent (grade II 70-294 μ) than the coarser adsorbent (grade I 294-710 μ). This is because the fine particles provide more surface area for adsorption. The increase in the rate of defluoridation is observed up to 8 and 5 g/L for grade I and II carbons respectively. Further increase in the dosage does not show any significant removal efficiency. This is due to the overlapping of the active sites at higher concentrations and thus reduce the net surface area. The results clearly indicate that the optimum carbon dosage of 7 and 5 g/L of grade I and II carbons respectively are required for 80.0% removal of fluoride. But in the case of CAC a higher dose of 14 g/L shows a lesser efficiency (56%).

**Effect of contact time**

Fig. 3 exhibits the variation of fluoride removal from aqueous solution CSC and CAC with respect to contact time. The removal of fluoride increases with time until an equilibrium fluoride concentration in the effluent is attained. It is observed that 30.8% removal takes place within 30 min of contact time with 8 g/L of grade I carbon and 50.4% removal of fluoride is observed within 2 h while a total of 91.6% removal is achieved only in the next 22 h. In the case of grade II carbon a dose of 5 g/L removes 40.5% fluoride within 30 min and 55.6% within 2 h while a total of 80.9% removal is achieved in the next 22 h. The increase in the rate of fluoride removal is not very significant after 16 and 12 h of contact time for grade I and II carbons respectively. In the case of CAC, 56% removal takes place within 4 h of contact time. This data clearly indicates that CSC is more effective than CAC for the removal of fluoride. The results of batch study experiments for the removal of fluoride are given in Table 2.

**Desorption of fluoride**

Dilute hydrochloric acid has been found to be the
suitable reagent for the desorption of fluoride. Various concentrations viz, 0.02, 0.04, 0.06, 0.08, 0.1, 0.2, 0.4, 0.5 and 1.0 N HCl were attempted for the desorption study. From the results (Fig. 4) it is observed that approximately 0.1 N HCl is required for quantitative desorption of fluoride from cashewnut sheath carbon. Above 0.1 N, there is no significant change in desorption capacity. Hence 0.1 N HCl has been chosen for regeneration. In the case of CAC 2% solution of aluminium sulphate showed good regeneration.

**Adsorption isotherms**

The Freundlich model was applied for adsorption equilibrium for both CSC and CAC.

\[
\log \left( \frac{x}{m} \right) = \log k + \frac{1}{n} \log C_e
\]

The results reveal that the adsorption of fluoride on CSC and CAC under optimum conditions at room temperature (27±1°C) obeys Freundlich adsorption isotherm. Freundlich adsorption isotherm represents the relationship between the amount of fluoride adsorbed by per unit mass of the adsorbent \((x/m)\) and the concentration of fluoride at equilibrium \((C_e)\). The constants \(k\) and \(n\) represent the adsorption capacity and intensity of adsorption respectively. The data obtained in this study fit well with Freundlich adsorption isotherm (Fig. 5). The plot of \(\log (x/m)\) versus \(\log C_e\) for various initial concentration is found to be linear indicating the applicability of Freundlich adsorption isotherm. The higher values of \(k\) (1.358 for CSC and 0.226 for CAC) indicates greater affinity for fluoride and the \(n\) value (1.92 for CSC and 1.89 for CAC) shows good adsorption character of the carbon\(^3\).

**Continuous flow column study**

The performance of CSC in the removal of fluoride has been studied in column operation by varying the
parameters viz., flow rate, initial fluoride concentration, particle size of the CSC and concentration of the regenerant. Fig. 6 shows the breakthrough curves for different initial fluoride concentrations. The saturated column is regenerated with 0.1 N hydrochloric acid. In order to fix the optimum flow rate of the influent for maximum fluoride removal, the fluoride solution is passed through the column at various flow rates. Table 3 shows the effect of flow rate of the influent on the de fluoridation capacity. The de fluoridation capacity is maximum for a flow rate of 300 mL/h. Though the de fluoridation capacity of grade II carbon is higher (2522 mg/kg) than grade I carbon (2256 mg/kg), the flow rate decreases with decreasing particle size. Hence grade I carbon is more suitable for fluoride removal as the flow rate is high and the adsorption capacity is also reasonable. CAC fluoride removal capacity is poor of 638 mg/kg.

An interesting and noteworthy feature of the column operation is that the total fluoride removal capacity of the bed appears to be higher for water having high fluoride content. Water containing 2.6 mg/L of fluoride shows low uptake capacity. However, the uptake capacity increases with increase in initial fluoride concentration up to 7.6 mg/L. Beyond this concentration, the adsorption capacity decreases considerably (Table 4). Similar studies conducted in the regeneration of the exhausted bed has shown that 0.1 N HCl is the suitable regenerant. The column operation was stopped when the effluent fluoride concentration exceeds the permissible limit of 1.5 mg/L to prevent overexhaustion of the bed. Each column was recharged 6 times before rejecting the bed material.

**Conclusion**

Activated carbon prepared from cashewnut sheath, a waste generated in the agricultural sector, is capable of removing fluoride effectively from aqueous solution. The removal of fluoride is more with finer variety of carbon rather than the coarse. The study indicates that removal of fluoride from aqueous solution depends on pH, contact time, particle size and dose of adsorbent. The adsorption of fluoride from aqueous solution with cashewnut sheath and commercial activated carbon conforms to a Freundlich equation based on the formation of mono layer. De fluoridation capacity is maximum at a flow rate of 300 mL/h. As this flow rate can be conveniently maintained with grade I carbon, this carbon is suitable for de fluoridation. 0.1 N HCl has been chosen for regeneration of the exhausted adsorbent. Each column is recharged 6 times before rejecting the carbon bed. An interesting feature of the study is that fluoride uptake capacity increases with higher initial fluoride concentration.

**Acknowledgement**

The authors gratefully acknowledge the Rajiv Gandhi National Drinking Water Mission, Ministry of Rural Areas and Employment, New Delhi for financial support to carry out this research work. Authors also wish to place on record the necessary facilities and congenial atmosphere provided by Anna University, Chennai.

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