Rubber seed shell carbon as sequestrant of heavy metals and organic compounds from aqueous solution

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Powdered activated carbon was prepared from ammonium chloride activated rubber seed shell at 500 °C and characterized in terms of pH, bulk density, surface area, abrasion resistance and total surface charge. The sorption behaviour of zinc ions and alcohols (methanol, ethanol and n-propanol) on the shell carbon was studied. The removal efficiency of the metal ions was found to depend upon the initial metal ion concentration, with efficiency decreasing with increase in concentration of the metal ions. By fitting the equilibrium sorption data obtained into the Langmuir isotherm equation, values for maximum metal ions binding capacity and affinity (binding) constant of 0.425 mmol/g and 2.614 respectively were determined. The sorption data also fitted the Freundlich isotherm equation, but with relatively lower correlation coefficient, and values for the coefficient and exponent of the isotherm equation of 0.19 and 0.59 respectively were determined. The removal efficiency of the alcohols was measured in terms of changes in the chemical oxygen demand of solutions containing various volume fractions of the alcohols before and after treatment with the shell carbon. Removal efficiency was generally lower than 30% and corresponded to about 5.82 mg/L/g decrease in chemical oxygen demand; and was highest for n-propanol and lowest for methanol.

Keywords: Activated carbon, rubber seed shells, adsorption capacity, zinc ions, alcohols.

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There is growing awareness of the potential hazards due to the presence of dissolved pollutants (inorganic and organic) in industrial and mining wastewaters and from agricultural and urban storm-water run-off to the environment and public health. Precipitation/coagulation and ion-exchange, the techniques widely used in the treatment of industrial wastewater require the use of chemicals and/or synthetic resins, which are expensive and do not allow compliance with statutory requirements, particularly in the treatment of large volumes of wastewaters containing low levels of pollutants. There is therefore a growing interest in cost-effective, innovative materials and methods that will be useful in the treatment of industrial wastestreams. Many agricultural by-products that are available at little or no cost have been reported to be capable of removing substantial amounts of metal ions from aqueous solutions. For instance, many of the locally available agricultural by-products such as maize cobs, groundnut and rice husks, melon seed husks, cassava and plantain peels, that constitute a substantial portion of the solid carbon waste, have been shown to be effective in removing heavy metals from aqueous solutions. Simple chemical treatments/modifications have also been shown to markedly enhance the metal ion binding capacity of agricultural by-products. Although agricultural by-products have been widely reported to be effective removers of metal ions from aqueous solution, there are few reports on their capacity to remove dissolved organic compounds from aqueous solution partly because the known binding sites in agricultural by-products are considered to be ineffective in the removal of organic compounds. In addition, agricultural by-products have low resistance to mechanical abrasion (with attrition levels reaching 30%) making them suitable only for a “once-and-for-all” application. In order to overcome these problems, much emphasis has been given to the treatment of wastewaters through adsorption technology using activated carbons.

Activated carbons are predominantly amorphous solids with large internal surface areas and pore volumes. This unique pore structure plays an important role in many different liquid- and gas-phase
Activated carbons can be made from a variety of precursor materials including coal, wood, coconut shells, etc., by some form of activation process. More recently, interest has been shown in the preparation of activated carbon using agricultural by-products as precursor materials. The production of activated carbons from agricultural by-products has both potential economic and environmental impacts. First, it converts unwanted, low-value agricultural waste to useful, high-value adsorbents. Second, activated carbons are increasingly used in water to remove organic chemicals and metals of environmental and/or economic concern. Activated carbons have become the most effective adsorbent in treating drinking water and industrial wastewater. Therefore, the use of agricultural by-products represents a source of cheaper activated carbons which may contribute to solving environmental pollution problems.

Rubber seed shells are waste products in natural rubber production. Earlier studies indicate that rubber seed oil can be processed into resins suitable for multi-purpose surface coating applications and additives that are useful in the processing of polymers. It has also been suggested that rubber seed cake (residue obtained after extracting the oil) can be used in animal feed formulations. Conversion of rubber seed shells into high-value activated carbons is of interest from economic viewpoint. There are no reports of previous attempts at producing activated carbons from rubber seed shells using ammonium chloride activation.

The objectives of this study include the preparation, characterization and evaluation of the adsorption properties of rubber seed shell carbon.

**Experimental Procedure**

**Precursor materials**

Rubber seed shells were obtained from the Rubber Research Institute of Nigeria, Iyanomon, Benin City. These materials are low-value agricultural waste that at present have no commercial value in this country. On account of its fluffy nature, the shells are often milled together with the seeds during mechanical extraction of the seed oil.

**Preparation of activated carbon**

Activated carbon was prepared from rubber seed shells using the method described by Ishak and Bakar. The rubber seed shell was steeped in saturated solution of ammonium chloride for 8 h and carbonized at 500 °C for 2 h. The activated carbon obtained was powdered and sieved. The portion of the shell carbon that passed through a 300 μm screen and retained on a 90 μm screen was used for the study.

**pH determination**

The pH of the carbon was determined by immersing 1.0 g sample in 100 mL of deionised/distilled water and stirring for 1 h.

**Bulk density determination**

Bulk density was determined by the tamping procedure described by Ahmedna et al.

**Abrasion resistance**

The resistance of the shell carbon to mechanical abrasion was determined by measuring the percent solids retained after the activated carbon was stirred in acetate buffer (pH 4.7) at 350 rpm for 2 h.

**Determination of total negative charge**

The determination of total negative charge was a modification of the Boehm method reported by Toles et al. The results are expressed as meq H⁺ neutralized by excess OH⁻ per gram sample.

**Surface area determination**

The surface area of the activated carbon was determined by the iodine adsorption method. The amount of iodine adsorbed from aqueous solution was estimated by titrating a blank with standard thiosulphate solution and compared with titrating against iodine solution containing the sample.

**Adsorption of zinc ions**

The activated carbon was evaluated for adsorption of Zn(II) ions using the method previously described. Residual metal ion concentration was determined by atomic absorption spectrophotometry. Adsorption efficiency was calculated as percent of the initial metal ion in solution removed, and adsorption capacity was calculated as mmols of the metal ions adsorbed per gram of the powdered activated carbon.

**Adsorption of organics**

The removal of methanol, ethanol and n-propanol from aqueous solution by the activated carbon was studied at 29 °C. It was thought that the alcohols being miscible with water in all proportions should provide a means of assessing the effectiveness of
rubber seed shell carbon in removing polar organic compounds from aqueous solution. The method involved the determination of chemical oxygen demand\textsuperscript{28,29} of aqueous mixtures containing various volume fractions of the alcohol before and after treatment with activated carbon. Chemical oxygen demand, COD, provides a measure of the total organic compounds present in wastewater. Chemical oxygen demand determination measures the oxygen necessary for the conversion of organic material to carbon dioxide and water. Measurement of oxygen uptake is an indirect method but has two advantages\textsuperscript{28}: oxygen uptake is a process operation parameter in aerobic biological processes, and oxygen uptake is an important characteristic in determining effluent quality. These reasons account partly for the general acceptance techniques based on oxygen demand for measuring organic concentration\textsuperscript{28}.

**Results and Discussion**

**Characteristics of rubber seed shell carbon**

Some characteristics of the powdered activated carbon prepared from rubber seed shells are given in Table 1. Previous studies\textsuperscript{28} showed that without a buffer in the system, activated carbons increased or decreased the pH of slurry to point out range of optimum metal adsorption. Carbons produced by physical activation, in particular CO\textsubscript{2}-activated carbons, have the tendency to raise pH to > 6.5, leading to precipitation of some metals as the hydroxides: while acid-activated carbons often lower pH to < 2.5, causing an increase in electrostatic repulsion between the metal cation and the surface of the carbon and thus decreasing the levels of metal ions uptake by the activated carbon\textsuperscript{13,30}. Optimum metal ions uptake levels by carbons prepared from agricultural by-products have been shown\textsuperscript{30} to occur above pH 4. It is however not envisaged that industrial/mining wastewaters would require to be buffered prior to treatment with activated carbon, as such a procedure would compromise the cost benefit deriving from the use of agricultural wastes. The pH of activated carbon prepared from rubber seed shell is well above the threshold for optimum metal ions uptake. The pH of Zn(II) ions was 6.8 (the solution was prepared using ZnCl\textsubscript{2} salt). The observed changes in the pH of mixture of activated carbon and metal ion solution at the end of the experiments were generally less than 1 pH unit. Therefore, the maximum pH of the slurry of the shell carbon in the Zn(II) ion solution as less than 7.8, levels at which precipitation of metal oxides would not be anticipated. The resistance of the shell carbon to mechanical abrasion is comparable with that of carbons prepared from other agricultural by-products\textsuperscript{11}. The total surface change of the shell carbon is not quite as large as for some commercial grade activated carbons.

The indications of the results in Table 1 are that rubber seed shells are a suitable precursor materials for the preparation of activated carbons.

**Adsorptive properties of rubber seed shell carbon**

**Sorption capacity of zinc ions**

The capacity and efficiency of rubber seed shell carbon in removing Zn(II) ions from aqueous solution are given Table 2. The removal efficiency of metal ion is affected by the initial metal ion concentration, the efficiency increases with increase in metal ion concentration. It is thought that at low metal/carbon ratio, the metal ion adsorption involves the high energy binding sites on the carbon, as the metal/carbon ratio increases, the higher energy sites are saturated and adsorption begins on lower energy sites, resulting in a decrease of adsorption.

### Table 1—Some characteristics of rubber seed shell carbon

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>7.38 ± 0.42</td>
</tr>
<tr>
<td>Bulk density (g/mL)</td>
<td>0.646 ± 0.024</td>
</tr>
<tr>
<td>Surface area (g C/mgI\textsubscript{2})</td>
<td>1.31 ± 0.08 × 10\textsuperscript{-2}</td>
</tr>
<tr>
<td>Attrition (%)</td>
<td>18.28 ± 0.92</td>
</tr>
<tr>
<td>Total negative charge (mmol H\textsuperscript{+} g\textsuperscript{-1} C)</td>
<td>0.362 ± 0.021</td>
</tr>
<tr>
<td></td>
<td>2.99 ± 0.010*</td>
</tr>
<tr>
<td></td>
<td>0.286 ± 0.020*</td>
</tr>
</tbody>
</table>

*Values for some commercial grade activated carbons\textsuperscript{10,26}

### Table 2—Sorption characteristics of Zn(II) ions on rubber seed shell carbon

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Efficiency of Zn(II) adsorption (%)</td>
<td>44.0 ± 2.0-15.6 ± 0.8</td>
</tr>
<tr>
<td>Amount of Zn(II) adsorbed (mmol/g)</td>
<td>0.22 ± 0.01-0.39 ± 0.02</td>
</tr>
<tr>
<td>Partition coefficient (L/mmol)</td>
<td>0.786 ± 0.006-0.190 ± 0.02</td>
</tr>
<tr>
<td>Maximum Zn(II) binding capacity (mmol/g)</td>
<td>0.43 (r\textsuperscript{2} = 0.9897)</td>
</tr>
<tr>
<td>Affinity (Binding) constant (L/mmol)</td>
<td>2.61 (r\textsuperscript{2} = 0.9897)</td>
</tr>
<tr>
<td>Exponent of the Freundlich isotherm model</td>
<td>0.28 (r\textsuperscript{2} = 0.9076)</td>
</tr>
<tr>
<td>Coefficient of the Freundlich isotherm model</td>
<td>0.19 (r\textsuperscript{2} = 0.9076)</td>
</tr>
</tbody>
</table>

Initial Zn(II) ion concentration (0.5-2.5 mmol/L)

*Determined from fitting data into the Lagmuir isotherm mode

r\textsuperscript{2} = correlation coefficients
The efficiency of an adsorbent in removing metal ions from wastewater may be assessed in terms of the number of sorption cycles required to reduce the metal ion content of the wastewater below intervention levels. Partition coefficient, defined as the ratio of the metal ion adsorbed to the amount in the liquid phase, provided quantitative estimate of efficiency of sorption; values of partition coefficient lower than 1.0 indicating low sorption efficiency. The values of partition coefficient of Zn(II) ions between the active carbon and continuous aqueous phase are in the range 0.786 – 0.190 L/g for the range of initial metal ion concentrations (0.5-2.5 mM) used in this study. Although these results suggest that treatment of wastewater, containing high levels of Zn(II) ions with rubber seed shell carbon may require several sorption cycles, the carbon would be suitable in the treatment of large volumes of wastewaters containing low levels of the metal ions. The sorption data were fitted into the Langmuir and Freundlich isotherm equations. The values of the constants of the isotherm equation are given in Table 2. The Langmuir isotherm better represented the distribution between the adsorbent and liquid phases of Zn(II) ions judging from the higher values of the correlation coefficient. Values of maximum Zn(II) ion adsorption capacity and binding capacity of the shell carbon derived from fitting the data into the Langmuir model were 0.425 mmol/g and 2.61 L mmol⁻¹ respectively. Large values of binding constant reflect the ability of the adsorbent to bind large amount of adsorbate.

Desorption studies

The rates of desorption of Zn(II) ions from activated carbon in dilute aqueous HCl solution were studied at different temperatures. The rate of desorption of metal ions from the surface of the carbon particles can be expressed as

\[ r_d = k_dC \]  

where \( r_d \) is the rate of description, \( k_d \) is the rate constant of desorption and \( C \) is the metal ion concentration in the liquid phase. Of course at time \( t = 0 \), \( C = 0 \). The desorption of metal ions from a previously saturated adsorbent surface may be given by the first-order rate law in which a semi-logarithmic plot of surface concentration of the metal ions versus time should allow the rate constant for desorption to be obtained. Figure 1 shows such plots for the desorption of Zn(II) ions from activated carbon in dilute HCl solution. The values of rate constant of desorption, of the order of \( 10^2 \) min⁻¹ obtained are given in Table 3. Activation energy of desorption \( \Delta E_{des} \) was obtained from the dependence of desorption rate constant on temperature. The values of \( \Delta E_{des} \) of 24.49 kJ mol⁻¹ correlates closely with the value of enthalpy of adsorption \( \Delta H_{des} \) (-26.05 kJ mol⁻¹) reported previously.

**Adsorption of alcohols**

The removal of methanol, ethanol and \( n \)-propanol from aqueous solution was estimated from measurement of changes in the values of chemical oxygen demand, COD. Chemical oxygen demand is a frequently determined parameter to indicate the pollution strength of wastewaters. Figure 2 shows the uptake levels of the alcohols from aqueous solution by the shell carbons. It would seem from the results...
that only moderate reductions, of less than 30%, in the value of COD resulted from the one-cycle equilibrium treatment of the aqueous alcohol mixtures with the shell carbon. Although the alcohols used in this study are miscible with water in all proportions, n-propanol appeared to have been most efficiently removed from the aqueous solution, while the uptake levels of methanol were the lowest. The ability of active carbons to remove organic compounds from aqueous solution depends on the structure/surface chemistry of the carbon and the nature (polarity) of the organic compound. Earlier studies indicated that oxidation produces oxygen-containing groups, such as carbonyl, quinonic and phenolic, on the carbon surface and that oxidation at temperatures up to 350 °C for several hours have little effect on the adsorptive properties of activated carbons towards organic compounds. It has been suggested that these properties taken together allow for the production of effective bi-functional activated carbon, with nonpolar surfaces available in finer micropores and the wider micropores and some mesopores. The rubber seed shell carbon used in the study was prepared in the presence of limited amount of oxygen, therefore allowing for oxidation of the carbon. The relative effectiveness of the shell carbon in reducing the COD of aqueous mixture of alcohols suggest that rubber seed shell can serve as precursor materials in the production of useful bi-functional activated carbons.

Figure 3 shows the trends of normalized COD concentration as a function of time. The slopes of the trends represent the observed constant of the pseudofirst-order model for the removal of COD and from linear regression values of 0.0024, 0.0027 and 0.0029 min⁻¹ were obtained as rate constants for the removal of methanol, ethanol and n-propanol respectively from aqueous solution by activated carbon derived from rubber seed shell.

Conclusion
Powdered activated carbon produced from using rubber seed shell and ammonium chloride as chemical activator has been used in removing Zn(II) ions and alcohols from aqueous solutions. The results show that the shell carbon is an effective remover of metal ions and organic compounds from aqueous solution. Although further work needs to be carried out to optimize the activation and carbonization process conditions. The potential for the production of activated carbons from rubber seed shells for

![Fig. 2](image2.png)

Fig. 2—Removal of alcohols from aqueous solution by rubber seed shell carbon at 29 °C.

![Fig. 3](image3.png)

Fig. 3—Rate of alcohol removal from aqueous solution by rubber seed shell carbon using 0.05 volume fraction of alcohol.
environmental remediation of metals and organics is indicated from the present study.

References