Select metal adsorption by activated carbon made from peanut shells

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Abstract

Agricultural by-products, such as peanut shells, contribute large quantities of lignocellulosic waste to the environment each growing season; but few, if any, value-added uses exist for their disposal. The objective of this study was to convert peanut shells to activated carbons for use in adsorption of select metal ions, namely, cadmium (Cd2+), copper (Cu2+), lead (Pb2+), nickel (Ni2+) and zinc (Zn2+). Milled peanut shells were pyrolyzed in an inert atmosphere of nitrogen gas, and then activated with steam at different activation times. Following pyrolysis and activation, the carbons underwent air oxidation. The prepared carbons were evaluated either for adsorption efficiency or adsorption capacity; and these parameters were compared to the same parameters obtained from three commercial carbons, namely, DARCO 12×20, NORIT C GRAN and MINOTAUR. One of the peanut shell-based carbons had metal ion adsorption efficiencies greater than two of the three commercial carbons but somewhat less than but close to Minotaur. This study demonstrates that peanut shells can serve as a source for activated carbons with metal ion-removing potential and may serve as a replacement for coal-based commercial carbons in applications that warrant their use.

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1. Introduction

Metal ion contamination of drinking water and wastewater, especially with metal ions such as cadmium, copper, lead, nickel and zinc, is a serious and ongoing problem. Cadmium, copper, lead, nickel and zinc, are toxic at high concentrations and are high frequency pollutants seen in municipalities and specific industries throughout the United States (Kosarek, 1981). Since contaminated wastewater can easily find its way into both surface water and ground water, this problem should be of great concern to anyone who obtains their drinking water from these sources.

In a typical residential water filter or in an industrial or municipal wastewater treatment system, cation exchange resins and, to a lesser extent, granular activated carbons (GACs) are used for removing metal ions to concentrations below the US EPA mandated levels (Chermisinoff, 1990; McKay, 1996). Commercial cation exchange resins are made from either styrene-divinylbenzene beads or cellulose with cationic functional groups grafted onto the beads or cellulose. Styrene and divinylbenzene are petroleum-derived products, and most of the GACs produced in the US are made from coal. GAC products for wastewater treatment can be easily reused with proper washing procedures. After repeatedly used, GACs can be burned off without any impact on the environment. However, petroleum and coal are non-renewable and expensive source materials and are being depleted in the US. Therefore, it is a noble idea to use renewable resources, such as peanut shells, as a low cost alternative.

Commodity crops, such as peanuts, generate considerable quantities of shells each year, which have little or no value. Peanut shells are low in density and high in volume, and are used in animal feed or burned for energy. North Carolina currently ranks fourth in peanut production,
producing 95.2 thousand metric tons or 6.3\% of the United States production (Agricultural Statistics, 2003). This represents a potential of 26 thousand metric tons of peanut shells produced each year that have little value. This leads to a need to convert these by-products to useful, value-added products, such as activated carbons.

There have been several reports that peanut shells can be converted into activated carbon and used to absorb various metal ions and organic compounds using sulfuric acid as the activant (Periasamy et al., 1993; Namasivayam and Periasamy, 1993; Periasamy and Namasivayam, 1994, 1995a,b, 1996). Johns et al., 1998) reported that granular activated carbons produced from agricultural by-products, including peanut shells, by a combination of carbon dioxide or steam activation followed by air oxidation was considered an excellent adsorbent for both organic and metal pollutants. The authors found that a granular activated carbon made from peanut shells adsorbed Cd, Cu, Ni, Pb, and Zn ions to a greater extent than comparable commercial carbons.

The purpose of this study was to extend the observations of Johns et al. (1998) and develop granular activated carbons with good metal ion adsorption characteristics from peanut shells using pyrolysis and steam activation, followed by air oxidation. The resulting carbons were evaluated for adsorption efficiency and adsorption capacity toward the metal ions copper, lead, cadmium, zinc, and nickel; and their metal ion adsorption properties were compared to those of commercial carbons.

2. Methods

2.1. Materials

Peanut shells were obtained from the Carolina-Virginia Peanut Growers Association (Suffolk, VA). They were milled to a 10 × 20 mesh (2.00–0.85 mm) US sieve particle size using a Retsch SK 100 cross-beater mill (Glen Mills, Clifton, NJ). The milled peanut shells were mixed with molasses (Golding Farm Food Inc., Winston Salem, NC) at a ratio of 1.5:1 by weight (shells:molasses). The mixture was conveyed to a stainless steel cylinder with a diameter of 5.7 cm and a height of 7 cm that was placed in a Carver Model C hydraulic press (Fred S. Carver, Inc., Wabash, IN). Five thousand psi was applied to the shells/molasses mixture; and the mixture was held at that pressure for 30 min, followed by removal from the cylinder to form a briquette of 5.7 cm diameter and an approximate thickness of 3 cm.

Three commercial carbons were used as reference carbons. DARCO 12 × 40 (Norit Americas, Atlanta, GA) is a general purpose granular carbon produced by steam activation of lignite coal and acid washed. NORIT C GRAN (Norit Americas, Atlanta, GA) is a chemically activated granular carbon produced by a phosphoric acid activation process applied to coal and used in the food, chemical, and pharmaceutical industries. MINOTAUR (Calgon Carbon Corp.) is a coal-based granular carbon used in water purification applications, especially the removal of lead ions from drinking water.

2.2. Preparation of granular activated carbon

2.2.1. Pyrolysis

The briquettes were placed in a ceramic evaporating dish and weighed. The ceramic dish was then placed in a Lindberg bench furnace equipped with a retort (Lindberg/Blue M, Waterton, WI). While allowing a stream of nitrogen gas to flow into the sealed retort, the briquettes were heated at 800 °C for 2 h.

2.2.2. Steam activation

While maintaining the furnace at 800 °C under nitrogen gas–water was pumped into the gas flow line and carried by the nitrogen into the retort. The flow rate used was 7.5 ml/min using a Carter Cassette Model pump (Model 74-046-00000; Cassette 72-560-100) (Manostat, Barrington, IL) for 2, 3 or 4 h. The briquettes were allowed to cool overnight under nitrogen gas.

2.2.3. Oxidation

After cooling in the retort, the briquettes were removed and weighed. One part of the sample was crushed with a mortar and pestle into small pieces of carbon (<1 mm). The carbon particles were then placed back into the furnace and heated at 300 °C for 4 h under compressed air. They were cooled overnight under compressed air. Another set of samples was prepared in exactly the same manner but was kept in the briquette form without crushing.

2.2.4. Ash removal

After the cooling, the non-crushed briquettes were now crushed to less than 1 mm particle size; and all the carbon samples were weighed and placed into a 500 ml beaker. The carbons were washed with 0.1 M HCl for 1 h in order to remove surface ash. The carbons were washed with 3 l of distilled water to remove the hydrochloric acid and dried in an oven at 110 °C overnight. The carbons were removed, placed in a desiccator, and allowed to cool for 24 h.

2.3. Determination of carbon properties

2.3.1. Yield

Carbon yield was calculated by the following equation:

\[
\text{Carbon yield (\%)} = \left[ \frac{W_{c}}{W_{ps}} \right] \times 100
\]

where \(W_{c}\) = dry weight in gram of the carbon after acid and water washes, and \(W_{ps}\) = dry weight of the peanut shells.

2.3.2. Surface area

Surface area measurements were obtained from nitrogen adsorption isotherms at 77 K using a Quantachrome Model 2000 surface analyzer (Boynton Beach, FL). Surface
area measurements were taken from adsorption isotherms using the BET equation (Brunauer et al., 1938).

2.4. Adsorption efficiency determination

Five metal ions (Cd^{2+}, Cu^{2+}, Ni^{2+}, Pb^{2+} and Zn^{2+}) frequently found in industrial and municipal wastewater were chosen for this study. All metal ion solutions were made to a concentration of 20 mM in 0.07 M sodium acetate and 0.03 M acetic acid buffer, pH 4.8.

For a given set of analyses, 0.3 g portions of each peanut based-carbon activated carbon and 0.3 g portions of each commercial GSA were placed in separate 80 ml beakers; and 30 ml of a metal ion solution was added to each. Each mixture was stirred at 300 rpm for 24 h using a Vario Mag Multipoint HP 15 multiple stirrer (Labortecnik GmbH, Germany). Aliquots of the resulting slurries were removed in disposable syringes and filtered through a 0.22 μm Milipore filters (Millipore Corp., Bedford, MA) to remove any carbon particles.

One ml of each of the resulting filtrates (one filtrate from each mixture) was diluted to 50 ml with 2% nitric acid and analyzed by a Liberty 150 inductively coupled emission spectrometer (ICP) in radial mode, equipped with a model SPS-5 autosampler (Varian, Sugarland, TX). The software used was Plasma 96. The flow rate was set at 15 ml/min, nebulizer pressure at 150 Kpa, and power at 1 KW. Standard solutions were prepared at concentrations of 5, 25, 50, 75, 100 ppm, and a standard was selected after every 10 samples as a quality control. The following wavelengths were used: 324.75 nm for copper, 231.60 nm for nickel, 213.85 nm for zinc, 327.75 for cadmium, and 261.41 nm for lead. The metal ions left in solution were determined, and the amount of metal ion adsorbed per gram of sample was calculated.

2.5. Adsorption capacity determination

Metal ion solution concentrations were 5, 10, 15, 20, 25, 30, 35, 40, 45, and 50 mM in 0.07 M sodium acetate and 0.03 M acetic acid buffer at pH 4.8. Metal ion adsorption was carried out and determined by ICP analysis as described above. Adsorption isotherms were constructed and adsorption capacities were calculated using the Langmuir model for monolayer saturation of metal ions on carbon binding sites. The non-linear form of the Langmuir equation is given as follows:

\[ q_e = K_C Q_0 / (1 + K_C C_e) \]

where \( q_e \) is the equilibrium cation concentration in solution, \( q_0 \) is the amount of cation adsorbed per unit mass, \( Q_0 \) is the adsorption maximum or adsorption capacity and \( K \) is the affinity or association constant of the cation for the adsorbent.

Adsorption capacities (\( Q_0 \)) were determined from the above equation employing non-linear regression analysis of the adsorption isotherms using Sigma Plot v. 8.0 (SPSS Inc., Chicago, IL). For all equilibrium isotherms, regression values (\( r^2 \)) were such that the Langmuir model predicted the data set at \( p < 0.05 \).

2.6. Statistical analysis

One-way analysis of variance (ANOVA) was used to analyze differences in the adsorption efficiency and adsorption capacity data between samples. A simple one-way analysis was done because the only difference among treatments was the steam activation time. The analysis of variance was done using a Statistical Analysis System (SAS) ANOVA program where \( x \) was set at 0.05 (v. 6.12 from the SAS Institute, Inc., Cary, NC).

3. Results and discussion

Table 1 gives select properties of the experimental and commercial carbons. In two out of three pairs of samples, yield values were lower for the non-crushed samples. Also, for the crushed samples, yields were highest for the 2 h steam activation and lowest for the 4 h steam activation. This trend would be expected, since a longer activation time would result in greater burn-off and lower mass yield (Johns et al., 1998). However, this trend was not observed for the non-crushed carbons, as sample 8-3-4-N showed an unusually high final yield.

The non-crushed samples had higher surface area and greater amount of titratable functional groups than the crushed samples. These observations may be related to the lower final product yields for the non-crushed samples. These samples apparently received a greater amount of burn-off due to either steam activation or air oxidation or both. The structure of the non-crushed briquettes may

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Yield (%)</th>
<th>Surface area (m²/g)</th>
<th>Titratable functional groups (mmol H⁺/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8-2-4-N</td>
<td>8.0</td>
<td>726</td>
<td>5.55</td>
</tr>
<tr>
<td>8-2-4-C</td>
<td>15.1</td>
<td>542</td>
<td>4.80</td>
</tr>
<tr>
<td>8-3-4-N</td>
<td>15.8</td>
<td>757</td>
<td>6.02</td>
</tr>
<tr>
<td>8-3-4-C</td>
<td>13.4</td>
<td>542</td>
<td>4.80</td>
</tr>
<tr>
<td>8-4-4-N</td>
<td>7.2</td>
<td>725</td>
<td>6.10</td>
</tr>
<tr>
<td>8-4-4-C</td>
<td>10.4</td>
<td>719</td>
<td>4.46</td>
</tr>
<tr>
<td>DARCO 12 x 40</td>
<td>N/A²</td>
<td>605</td>
<td>3.39</td>
</tr>
<tr>
<td>NORIT C GRAN</td>
<td>N/A</td>
<td>624</td>
<td>17.1</td>
</tr>
<tr>
<td>MINOTAUR</td>
<td>N/A</td>
<td>815</td>
<td>28.8</td>
</tr>
</tbody>
</table>

¹ Experimental sample designations are given as follows: (activation temperature-activation time-oxidation time-non-crushed (N) or crushed (C) carbon before oxidation, where \( 8 = 800 ^\circ C, 2, 3 \) and \( 4 = 2 \) h, \( 3 \) h and \( 4 \) h and \( 4 = 4 \) h).

² N/A = not available.
be more porous than the crushed particles, allowing greater interaction with the activating agent, steam, and the oxidizing agent (air).

The metal ion adsorption efficiencies of the peanut shell-based carbons prepared under different activation times and adsorption efficiencies for the commercial carbons in Table 2. In terms of the experimental samples, there were significant differences in metal ion adsorption among treatment types, while the mean values were calculated across the different treatment types. The peanut shell-based carbons which were steam activated for 4 h and not crushed (8-4-4-N) or crushed (8-4-4-C), showed significantly higher adsorption for all five metal ions (copper, lead, nickel, zinc, and cadmium) than all of the other peanut shell-based carbons. The 8-4-4-N sample adsorbed the greatest amount of metal ions. The 8-2-4-C sample adsorbed the least amount of metal ions among the peanut shell-based carbons except for lead ion, where carbon 8-3-4-C had the lowest adsorption value. The non-crushed carbons showed higher metal ion adsorption than their crushed counterparts in each group. However, the carbon with the greatest metal ion binding in Table 2 was the commercial carbon, MINOTAUR. The commercial carbon designated NORIT C GRAN was also good at metal ion adsorption and came behind the experimental carbon 8-4-4-N in amount of metal ion adsorbed. The other carbon, DARCO 12 × 40, was the poorest adsorber of metal ions among the commercial carbons.

Metal ion binding appears to be dependent on the number of titratable functional groups or the amount of negative charge on the carbon surface. The titratable groups in the carbon designated 8-4-4-N was the highest of all the experimental carbons, while MINOTAUR had the greater number of titratable functional groups of any of the carbons. Carbons with higher titratable functional groups are better at binding metal ions than carbons with lower amounts of titratable functional groups (Tolles et al., 1999). Moreover, the non-crushed samples in each pair had greater negative surface charge than the crushed carbons and also possessed greater metal ion binding. Surface area appears to play little if any role in metal ion adsorption, as no correspondence between the two variables could be observed.

The data for the adsorption capacities based on the Langmuir isotherm for the experimental peanut shell-based carbon (8-4-4-N), that showed the highest adsorption efficiency among the experimental carbons are presented in Table 3. Two of the commercial carbons, NORIT C GRAN and MINOTAUR, that showed the highest adsorption efficiencies among the reference carbons (Table 2) are compared with the 8-4-4-N carbon. DARCO 12 × 40 carbon was not considered further for evaluation of adsorption capacity and therefore not included in Table 3 because of its poor adsorption efficiency performance (Table 2) compared to NORIT C GRAIN and MINORTAUR. MINOTAUR had the highest adsorption capacities of the

Table 2
Metal ion adsorption efficiency¹ among peanut shell-based carbons and commercial carbons

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Metal ion adsorption (mmol/g of carbon)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cu²⁺</td>
</tr>
<tr>
<td>8-2-4-N</td>
<td>0.440 ± 0.027²</td>
</tr>
<tr>
<td>8-2-4-C</td>
<td>0.203 ± 0.025</td>
</tr>
<tr>
<td>8-3-4-N</td>
<td>0.598 ± 0.021</td>
</tr>
<tr>
<td>8-3-4-C</td>
<td>0.301 ± 0.038</td>
</tr>
<tr>
<td>8-4-4-N</td>
<td>0.843 ± 0.027</td>
</tr>
<tr>
<td>8-4-4-C</td>
<td>0.600 ± 0.024</td>
</tr>
<tr>
<td>DARCO 12 × 40</td>
<td>0.410 ± 0.011</td>
</tr>
<tr>
<td>NORIT C GRAN</td>
<td>0.752 ± 0.010</td>
</tr>
<tr>
<td>MINOTAUR</td>
<td>0.964 ± 0.014</td>
</tr>
</tbody>
</table>

¹ Data are presented as the means of duplicate samples ± standard deviation. Means with the same letter in each column are not significantly different at the 5% level.
² Standard deviation.

Table 3
Adsorption capacities¹ of peanut shell-based carbons and commercial carbons

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Adsorption capacity (Q₀) (mmol/g carbon)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cu²⁺</td>
</tr>
<tr>
<td>8-4-4-N</td>
<td>0.793 ± 0.020²</td>
</tr>
<tr>
<td>NORIT C GRAN</td>
<td>0.874 ± 0.028</td>
</tr>
<tr>
<td>MINOTAUR</td>
<td>1.016 ± 0.021</td>
</tr>
</tbody>
</table>

¹ Data are presented as the means of duplicate samples ± standard deviation. Means with the same letter in each column are not significantly different at the 5% level.
² Standard deviation.

three carbons for all metal ions except the zinc ion. The adsorption capacity of 8-4-4-N for lead, nickel, zinc, and cadmium ions was higher than the adsorption capacity of NORIT C GRAN for these ions and higher than MINOTAUR with respect to zinc only.

As mentioned above, NORIT C GRAN is a granular carbon produced by chemical activation using phosphoric acid. This carbon had a high concentration of titratable functional groups and was generally a good metal ion adsorbent (Tables 2 and 3). However, NORIT C GRAN showed strong evidence of residual phosphoric acid in the carbon as evidenced by the immediate formation of a white precipitate of lead phosphate when a slurry of the carbon in water was tested for the presence of phosphate with lead nitrate solution. The presence of residual phosphoric acid can result in a greater amount of titratable functional groups than in the absence of residual phosphate groups and also leads to higher metal ion binding. If the residual phosphate were removed, NORIT C GRAN would likely show reduced metal ion binding. MINOTAUR, however, showed no residual phosphate when subjected to the lead nitrate test. The manufacturer will not divulge manufacturing information on this carbon other than to say that coal is the feedstock. Based on our results (Tables 2 and 3), Calgon's manufacturing process was able to create a carbon with high negative surface charge and high metal ion binding.

The adsorption capacity data (Table 3) indicate that with judicious control of steam activation time, peanut shell-based carbons can be developed with high adsorption capacity toward metal ions in solution and could potentially replace coal-based commercial carbons currently sold in the marketplace. Although peanut shell-based carbons could potentially replace coal-based commercial carbons, they would still require desorption of metal ions with suitable mineral acid for reuse or the spent carbons could be transported to a hazardous waste landfill, as would the commercial carbons under similar circumstances.

4. Conclusions

In conclusion, granular activated carbons made by steam activation, followed by air oxidation of peanut shells have been shown to individually bind a set of potentially toxic metal ions commonly found in the environment. Compared to metal ion binding by three reference carbons, steam-activated, air-oxidized peanut shell carbons showed adsorption properties similar to the best commercial, coal-based carbons. Production advantages compared to the coal-based carbons would include: (1) a less costly feedstock, peanut shells versus coal, (2) activation with steam and air rather than with a more costly activant, such as phosphoric acid, and (3) a generally simpler manufacturing process with no need for removal and recycling of the acid activant.

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