Removal of Heavy Metals by Using Activated Carbon Produced from Cotton Stalks

Mohamed El Zayat and Edward Smith
Environmental Engineering Program, the American University in Cairo

Abstract
Utilization of agricultural waste to produce valuable products has opened opportunities in Egypt to minimize serious public health risks from exposure to dangerous fumes that come from burning the agricultural wastes in open fields. In this study, activated carbon produced locally from cotton stalks was examined for the removal of target heavy metal contaminants from water and wastewater. Adsorption studies conducted in completely mixed batch reactors showed the ability of the produced activated carbon to remove heavy metals; namely lead, cadmium and copper; from aqueous solutions in a pH range below that of precipitation and with high uptake capacity after an equilibrium reaction time of 72 hours. The surface titration experiment indicated a negative surface charge of the produced activated carbon in solution at pH as low as 6, meaning that electrostatic attraction of the divalent heavy metals can occur below the pH required for precipitation. The highest adsorption capacity was for lead, followed by copper and then cadmium. Multicomponent metal adsorption experiments indicated a competition for the available surface sites. Adsorption capacities in the mixture were reduced from their single-solute values for all metals.

Introduction
Heavy metals are any element in the d-block of the periodic table, or transition metals. Many are also known to be toxic to both humans and other living forms, with their accumulation over time causing damage to the kidney, liver, and reproductive system in addition to cancer (Lentech, 1998). Heavy metal pollution derives from a number of sources, including lead in petrol, industrial effluents, and leaching of metal ions from the soil into lakes and rivers by acid rain. Moreover, they arise from the purification of metals, for instance smelting of ores, preparation of nuclear fuels, and electroplating (Lef, 1998). They precipitate into soil, underground water, and surface water. Unlike organic contaminants, heavy metals do not normally undergo biological decay and are thus considered a challenge for remediation. Many governments have enacted laws to hinder discharging heavy metals into water bodies and using toxic substances such as lead (Abdelshafi, 2007). However, heavy metals still find their way to water supplies. Accordingly, many studies have been done for removal of heavy metals. Ion exchange, reverse osmosis, and chemical precipitation have been investigated for the removal process, but they are too expensive or incapable of meeting treatment objectives. Adsorption has been proved to be a potentially feasible alternative. Adsorption by using activated carbon is the most common method, but this too may be expensive, particularly if proper raw materials are not available and therefore the carbon has to be imported.

Motivated by cost considerations, locally generated agricultural wastes such as cotton stalks, rice straw, sugar cane bagasse, and others have been tested in the production of activated carbon in developing countries (Logan, 2002). The use of these raw materials in carbon production shows from the past studies that they are available at low cost, contain high carbon content, and may be effective in the removal of heavy metals and other toxic pollutants. This research investigated the effectiveness of activated carbon produced from cotton stalks in the adsorption of three target heavy metals – lead, cadmium, and copper – from aqueous solution in both single and multicomponent metal cases.

Materials and Methods
Activated Carbon
The activated carbon used in this work was produced from cotton stalks, with the production procedure and carbon properties described in Louis (2006). The carbon had a surface area of approximately 850 m$^2$/g. For this research, a sample of the produced carbon was sieved using U.S standard sieves. The pass 200 fraction was used for the surface titration experiment, and 35-50 mesh fraction was used in the adsorption experiments.
**Surface Titration**

Sorbent samples were titrated potentiometrically in order to estimate surface charge characteristics. A 0.5 g dry sample (200 x 325 mesh) was suspended in a Teflon reaction vessel containing 50 ml of deionized distilled water (DDW) at room temperature to yield a solid concentration of 10 g/L. The suspension was continuously stirred and purged by ultra pure nitrogen gas prior to titration in order to remove CO$_2$ that would interfere with an acid-base titration. Standard HNO$_3$ (0.1 M) and NaOH (0.1 M) were added precisely to adjust the pH. NaNO$_3$ was used as an ionic background in order to standardize the solution. The NaOH was incrementally added to the suspended solution to raise the pH, and the HNO$_3$ was incrementally added to lower the pH. The total volume of acid and base added was less than 5% of the sample volume to minimize dilution effects. The pH was measured for increments of 0.1 mL, for both acid and base. The experiment was done for ionic backgrounds of 0.1M, 0.01M, and 0.001M to examine the impact of background total dissolved solids concentration on surface charge of the carbon.

**Batch Equilibrium Experiments**

All the synthetic solutions had the same molar concentration of metal of 0.0048 M. The same molarity was used so that the relative adsorption capacity of the target metals can be compared in a meaningful way. The purposes of this set of experiments were to determine the pH-adsorption edge for the three target heavy metals in single versus multicomponent systems and the impact of system variables on adsorption capacity. Typical parameters for the equilibrium experiments conducted are presented in Table 1.

<table>
<thead>
<tr>
<th>Carbon Dose (gm/L)</th>
<th>Carbon Size (mesh)</th>
<th>Cadmium Concentration (mg/L)</th>
<th>Lead Concentration (mg/L)</th>
<th>Copper Concentration (mg/L)</th>
<th>pH Range</th>
<th>Reaction Time (Days)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>No Carbon</td>
<td>5.4</td>
<td>10</td>
<td>3.05</td>
<td>3-11</td>
<td>3</td>
</tr>
<tr>
<td>0.5</td>
<td>35-50</td>
<td>5.4</td>
<td>10</td>
<td>3.05</td>
<td>3-11</td>
<td>3</td>
</tr>
<tr>
<td>1.0</td>
<td>35-50</td>
<td>5.4</td>
<td>10</td>
<td>3.05</td>
<td>3-11</td>
<td>3</td>
</tr>
<tr>
<td>1.0</td>
<td>35-50</td>
<td>Mixture of the three metals(Cd, Pb, and Cu)</td>
<td>3-11</td>
<td>3</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

5.4 10 3.05

**Results and Discussion**

**Surface Titration**

Sorbent samples were titrated potentiometrically at room temperature in order to observe the acid-base nature of the carbon surface. The experiment was conducted for ionic backgrounds of 0.1M, 0.01M, and 0.001M, where Figure 1 shows the surface titration data of activated carbon for the different ionic strengths. Figure 1 indicates that the acid-base titration curve of the aqueous solution with the suspended activated carbon is characteristic of a weak acid-base system for the different ionic strengths. The three curves intersect at $\approx$ pH 5.6 meaning that thermodynamically, the system will try to drive toward this point. It also signifies that the surface charge on the sorbent surface is zero at pH 5.6, which is referred to as the $pH_{zpc}$, or pH of zero point of charge (Chris et al., 2000).

The surface titration data were used to calculate the surface charge of the sorbent by using the following equation:

$$\sigma = \frac{F}{AS} [C_A - C_B - (H^+) + (OH^-)]$$

where $F$: Constant = 96485.339 Coulomb/mole

$S$: Sorbent concentration = 10 g/l according to this study
A: Surface area of sorbent = 838 m$^2$/g

$H^+ : 10^{(\text{pH value})}$

$OH^- : 10^{(14-\text{pH value})}$

$C_A, C_B$: Acid or base added (moles/L)

$\sigma$: The surface charge density

The results showed that the activated carbon used in the experiments has negative surface charge at pH greater than 5.5 for different ionic backgrounds as shown in Figure 2.

**Figure 1: Surface Titration Data of Activated Carbon for Three Ionic Strengths.**

**Figure 2: The Sorbent Surface Charge at different pH values for different Ionic Backgrounds**

**Batch Equilibrium Experiments**

An experiment without activated carbon was carried out to investigate the precipitation pH range of the heavy metal so that the impact of the presence of carbon alone can be investigated. Figures 3 to 5 show the removal efficiency of Cd, Cu, and Pb from aqueous solution due to precipitation as a function of equilibrium pH. Smith (1998) obtained similar results as shown in the same charts.
Figure 3: Cadmium Removal by Precipitation

![Figure 3](image1.png)

**Equilibrium pH**

- % Removal of Cd

- Co(Cd) = 5.4 mg/l
- Ionic Background = 0.01 M
- Smith 1998

Figure 4: Lead removal by precipitation

![Figure 4](image2.png)

**Equilibrium pH**

- % Removal of Pb

- C₀(Pb) = 10 ppm
- Ionic background = 0.01 M
- Smith 1998

Figure 5: Copper Removal by Precipitation

![Figure 5](image3.png)

**Equilibrium pH**

- % Removal of Cu

- C₀ (Cu) = 3.05 ppm
- Ionic background = 0.01 M
A carbon dose of 0.5 g/l of the 35-50 mesh fractions was used with each element individually to determine the pH-adsorption edge for the produced carbon as shown in Figures 6 to 8. This indicates that the adsorption process took place well before substantial precipitation began to occur with respect to the pH scale. According to the surface charge results that showed the negative charge of the sorbent at pH > 5.6, a surface reaction involving electrostatic attraction of M²⁺ is likely responsible for the sharp increase in the adsorption of heavy metals onto the surface of the activated carbon. However, the notable removal of metal below this pH value indicates that surface complexation reactions are also important.

The experiments were repeated to investigate the impact of carbon dose on heavy metals uptake from aqueous solution. Figures 9 to 11 indicate that the heavy metals removal increases for the higher dose (1.0 versus 0.5 g/l), especially for pH values greater than 5.0. It is difficult to know with certainty whether heavy metals removal for higher pH values is dominated by adsorption, precipitation of metals, or a more complex surface interaction. It is likely a combination of several processes occurring simultaneously (Smith et al., 1996).
Figure 8: Copper Removal for Carbon Dose 0.5g/l

Figure 9: Comparison of pH adsorption edges for different carbon doses for Cadmium

Figure 10: Comparison of pH adsorption edges for different carbon doses for Lead
Figure 11: Comparison of pH Adsorption Edges for Copper for Different Carbon Doses

Figure 12 shows that the uptake capacity followed the trend of $Cu \geq Pb > Cd$, which is consistent with the electronegativity where the electronegativity of these metals are 1.85, 1.854, and 1.52 respectively (from the periodic table). Since the activated carbon is negatively charged, the potential of the electrostatic adsorption among the three adsorbates increases directly proportional to their electronegativity.

Figure 13 shows the pH-adsorption edge for the multicomponent experiment when a carbon dose of 1.0 g/l was used for a mixture solution of Pb, Cd, and Cu with the same concentrations as the previous experiments ($10 \text{ mg/l Pb}; 5.4\text{ mg/l Cd}; 3.05\text{ mg/l Cu}$). This experiment has shown that the lead removal reaches almost 99% at pH>5.0. The removal for copper reaches almost 99% starting from pH=6.3, while the percentage removal is greater than 80% for pH>5.5. For cadmium, the removal efficiency barely reaches 80% for pH=9.0. The results of this experiment show that the percent removal uptake followed the trend of Pb$>$Cu$>$Cd which gives insight into competition effects among the three solutes during the adsorption process by the activated carbon. Furthermore, the results of the removal percentage of each element have slightly changed either in the percentage uptake or the pH-adsorption range where it may be considered due to a competition among the elements in the adsorption process. The pH adsorption edge investigations suggest that there is potential for the use of the produced carbon to remove certain heavy metals from both waste water and drinking water. It also indicates that the suitable pH for Pb and Cu removal by adsorption is 5.5-6.5, while for Cd removal it is almost 8.0.
Based on batch equilibrium studies, the uptake capacity of the three heavy metals studies appears to be greatest for Pb, followed by Cu and then Cd. The presence of multiple heavy metals in solution promoted a competition among them during the adsorption process. The uptake capacity was greater for single solutes than in the multicomponent case, especially for Cu and Cd. By checking the uptake of the three heavy metals in the single component experiments on a molar basis, the greatest removal was for Cu followed closely by Pb and then Cd. In the multi-component experiment for the same carbon dose of 1.0 g/l, one can find that the uptake capacity was greater for Pb than Cu followed by Cd. To conclude, Cd was significantly affected by the presence of other heavy metals. Cu was affected to a lesser degree. Amazingly, the Pb removal improved as shown in Table 3.

Table 3: Adsorption Capacity of Cd, Pb, and Cu at different pH values (carbon dose of 1.0 g/l)

<table>
<thead>
<tr>
<th>pH</th>
<th>5.0</th>
<th>5.5</th>
<th>6.0</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Single Solute</td>
<td>Multi-component</td>
<td>Single Solute</td>
</tr>
<tr>
<td>Cd (µM/g)</td>
<td>10.7</td>
<td>2.88</td>
<td>19.2</td>
</tr>
<tr>
<td>Pb (µM/g)</td>
<td>35.23</td>
<td>41.02</td>
<td>38</td>
</tr>
<tr>
<td>Cu (µM/g)</td>
<td>36</td>
<td>27.86</td>
<td>42.16</td>
</tr>
</tbody>
</table>

Conclusions

- The produced activated carbon demonstrates potential to adsorb heavy metals in batch equilibrium studies from both single and multicomponent aqueous solutions, especially at pH higher than 5.5. The activated carbon has high negative charge above pH 5.5 for different ionic backgrounds. Also, the surface titration experiment shows that the zero point of charge for the produced activated carbon is at pH 5.5.

- The high removal at pH values greater than 5.5 is motivated by the electrostatic interaction between the activated carbon with its high negative charge and the heavy metal elements with their positive charge (+2). However, in some cases a notable removal has occurred at lower pH values which may be due to surface complexation.

- Single solute pH adsorption edges for the same molar concentration of metal and same carbon dose indicated that the adsorption capacity was nearly the same for Cu and Pb, with values for Cu...
being only slightly higher at certain pH values on a molar basis. Adsorption capacity of Cd was considerably less than for Cu and Pb.

- The mixed heavy metals compete with each other during the adsorption process. The heavy metal capacity followed a similar trend as in the single solute studies, except that Pb clearly competed better than Cu in the multicomponent case in the pH range of study. Pb was the least affected by competition, followed by Cu and then Cd.

References