THE PERFORMANCE OF ACTIVATED CARBONS FROM SUGARCANE BAGASSE, BABASSU, AND COCONUT SHELLS IN REMOVING RESIDUAL CHLORINE

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Abstract - The capacity of activated carbons obtained from different raw materials, such as sugarcane bagasse, babassu (Orbygnya speciosa), and coconut (Cocus nucifera) shells, to remove residual chlorine is studied. The influence of particle size and time of contact between particles of activated carbon and the chlorinated solution were taken into account. The adsorptive properties of the activated carbons were measured by gas adsorption (BET method), using an ASAP 2010 porosimeter, and liquid phase adsorption, employing iodine and methylene blue adsorbates. The activated carbon from sugarcane bagasse was the only adsorbent capable of removing 100% of the residual chlorine.

Keywords: Activated carbon; Adsorption; Removal of residual chlorine.

INTRODUCTION

The water used directly in almost all food or beverage production processes is potable. The World Health Organization, WHO, defines potable water as water that is limpid and transparent, odorless, with no objectionable taste, and free from any kind of microorganism or chemical substance in concentrations that can cause a risk to human health.

For disinfection in many public water treatment facilities, chlorine and chlorine compounds (sodium hypochlorite, chlorine dioxide, and calcium hypochlorite) are used. Chlorine is a powerful oxidizing agent, able to penetrate cells and to act on vital cellular substances, killing microorganisms. The concentration of free residual chlorine in drinkable water should be in the range of 1.5 to 2.0 mg L⁻¹ (U.S. EPA, 1999).

Many food and beverage industries use water in their processes that has been treated with chlorine in city facilities and therefore still contains active chlorine, i.e. some residual chlorine. In other industries, the water from city water distribution plants receives an additional dosage of chlorine so as to guarantee the level of quality required by the process. It is known that there is a natural tendency for chlorine to react with organic substances, forming chloramine, which alters characteristics of the final product such as taste and odor, and total trihalomethanes, (TTHM), associated with an increased risk of cancer as well as damage to heart, lung, kidney, liver, and central nervous system. For

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this reason, these food and beverage industries have
to keep the water used in all processes in which it
comes into direct contact with the products free from
residual chlorine. That residual chlorine is removed
with activated carbon.

Activated carbon is a porous carbonaceous
material prepared through the carbonization and
activation of organic substances, mainly of vegetable
origin. During carbonization of raw lignocellulosic
material, a solid residue (charcoal) and volatile gases
are produced. During this process pores, i.e., voids
between the graphite crystals, are formed. Activation
occurs immediately after carbonization. Activation
may be chemical or physical. The intermediate
product is removed and the graphite crystals become
exposed to the activating agent (Smíšek and Černý,
1970). This increases the number and the
dimensions of the pores during activation.

Due to its well-developed pore structure,
activated carbon in either powder or granules has an
excellent adsorbent capacity. Depending on the
nature of the raw material, on the size of the particles
(granules or powder), and obviously on the chosen
production process, activated carbons have different
adsorption capacities.

The quality of activated carbons is evaluated in
terms of their physical properties of adsorption and
of superficial area, using different analytical methods
for liquid and for gas phase adsorption (Smíšek and
Černý, 1970; Gergova et al., 1993; El-Hendawy et
al., 2001). For the gas phase, characterization may
rely on measurement of the adsorption of nitrogen
and application of one of the different procedures
available to determine superficial area, such as the
BET method (Brunauer et al., 1938) or that of
Langmuir (JIS K 1474). For the liquid phase, the
characterization may be achieved with iodine or with
methylene blue adsorption.

All of the raw materials used in this work,
coconut, probably the most typical and traditional
raw material for the preparation of biomass activated
carbon; babassu; and sugarcane bagasse, are very
abundant in the Brazilian Northeast.

**EXPERIMENTAL**

**Process Variables**

In the pyrolysis and activation processes, there
are some variables that may be controlled, allowing
optimization of some parameters such as yield and
the structural characteristics of the activated carbon.
In this study, five variables of the activation process
were considered: 1. carbonization temperature, 2.
heating rate, 3. steam flow, 4. activation
temperature, and 5. residence time. The choice of a
carbonization temperature of 500 °C, i.e., the
temperature at which the matter should be totally
pyrolyzed, was possible by taking into account the
thermogravimetric curves of all raw materials used
in this study. The heating rate in all experiments was
set to 10 K min^{-1}. Physical activation with steam at
the rate of 0.8 kg h^{-1} was used. Lower steam flow
reduces the formation of the pores, while higher
flows may drop the temperature in the reactor and
produce very humid activated carbon. In general, the
choice of the residence time for the activation
depends on the desired porous structure distributions,
and yield. The maximum activation temperature in
this study was 800 °C for sugarcane bagasse and 900
°C for the coconut and babassu shells. In all cases the
residence time for activation was 20 min.

**Carbonization and Activation**

The raw materials were pyrolyzed in a rotary kiln
inside a fixed-bed tubular reactor. The kiln allows
the establishment of pyrolysis and of activation
programs, through which temperature profiles and
heating rates are established. The steam at 110 °C,
necessary for activation, was generated by an electric
furnace coupled to the rotary kiln. An activated
carbon production scheme is shown in Fig. 1.

![Figure 1: Diagram showing the steps in production of activated carbon used in the present work.](image-url)
Characterization of the Activated Carbons

The adsorption isotherms for N\textsubscript{2} at 77 K as well as the BET and Langmuir surface areas, the Harkins and Jura t-graph, and the BJH chart from which the pore size distributions in the mesopore and macropore regions are evaluated were determined using a Micromeritics ASAP 2010 surface area analyzer for all the activated carbons in powder form (< 0.35 mm). Micropore volume was obtained from the t-graph.

The pH and the ash content of each sample were also determined. pH was measured using a pH-meter Quimis Q 400-A and the ash content was determined by a gravimetric method, following a JIS (JIS, 1992) norm.

To study the influence of particle dimensions on aqueous phase adsorption, all the activated carbons from the three raw materials were classified according to the following ranges of particle size, expressed in mm: a) 1.00 – 1.18, b) 1.18 – 1.68, c) 1.68 – 2.00, and d) 2.00 – 2.36.

For each activated carbon considered in this work, the iodine number and the methylene blue index were calculated, employing a four-point Freundlich isotherm. The iodine residual concentration was determined by titration with standard Na\textsubscript{2}S\textsubscript{2}O\textsubscript{2} solution, JIS (JIS K 1474), and the remaining methylene blue concentration was evaluated with a Hewlett Packard 845 UV/VIS spectrophotometer.

Residual Chlorine Adsorption

Sodium hypochlorite solutions of 10%, with residual chlorine concentrations between 2.5 to 3.0 mg L\textsuperscript{-1} were prepared with deionized water. Then 5 g of a granular activated carbon was poured into a bucket containing 8 L of the sodium hypochlorite solution. The bucket had rotary blades to stir and homogenize the solutions, from which 500 mL sample were taken at five-minute intervals during the period of one hour. Each sample was titrated with 0,001 mol L\textsuperscript{-1} of tiosulfate (cf. Streat et al., 1995) and its residual chlorine was determined.

RESULTS AND DISCUSSION

In Table 1 the BET superficial area, the iodine number, and the methylene blue index for powdered activated carbons are presented.

In Table 1 it can be seen that all activated carbons have BET superficial areas larger than 700 m\textsuperscript{2}g\textsuperscript{-1}, the smallest allowed for the majority of commercial activated carbons. (Streat et al., 1995; Bernardo et al., 1997; Sieh and Teng, 2000; Nevksaia et al., 1999). The activated carbons from babassu and bagasse had BET superficial areas larger than 800 m\textsuperscript{2}g\textsuperscript{-1}, and in all cases the activated carbon figures for babassu were higher than those for coconut.

The minimum iodine number recommended by the American Water Works Association (AWWA), for use of an activated carbon in removing compounds of low molecular weight is 500 mg g\textsuperscript{-1} (Warhurst et al., 1997). In Table 1 it is possible to see that all iodine numbers are more than 70% higher than the value considered by the AWWA.

The activated carbon that was most efficient in adsorbing methylene blue was the one from bagasse. Therefore, knowing that methylene blue is used to characterize mesoporous activated carbons, it can be inferred that of the three activated carbons studied the most mesoporous was the one from bagasse.

<table>
<thead>
<tr>
<th>Samples</th>
<th>S\textsubscript{BET} (m\textsuperscript{2}g\textsuperscript{-1})</th>
<th>I (mg g\textsuperscript{-1})</th>
<th>MB (mg g\textsuperscript{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coconut</td>
<td>712</td>
<td>854</td>
<td>48</td>
</tr>
<tr>
<td>Babassu</td>
<td>874</td>
<td>880</td>
<td>79</td>
</tr>
<tr>
<td>Bagasse</td>
<td>806</td>
<td>894</td>
<td>152</td>
</tr>
</tbody>
</table>

Tables 2 to 4 show figures on iodine and methylene blue adsorption for the four ranges of particle size.

As expected, for all activated carbons, an inverse relationship between adsorption capacity and the size of adsorbent particle was found. Independent of the range of particle sizes as well as of adsorbate, the adsorption capacities of the activated carbons from coconut and babassu were very similar. For the activated carbon from bagasse, for the three first
ranges of particle sizes the iodine numbers were at least 80% higher than the numbers for the activated carbon from babassu and coconut. The results for methylene blue adsorption show that activated carbon from bagasse has many more mesopores than that from the other two materials.

In Table 5 results on pH and ash content for the three activated carbons are shown.

Ash content is an indicator of the quality of an activated carbon. In general, the percentage of ash in a commercial activated carbon is higher than 10% (Bernardo et al., 1997). In the present study all activated carbons had ash contents lower than 7%.

All activated carbons considered in this work proved to be alkaline. The acid or basic nature of an activated carbon depends on its preparation and the inorganic matter and chemically active oxygen groups on its surface as well as the kind of treatment to which the activated carbon was submitted (Jankowska et al., 1991; Nev skaia et al., 1999).

### Table 2: Iodine (I) and methylene blue (MB) adsorption figures for the activated carbon from coconut for four ranges of particle size.

<table>
<thead>
<tr>
<th>Range (mm)</th>
<th>I (mg g(^{-1}))</th>
<th>MB (mg g(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.00-1.18</td>
<td>455</td>
<td>10.47</td>
</tr>
<tr>
<td>1.18-1.68</td>
<td>431</td>
<td>8.33</td>
</tr>
<tr>
<td>1.68-2.00</td>
<td>407</td>
<td>4.72</td>
</tr>
<tr>
<td>2.00-2.36</td>
<td>379</td>
<td>3.32</td>
</tr>
</tbody>
</table>

### Table 3: Iodine (I) and methylene blue (MB) adsorption figures for the activated carbon from babassu for four ranges of particle size.

<table>
<thead>
<tr>
<th>Range (mm)</th>
<th>I (mg g(^{-1}))</th>
<th>MB (mg g(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.00-1.18</td>
<td>467</td>
<td>14.11</td>
</tr>
<tr>
<td>1.18-1.68</td>
<td>447</td>
<td>13.65</td>
</tr>
<tr>
<td>1.68-2.00</td>
<td>432</td>
<td>6.16</td>
</tr>
<tr>
<td>2.00-2.36</td>
<td>391</td>
<td>5.79</td>
</tr>
</tbody>
</table>

### Table 4: Iodine (I) and methylene blue (MB) adsorption figures for the activated carbon from bagasse for four ranges of particle size.

<table>
<thead>
<tr>
<th>Range(mm)</th>
<th>I (mg g(^{-1}))</th>
<th>MB (mg g(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.00-1.18</td>
<td>815</td>
<td>79.57</td>
</tr>
<tr>
<td>1.18-1.68</td>
<td>803</td>
<td>40.11</td>
</tr>
<tr>
<td>1.68-2.00</td>
<td>789</td>
<td>35.12</td>
</tr>
<tr>
<td>2.00-2.36</td>
<td>708</td>
<td>34.86</td>
</tr>
</tbody>
</table>

### Table 5: pH and ash content of the three activated carbons.

<table>
<thead>
<tr>
<th>Active carbon</th>
<th>pH</th>
<th>Ash (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coconut</td>
<td>9.44</td>
<td>5.65</td>
</tr>
<tr>
<td>Babassu</td>
<td>9.25</td>
<td>6.49</td>
</tr>
<tr>
<td>Bagasse</td>
<td>9.04</td>
<td>1.65</td>
</tr>
</tbody>
</table>
Figures 2 to 5 show curves, which give the percentage of residual chlorine removed in terms of the time of contact between the activated carbon particles and the chlorinated solution. The effect of the three different activated carbons was evaluated, taking into account all the particle size ranges considered.

An analysis of Figs. 2 to 5 shows that for all particle size ranges the activated carbon from bagasse was the most efficient. This capacity may be higher than to 70%, when total removal of the residual chlorine by the activated carbon from bagasse is achieved.

The activated carbon from babassu is slightly more efficient than that from coconut in removing residual chlorine. For the range of particle sizes that was most efficient in babassu adsorption, i.e., 1.18 mm – 1.68 mm, the capacity of the babassu was about 15.4% higher. The lowest percentage was 9.1% for the range of smallest particle size.

**Figure 2:** Percentage of residual chlorine removal versus contact time for the three activated carbons with particle sizes in the range of 1.00 mm – 1.18 mm.

**Figure 3:** Percentage of residual chlorine removal versus contact time for the three activated carbons with particle sizes in the range of 1.18 mm – 1.68 mm.
Figure 4: Percentage of residual chlorine removal versus contact time, for the three activated carbons particle sizes in the range of 1.68 mm – 2.00 mm.

Figure 5: Percentage of residual chlorine removal versus contact time for the three activated carbons with particle sizes in the range of: 2.00 mm – 2.36 mm.

CONCLUSIONS

The activated carbon from babassu had the largest BET superficial area. All the powdered activated carbons had similar iodine adsorption capacities. However, for methylene blue adsorption, the activated carbon from bagasse was shown to be much better.

The granular activated carbons from coconut and babassu had very similar capacities to adsorb iodine, methylene blue, and residual chlorine, but that from sugarcane bagasse was the most efficient.

The activated carbon from bagasse was also the only one, which succeeded in completely eliminating the residual chlorine. For the other activated carbons, the maximum removal obtained was around 40% for a time of 60 min.

NOMENCLATURE

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>BET</td>
<td>Brunauer, Emmett, and Teller</td>
<td>(-)</td>
</tr>
<tr>
<td>BJH</td>
<td>Barrett, Joyner, and Halwnda</td>
<td>(-)</td>
</tr>
<tr>
<td>PA</td>
<td>Environmental Protection Agency</td>
<td>(-)</td>
</tr>
<tr>
<td>I</td>
<td>Iodine number, mg g⁻¹</td>
<td></td>
</tr>
<tr>
<td>JIS</td>
<td>Japanese Industrial Standards</td>
<td>(-)</td>
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</table>
REFERENCES


