EFFECT OF OZONATION ON THE ACTIVATED CARBON SURFACE CHEMICAL PROPERTIES AND ON 2-MERCAPTOBENZOTHIAZOLE ADSORPTION

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Abstract—Benzothiazoles are organic compounds that may produce negative environmental impact when released into watercourses. In particular, 2-mercaptobenzothiazole (MBT) are known to be toxic and hard to biodegrade. Activated carbon adsorption and ozonation have been identified as suitable treatment for those contaminants. However, there is some controversy about the effect of carbon surface chemical composition on the MBT adsorption. This paper focuses on this issue and presents experimental adsorption isotherms for MBT on Filtrasorb-400 activated carbon treated with different ozone doses. The activated carbon surface chemical properties were assessed by acid/basic neutralization, temperature programmed desorption (TPD), X-ray photoelectron spectroscopy (XPS), and the point of zero charge (pH\textsubscript{PZC}). Results show that ozone treatment modified the oxygenated groups on the activated carbon surface, increasing the concentration of acid groups, and reducing the pH\textsubscript{PZC}. Finally, ozone treatment led to a significant reduction of the carbon’s MBT adsorption capacity, due to the increase in polar hydrophilic groups.

Keywords—2-Mercaptobenzothiazole, Ozone, Activated Carbon, Surface Properties, Adsorption.

I. INTRODUCTION

2-Mercaptobenzothiazole (MBT) is a toxic xenobiotic compound widely used in the rubber industry, where effluents may be greater than 200 mg/dm\textsuperscript{3} (de Wever and Verachtert, 1997). It is also used as a biocorrosion inhibiting agent, as an anti-fungal drug in medical applications, as a metallic surface coating agent (Fiehn et al., 1998); as a fungicide in leather and wood industries (Paxeus, 1996). Leachate from hospital solid waste has been found to contain significant amount of MBT, probably derived from rubber seals (Airaudo et al., 1990). Moreover, MBT is highly resistant to biological attack in enriched activated sludge systems and tend to adsorb on the cell membrane leading to bioaccumulation (Gaja and Knapp, 1998).

On the other hand, ozonation combined with activated carbon adsorption offers an attractive option for MBT removal. Indeed, activated carbon presents a large surface area where ozone and MBT could adsorb and react. Ozone readily destroys adsorbed aromatic molecules, which may help to regenerate the activated carbon adsorption capacity (McKay and McAleavey, 1988; Kainulainen et al., 1995; Cannon et al., 1996; Croll, 1996). Also, activated surface groups may be responsible for catalytic effects found in ozonation in presence of activated carbon (Zaror, 1997).

However, ozone has been showed to oxidize the carbon and modify its surface chemical composition (Sutherland et al., 1996; Zaror et al., 2001). Unfortunately, little is known about the effect of such chemical modifications on the carbon adsorption capacity, which is key to process design. Surface properties may have a strong effect on both adsorptive and regenerative capacities.

Within this context, this paper reports experimental results on the chemical and physical modifications of activated carbon due to ozonation, and their effect on the MBT adsorption capacity. This work is part of a wider ongoing project to investigate the possibilities of the combined use of ozone and activated carbon in the elimination of contaminants from water.

II. EXPERIMENTAL

Commercial granulated activated carbon Filtrasorb 400 supplied by Calgon Carbon Corporation (Pittsburgh, USA) was used as starting material in this study. A batch of 500-800 µm particle size activated carbon was washed several times with deionized water to remove fines, oven dried at 170 °C during 24 hours, and stored in a desiccator until use. MBT and all chemicals used for analysis were purchased from Merck. Ozone was monitored by UV spectrophotometry (Spectronic...
Acid and base properties shown in Table 1 indicate that acid groups are massively formed due to ozonation, whereas basic groups are significantly reduced. Acid groups appear to be associated with oxygenated functional groups such as carboxyl, phenol, carbonyl, lactone and carboxylic anhydride (Barton et al., 1997). On the other hand, the basic behavior of activated carbon has been related with oxygen containing species, such as chromene and γ-pyrene-like structures (Boehm, 1994), and with electron system of the basal planes of the carbon (Leon y Leon et al., 1992).

TPD analysis showed in Fig. 1 indicate that ozonation leads to an increase in peaks both in the CO and CO₂ desorption profiles. Moreover, low temperature

### Table 1. Textural characterization and acid/base properties of the carbon samples

<table>
<thead>
<tr>
<th>Carbon</th>
<th>Textural characterization</th>
<th>Acid/base properties</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$A_{BET}$, m²/g $\alpha_m$ m²/g $V_{micro}$ cm³/g $V_{meso}$ cm³/g</td>
<td>Acidic sites, µeq/g Basic sites, µeq/g pHₚₑₑₑₑ</td>
</tr>
<tr>
<td>untreated</td>
<td>1000 54 0.474 0.019</td>
<td>234 570 8.82</td>
</tr>
<tr>
<td>OZ10</td>
<td>1023 87 0.472 0.031</td>
<td>702 437 5.96</td>
</tr>
<tr>
<td>OZ20</td>
<td>943 75 0.437 0.027</td>
<td>1030 399 5.12</td>
</tr>
<tr>
<td>OZ30</td>
<td>940 80 0.436 0.028</td>
<td>1498 304 4.76</td>
</tr>
<tr>
<td>OZ60</td>
<td>815 72 0.380 0.025</td>
<td>2059 171 3.89</td>
</tr>
<tr>
<td>OZ120</td>
<td>632 64 0.297 0.023</td>
<td>3370 - 2.59</td>
</tr>
</tbody>
</table>

where OZk refers to treated samples for k minutes ozonation.
peaks in the CO₂ curve (500-650 K) increase with ozone treatment which may show the presence of carboxylic and lactone groups (Zielke et al., 1996). This is supported by the significant decrease shown by the CO/CO₂ ratio, from 4.64 in the untreated carbon to 1.68 after 60 min. ozonation.

A fraction of acid sites generated by ozonation seems to be associated with the oxidation of basic groups present in the untreated carbon, as shown by the CO peak register at 1200 K, indicating the presence of γ-pyrone-like structures (Fritz et al., 1993). Other acid groups, such as ethers and lactones, may be generated by ozone addition to double bonds in the carbon structure, like in the reaction between ozone and alkenes (Deitz and Bitner, 1973).

The XPS spectra of both treated and untreated samples present two distinct peaks, due to carbon (C 1s) and oxygen (O 1s). Peaks were deconvoluted after the base line was subtracted (Biniak et al., 1997). The curve-fitting was performed using the non-linear least-squares algorithm with a Lorentzian-Gaussian functions 85:15 ratio. As shown in Table 2, the C 1s spectra have been resolved into five individual component peaks, namely the following: (1) graphitic, aromatic, or aliphatic carbon; (2) ether or phenol groups; (3) carbonyl groups; (4) carboxyl or esters groups; and (5) shake-up satellite peaks due to a π-π* transitions in aromatic rings. These results are in agreement with those reported by Biniak et al. (1997) and Zielke et al. (1996).

Moreover, the high-resolution O 1s spectra show the presence of 4 peaks, summarized in Table 2: (1) oxygen in carbonyl groups (C=O); (2) oxygen atoms in hydroxyl or ethers; (3) oxygen in anhydride, lactone, or carboxylic acids; (4) chemisorbed oxygen or water. These results agree with those reported by Figueiredo et al. (1999), using a commercial activated carbon modified with different procedures. It is interesting to note that the surface oxygen fraction increases from about 14% to more than 24% due to ozonation. Moreover, the O 1s:C 1s ratio, which indicates the degree of surface oxidation, increases from 0.16 to 0.34 after ozonation. Lactone, anhydride, and carboxylic acids surface concentrations increase due to ozonation, whereas carbon in graphitic or aromatic surface structures is significantly reduced as a result of the increase in the oxidation level. These results confirm those obtained by TPD and acid/basic neutralization.

### B. MBT adsorption analysis

MBT adsorption isotherms corresponding to activated carbon ozonated at different doses are shown in Fig. 2.

![Fig. 2. MBT adsorption isotherms at pH = 7 for: untreated, □; OZ30, ◊; OZ60, Δ; OZ120, ×.](image)

![Fig. 3. Relationship between adsorption capacities of MBT and the surface chemistry of the carbon samples.](image)

| Table 2. XPS Results. Surface composition for untreated and 60 minutes ozonated carbon |
|-----------------------------------------------|-----------------|------------------|-----------------|-----------------|
| **Element** | **Peak** | **Functional groups** | **Binding energy (eV)** | **Activated carbon (% atomic)** |
| | | | **untreated** | **OZ60** |
| C 1s | 1 | graphitic, aromatic (C-C) | 284.6 | 52.28 | 41.57 |
| C 1s | 2 | C in hydroxyl, ethers (C-OH, C-O-C) | 286.0 | 16.07 | 14.55 |
| C 1s | 3 | C in carbonyl (C=O) | 287.3 | 5.03 | 2.29 |
| C 1s | 4 | C in COOR (R=H or alkyl) | 288.6 | 3.58 | 10.27 |
| C 1s | 5 | π-π* transitions in aromatic | 291.0 | 3.95 | 3.03 |
| O 1s | 1 | carboxyl, quinone (C=O) | 530.7 | 5.30 | 1.59 |
| O 1s | 2 | Hydroxyl, ethers (C-OH, C-O-C) | 532.1 | 6.96 | 12.15 |
| O 1s | 3 | anhydride, lactone, carboxylic acids | 533.3 | 1.95 | 9.86 |
| O 1s | 4 | chemisorbed H₂O or O₂ | 535.5 | - | 0.67 |
It is seen that the adsorption capacity decreases as the ozonation time increases. Indeed, the untreated carbon is mainly hydrophobic (type-H) and is turned hydrophilic (type-L) due to ozonation since polar groups are formed. This is illustrated in Fig. 3, where the MBT maximum adsorption capacity decreases as the acid groups content of activated carbon increases. Those polar groups adsorb water reducing the number of active sites available for MBT adsorption.

IV. CONCLUSIONS

Ozonation of activated carbon leads to a modification of both textural and chemical surface properties. The extensive oxidation undergone by the carbon generates acid groups, such as anhydride, lactones and carboxylic acid, which in turn reduce the surface hydrophobicity. As a consequence of these changes, the MBT adsorption capacity of activated carbon is significantly reduced by ozonation. This aspect should be taken into consideration when dealing with the design of treatment processes based on ozonation activated carbon adsorption.

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