

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

H. VALDES[†], M. SANCHEZ-POLO[‡] and C.A. ZAROR[†]

[†] *Departamento de Ingeniería Química, Universidad de Concepción, Casilla 160-C, Correo 3 Concepción, Chile.*
hvaldez@udec.cl, czaror@diq.udec.cl

[‡] *Departamento de Química Inorgánica, Universidad de Granada, 18071 Granada, España.*
msanchez@ugr.es

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_{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_{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/dm³ (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 (Airaud *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 produced from pure O₂ supplied by AGA using a generator rated at 5 g of O₃/h.

MBT was determined by High Performance Liquid Chromatographic (HPLC), Merck-Hitachi, L7100, using a RP18 LiChrospher column as the stationary phase. Mobile phase was acetonitrile-sodium phosphate buffer pH 2.3 (60:40), 0.7 cm³/min, reading at 215 nm. Ozone was monitored by UV spectrophotometry (Spectronic

Genesis 5) at 253.7 nm using a gas flow cell (Masschelein, 1998).

Activated carbon textural properties were obtained by N₂ adsorption at 77 K, using a Micromeritics Gemini 2370 sorptometer. Approximately 0.2 g carbon samples, previously degassed at 623 K for 3 hours under N₂ flow, were used. The apparent solid surface area (A_{BET}) was calculated following procedure described by (Emmett and McIver, 1956). The micropore (V_{micro}) and mesopore (V_{meso}) volume and mesopore surface area (α_s) were determined by α -method, using the standard isotherm for carbon materials proposed by Rodriguez-Reinoso *et al.* (1987). The activated carbon surface chemical properties were assessed by of acid/basic neutralization (Boehm, 1966), mass spectroscopy-temperature programmed desorption (TPD) (in He, at 50 K/min, up to 1273 K) (Moreno-Castilla *et al.*, 1998), X-ray photoelectron spectroscopy (XPS) (4×10^{-9} mbar, 25-50 eV pass energy) (Zaror *et al.*, 2001), and the point of zero charge (pH_{PZC}) (Noh and Schwarz, 1990).

Ozonation was carried out in a fixed bed reactor, loaded with 2 g carbon samples (Valdés *et al.*, 2001). After pretreatment, samples were oven dried following a thermal program that allowed drying for 1 h at 60 °C, 1 h at 100 °C, 1 h at 150 °C, and 24 h at 170 °C. Dried samples were coded and stored in a desiccator until use.

MBT equilibrium adsorption isotherms on activated carbon in aqueous solution were determined by the bottle-point method described by Leng and Pinto (1997). Experiments were conducted at $30 \pm 1^\circ\text{C}$, using 50 mg of MBT/dm³ stock solution, at pH 7.

III. RESULTS AND DISCUSSION

A. Textural and Chemical Surface Characterization

The effect of ozonation on textural and chemical surface properties is summarized in Tables 1 and 2.

Clearly, as the extent of ozonation increases, BET area and micropore volumes tend to decrease. On the other hand, the external surface area and mesopore volume show a slight increase due to ozonation, although it does not grow proportional to the extent of ozonation. Oxidation reactions between ozone and carbon surface seem to be responsible for those effects, since extended ozonation leads to the formation of volatile species (Deitz and Bitner, 1972).

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 -pyrone-like structures (Boehm, 1994), and with π 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

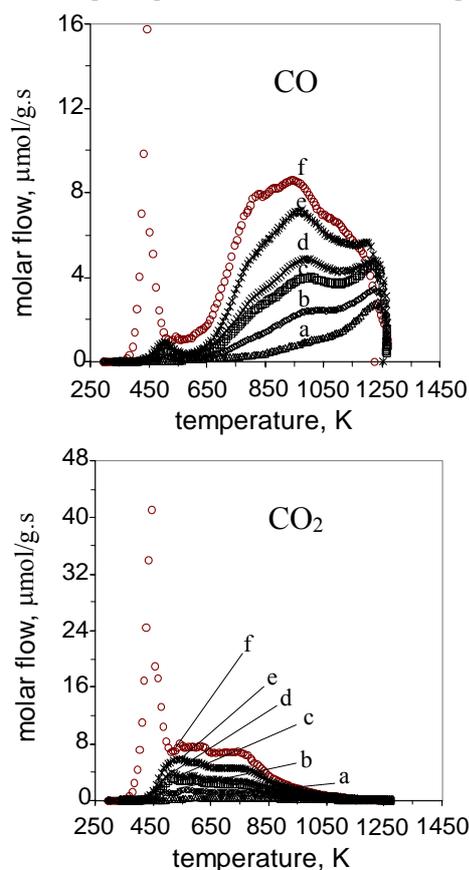


Fig. 1. Thermal desorption of CO and CO₂ for untreated (a), OZ10 (b), OZ20 (c), OZ30 (d), OZ60 (e), and OZ120 (f).

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

Carbon	Textural characterization				Acid/base properties		
	A_{BET} , m ² /g	α_s , m ² /g	V_{micro} , cm ³ /g	V_{meso} , cm ³ /g	Acidic sites, μeq/g	Basic sites, μeq/g	pH_{PZC}
untreated	1000	54	0.474	0.019	234	570	8.82
OZ10	1023	87	0.472	0.031	702	437	5.96
OZ20	943	75	0.437	0.027	1030	399	5.12
OZ30	940	80	0.436	0.028	1498	304	4.76
OZ60	815	72	0.380	0.025	2059	171	3.89
OZ120	632	64	0.297	0.023	3370	-	2.59

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.

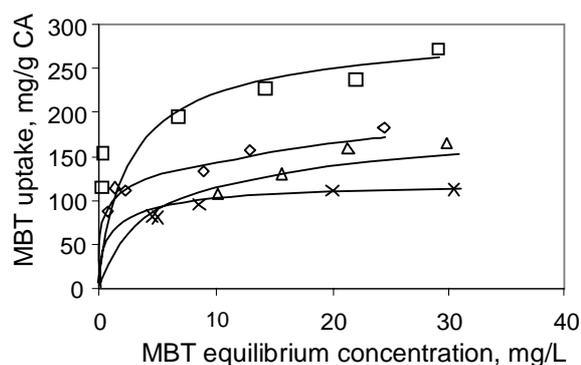


Fig. 2. MBT adsorption isotherms at pH = 7 for: untreated, \square ; OZ30, \diamond ; OZ60, Δ ; OZ120, \times .

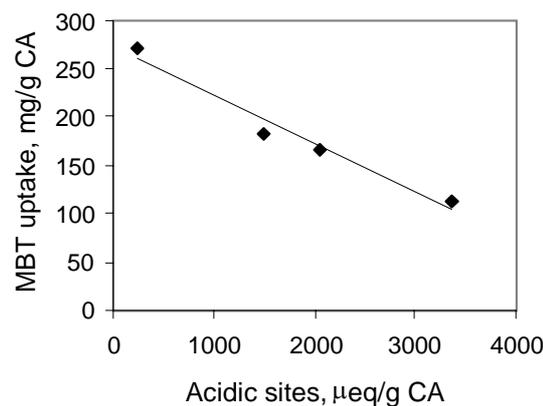


Fig. 3. Relationship between adsorption capacities of MBT and the surface chemistry of the carbon samples.

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	carbonyl, 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 H ₂ O or O ₂	535.3	-	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.

Acknowledgments

This research was financially supported by FONDECYT (Grants N° 2000130 and 1010881). The authors would like to thank Prof. Pedro Toledo and Dr. Nelson Alarcón, of the Surface Analysis Laboratory at the Chemical Engineering Department, University of Concepcion, who conducted the XPS assessment.

REFERENCES

- Airaudo, C. B., A. Gayt -Sorbier, R. Momburg and P. Laurent, "Leaching of Antioxidants and Vulcanization Accelerators from Rubber Closures into Drug Preparations," *J. Biomat. Sci. Polym. Ed.* **1**, 4, 231-241 (1990).
- Barton, S.S., M.J.B. Evans, E. Halliop and J.A.F. MacDonald, "Acidic and Basic Sites on the Surface of Porous Carbon," *Carbon* **35**, 1361-1366 (1997).
- Biniak, S., G. Szymanski, J. Siedlewski and A. Swiatkowski, "The Characterization of Activated Carbons with Oxygen and Nitrogen Surface Groups," *Carbon* **35**, 1799-1810 (1997).
- Boehm, H.P., "Chemical Identification of Surface Groups," *Advances in Catalysis* **16**, 179-274 (1966).
- Boehm, H.P., "Some Aspects of the Surface Chemistry of Carbon Blacks and Others Carbons," *Carbon* **3**, 759-769 (1994).
- Cannon, F. S., J. Dusenbury, P.D. Paulsen, J. Singh, D. W. Mazyck and D.J. Maurer, "Advanced Oxidation Regeneration of Granular Activated Carbon for Controlling Air-Phase VOCs," *Ozone: Sci. & Eng.* **18**, 417-441 (1996).
- Croll, B.T., "The installation of GAC and Ozone Surface Water Treatment Plants in Anglian Water, UK," *Ozone: Sci. & Eng.* **18**, 19-40 (1996).
- de Wever, H. and H. Verachtert, "Biodegradation and Toxicity of Benzothiazoles," *Wat. Res.* **31**, 11, 2673-2684 (1997).
- Deitz, V.R. and J.L. Bitner, "The Reaction of Ozone with Adsorbent Charcoal," *Carbon* **10**, 145-154 (1972).
- Deitz, V.R. and J.L. Bitner, "Interaction of Ozone with Adsorbent Charcoals," *Carbon* **11**, 393-401 (1973).
- Emmett, P.H. and D.S. McIver, "Adsorption of Nitrogen on Pure Sodium Chloride," *J. Phys. Chem.* **60**, 824-825 (1956).
- Fiehn, O., J. Wegener, J. Jochimsen and M. Jekel, "Analysis of the Ozonation of 2-Mercaptobenzothiazole in Water and Tannery Wastewater Using Sum Parameters, Liquid- and Gas Chromatography and Capillary Electrophoresis," *Wat. Res.* **32**, 4, 1075-1084 (1998).
- Figueiredo, J.L., M.F.R. Pereira, M.A.A. Freitas and J.J.M.  rf o, "Modification of Surface Chemistry of Activated Carbons," *Carbon* **37**, 1379-1389 (1999).
- Fritz, O.W. and K.J. H ttinger, "Active Sites and Intrinsic Rates of Carbon-Gas Reactions: a Definite Confirmation with the Carbon-Carbon Dioxide Reaction," *Carbon* **31**, 923-930 (1993).
- Gaja, M.A. and J.S. Knapp, "Removal of 2-Mercaptobenzothiazole by Activated Sludge: a Cautionary Note," *Wat. Res.* **32**, 12, 3786-3789 (1998).
- Kainulainen, T.K., T.A. Tuhkanen, T.K. Vartiainen and P.J. Kalliokoski, "Removal of Residual Organic from Drinking Water by Ozonation and Activated Carbon Filtration: A pilot plant study," *Ozone: Sci. Eng.* **17**, 449-462 (1995).
- Leng, C.-C. and N.G. Pinto, "Effects of Surface Properties of Activated Carbons on Adsorption Behavior of Selected Aromatic," *Carbon* **35**, 1375-1385 (1997).
- Leon y Leon, C.A., J.M. Solar, V. Calemma and L.R. Radadovic, "Evidence for the Protonation of Basal Plane Sites on Carbon," *Carbon* **30**, 797-811 (1992).
- Masschelein, W.J., "Measurement of High Ozone Concentrations in Gases by KI Titration and Monitoring by UV-Absorption," *Ozone: Sci. Eng.* **20**, 489-493 (1998).
- McKay, G. and G. McAleavey, "Ozonation and Carbon Adsorption in a Three-Phase Fluidised Bed for Colour Removal from Peat Water," *Chem. Eng. Res. Des.* **66**, 532-536 (1988).
- Moreno-Castilla, C., F. Carrasco-Marin, F.J. Maldonado-H dar and J. Rivera-Utrilla, "Effects of Non-Oxidant and Oxidant Acid Treatment on the Surface Properties of an Activated Carbon with

- Very Low Ash Content," *Carbon* **36**, 145-151 (1998).
- Noh, J.S. and J.A. Schwarz, "Effect of HNO₃ Treatment on the Surface Acidity of Activated Carbons," *Carbon* **28**, 675-682 (1990).
- Paxeus, N., "Organic Pollutants in the Effluents of the Large Wastewater Treatment Plants in Sweden," *Wat. Res.* **30**, 1115-1122 (1996).
- Rodriguez-Reinoso, F., J.M. Martin-Martinez, C. Prado-Burguete and B. McEnaney, "A Standard Adsorption Isotherm for the Characterization of Activated Carbons," *J. Phys Chem.* **91**, 515-516 (1987).
- Sutherland, I., E. Sheng, R.H. Bradley and P.K. Freakley, "Effects of Ozone Oxidation on Carbon Black Surfaces," *J. of Materials Science* **31**, 5651-5655 (1996).
- Valdés, H., M. Sánchez-Polo, J. Rivera-Utrilla and C.A. Zaror, "Effect of Ozone Treatment on Surface Properties of Activated Carbon," *Langmuir* **18**, 2111-2116 (2001).
- Zaror, C.A., "Enhanced Oxidation of Toxic Effluents Using Simultaneous Ozonation and Activated Carbon Treatment," *J. Chem. Tech. Biotechnol.* **70**, 21-28 (1997).
- Zaror, C.A., G. Soto, H. Valdés and H. Mansilla, "Ozonation of 1,2 Dihydroxybenzene in the Presence of Activated Carbon," *Wat. Sci. & Tech.* **44**, 5, 125-130 (2001).
- Zielke, U., K.J. Hüttinger and W.P. Hoffman, "Surface-Oxidized Carbon Fibers: I. Surface Structure and Chemistry," *Carbon* **34**, 983-998 (1996).

Received: September 16, 2001.

Accepted for publication: November 14, 2002.

Recommended by Guest Editors J. Cerdá, S. Díaz and A. Bandoni