Ozonation of benzothiazole saturated-activated carbons: Influence of carbon chemical surface properties

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Abstract

The combined or sequential use of ozone and activated carbon to treat toxic effluents has increased in recent years. However, little is known about the influence of carbon surface active sites on ozonation of organic adsorbed pollutants. This paper presents experimental results on the effect of metal oxides and oxygenated surface groups on gaseous ozonation of spent activated carbons. Benzothiazole (BT) was selected as a target organic compound in this study due to its environmental concern. Activated carbons with different chemical surface composition were prepared from a Filtrasorb-400 activated carbon. Pre-treatment included: ozonation, demineralisation, and deoxygenation of activated carbon. Ozonation experiments of BT saturated-activated carbons were conducted in a fixed bed reactor loaded with 2 g of carbon samples. The reactor was fed with an O_2/O_3 gas mixture (2 dm^3/min, 5 g O_3/h), for a given exposure time, in the range 10–120 min, at 298 K and 1 atm. Results show that extended gaseous ozonation of activated carbon saturated with BT led to the effective destruction of the adsorbate by oxidation reactions. Oxidation of BT adsorbed on activated carbon seemed to occur via both direct reaction with ozone molecules, and by oxygen radical species generated by catalytic ozone decomposition on metallic surface sites.
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1. Introduction

Benzothiazole and its derivatives are widely used as industrial chemicals in: fungicides in leather and wood industry, bio-corrosion inhibitors in cooling systems, ingredients in antifreezing agents for automobiles, and mainly as vulcanisation accelerators in rubber production [1]. Because of their application great variety, benzothiazoles have been not only detected in industrial and municipal wastewaters, but also in soils, estuarine sediments, and superficial waters, posing environmental concern [2,3].

Unfortunately, conventional biological wastewater treatment processes could not effectively remove such contaminants since they are resistant to biodegradation and tend to adsorb on cell membrane, leading to bio-accumulation [3,4]. Ozonation has been shown to remove benzothiazoles in aqueous solution [5,6]. However, high ozone consumption is required for the improvement of biodegradability of formed oxidation by-products, impairing its application at industrial scale.

Activated carbon adsorption combined with ozone oxidative regeneration of adsorbent offers an attractive option for benzothiazoles removal. Indeed, activated carbon presents a large surface area where benzothiazoles could adsorb [7,8], while ozone readily destroys adsorbed aromatic molecules, helping to regenerate the activated carbon adsorption capacity [9]. In this combined treatment, activated surface groups may be responsible for catalytic effects found in ozonation of toxic organic contaminants in presence of activated carbon [10–12]. However, the mechanism of gaseous ozone regeneration of activated carbon adsorption column has not been fully elucidated nor the influence of chemical surface properties on the oxidation of adsorbed organic pollutants has been analysed. These basic aspects are crucial for the design and optimisation of ozone and activated carbon based treatment systems.

Within such context, this article presents experimental data on gaseous ozonation of BT saturated-granular activated carbons,

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with different chemical surface composition. In particular, the effect of activated carbon chemical surface properties on BT degradation is discussed. The results presented in this article are part of a wider ongoing project on the fundamental study of the degradation of toxic organic compounds using ozone combined with activated carbon.

2. Experimental

2.1. Materials

A commercial granulated bituminous coal-based activated carbon Filtrasorb-400 (Calgon Carbon Corp., USA), was used as a starting material (here, referred as "F" sample), with particle size of 0.5–0.8 mm. The carbon was washed with de-ionised water, oven-dried at 443 K for 24 h, and stored in a desiccator until its use. BT (95% purity) was supplied by Fluka. All chemicals used for analysis were purchased from Merck. All solutions were prepared with ultrapure water obtained from a Millipore MilliQ system. Ozone was produced from pure O_2 supplied by AGA using an Ozocav generator.

2.2. Pre-treatment of carbon samples

Activated carbons with different chemical surface composition were prepared from a Filtrasorb-400 activated carbon (F). Three kinds of pre-treatment were applied: ozonation, demineralisation, and deoxygenation of activated carbon. Ozonation pre-treatment was carried out in a fixed bed reactor loaded with 2 g of activated carbon. The reactor was fed with an O_2/O_3 gas mixture (2 dm^3/min) from an Ozocav generator (5 gO$_3$/h), for 60 min, at 298 K and 1 atm. The ozonated carbon was identified as F-60. Demineralised activated carbon (F-D) was obtained by shaking a 3 g sample of carbon F in 50 cm^3 of concentrated hydrofluoric acid for 12 h. The demineralised carbon was then washed with de-ionised water in a Soxhlet extraction apparatus until AgNO$_3$ could no longer detect fluoride in the washing water. Activated carbon surface deoxygenation was achieved in a horizontal tubular furnace through stream of nitrogen at 1273 K. A 13 g sample of carbon F was placed in a quartz container, which was put in the furnace. Deoxygenation was carried out by heating the sample at a 10 K/min-rate, in a constant nitrogen flow (5 dm^3/min) and holding it at 1273 K for 60 min. Then, the sample was cooled under nitrogen flow until room temperature was reached. Finally, it was stored in a desiccator under vacuum until its use. This carbon sample was named F-G.

2.3. Adsorption experiments

Adsorption isotherms of BT on activated carbon samples were obtained at 298 K in unbuffered aqueous solution. The solutions were prepared using de-ionised water with pH 5 ± 0.5. Equilibrium isotherms were conducted using the bottle point method. Different amounts of carbon were added to Erlenmeyer flasks containing 50 mL of solution of BT with a concentration of 30 mg/dm^3, and shaked until the equilibrium was reached (ca. 48 h). Then, samples were filtrated using nylon membrane filter

Nylaflo$^®$ (0.2 μm) and analysed by UV spectroscopy (Spectronic Genesys 5) at 220 nm for BT concentration. The amount of adsorbed BT was deduced from a mass balance as follows:

$$q_e = \frac{(C_0 - C_e) V}{M} \tag{1}$$

where C_0 is the BT initial concentration in liquid phase (typically 30 mg/dm^3), C_e the BT concentration remaining in solution after the equilibrium was reached, V the volume of solution in the equilibrium bottle and M stands for the mass of activated carbon sample used in each bottle.

2.4. Saturation of carbon samples with BT prior to ozone regeneration

Saturation of activated carbons was conducted by adding 2–4 g (dry weight) of carbon in adsorption flasks containing 150 cm^3 of BT aqueous solutions (7.0 mmol/L). The amount of carbon added to the solution was adjusted to attain a similar adsorbed BT concentration. The pH was set at 2 with phosphoric acid. The suspensions were shaken at 298 K during 48 h. After that time, the amount of BT adsorbed was calculated from the mass balance (see Eq. (1)). According to the experimental adsorption, mean BT adsorbed on activated carbon samples F, F-60, F-D, F-G resulted in 66, 68, 66, 65 mg BT/g, respectively.

2.5. Ozonation of BT saturated-carbon samples

BT saturated-carbon samples were placed in a fixed bed reactor and dried with a constant flow rate of nitrogen (2 dm^3/min) for 2 h. Later, the reactor was connected to an Ozocav ozone generator rated at 5 g O$_3$/h using pure O$_2$. The reactor was fed with an O$_2$/O$_3$ gas mixture (2 dm^3/min) for 10 min exposure, at 298 K and 1 atm. Additionally, a set of runs was conducted with extended ozonation, up to 120 min, in order to determine the effect of exposure time on BT removal. After each run, activated carbon samples were taken for chemical essays. Surface analysis was conducted for samples ozonated during 10 min. Soluble organic compounds present on activated carbon surface were desorbed following the procedure described below. Before surface analysis, samples were oven dried following a thermal program that allowed drying for 1 h at 333 K, 1 h at 373 K, 1 h at 423 K, and 24 h at 443 K, in a N$_2$ atmosphere. This procedure leads to a removal of water and more volatile low molecular weight organic compounds adsorbed on the carbon surface. Dried samples were stored in a desiccator until analysis.

2.6. BT desorption procedure

Desorption of unreacted BT and BT oxidation by-products was conducted in 250 cm^3 Erlenmeyer flasks, containing treated activated carbon samples and filled with 100 cm^3 of acetonitrile/water solution (50/50). The acetonitrile/water extraction procedure achieved over 50% BT desorption from all (unozonated) carbon samples saturated with BT. It is assumed here that the same recovery ratio is achieved in the case of carbon-

Table 1
Textural and chemical characteristics of activated carbon samples

Sample	S_{N_2} (m²/g)	V_{mi} (cm³/g)	S_{meso} (m²/g)	Acidic sites[a] (μeq/g)	Basic sites[b] (μeq/g)	pH$_{PZC}$
F	1000	0.47	54	234	570	8.8
F-60	815	0.38	72	2059	171	3.9
F-D	1180	0.55	88	296	646	7.9
F-G	1100	0.51	94	0	801	10.4

[a] Determined by NaOH (0.1 N) neutralisation [13].
[b] Determined by HCl (0.02 N) neutralisation [13].

BT ozonated samples. The suspensions were placed in an orbital temperature-controlled shaker, and mixed at 150 rpm for 6 days at 298 K. After that, activated carbon samples were filtered using nylon membrane filter Nylaflo® (0.2 μm). BT concentration in the filtrates was determined by high-pressure liquid chromatography (HPLC) (Merck-Hitachi, L7100), as reported elsewhere [6]. Since complete BT desorption was not possible to achieve with this extraction procedure, the amount of unreacted BT was expressed in dimensionless terms as a ratio between desorbed unreacted BT concentration at an specific time and desorbed unreacted BT concentration at time zero for each carbon samples.

2.7. Textural and chemical surface analysis

Textural characteristics of activated carbons were obtained by N₂ adsorption at 77 K as described in previous publication [13]. The apparent carbon surface area (S_{N_2}) was calculated from the nitrogen adsorption data using the BET equation. Micropore volume (V_{mi}) and mesopore surface area (S_{meso}) were calculated by α-method [14]. Chemical surface properties of activated carbons were assessed by: acid/basic neutralisation, X-ray photoelectron spectroscopy (XPS) (4×10^{-9} mbar, 25–50 eV pass energy), and the point of zero charge (pH$_{PZC}$) [13].

Temperature programmed desorption (TPD) of fresh and treated activated carbon samples were carried out by heating the samples in a He flow up to 1273 K at a heating rate of 50 K/min. Gas evolved was monitored with a thermal conductivity detector (TCD). The activated carbon thermal desorption profiles for different samples were conducted, namely: untreated activated carbon (F), preozonated (F-60), demineralised (F-D), deoxygenated (F-G), untreated activated carbon with BT adsorbed (F-BT), and activated carbon samples ozonated for 10 min with BT adsorbed (F-BT-10), (F-60-BT-10), (F-D-BT-10), (F-G-BT-10). Additionally, a blank thermal desorption profile was obtained for activated carbon ozonated during 10 min without BT adsorbed (F-10).

Total ash content was determined by incineration of the carbon. Ash components were analysed by X-ray fluorescence.

3. Results and discussion

3.1. Characterisation of carbon samples

Table 1 summarises the effect of pre-treatments on activated carbon textural and acid/basic characteristics. Oxidation reactions between ozone gas and carbon surface seem to be responsible for a reduction in BET area and a slight increase in mesopore surface area, since extended oxidation leads to the destruction of pore walls, forming volatile species [15]. Overall, 20–30% original mass was lost when virgin activated carbon was ozonated during 60 min with 5 g O₃/h.

In turn, acid demineralisation extracts mineral and other soluble materials, resulting in an increase in BET and mesopore surface area [16]. Demineralisation treatment reduced carbon ash content from 6.6% to less than 0.1%. Major metallic oxides present in the ash of untreated carbon are listed in Table 2.

Deoxygenated carbon samples also showed an increase in surface area since significant gasification of oxygenated surface complexes occurred due to thermal treatment at 1273 K in a N₂ atmosphere.

Table 3 shows a detailed chemical characterisation of carbon surface samples obtained by XPS. It is seen that the nature of active groups on the carbon surface was greatly modified by the applied pre-treatments. The XPS spectra of activated carbon samples presented two different peaks, due to carbon (C 1s) and oxygen (O 1s). Peaks were deconvoluted after the baseline was subtracted according to Biniak et al. [17]. The curve fitting was performed using the non-linear least-squares algorithm with a Lorentzian–Gaussian functions 85:15 ratio. Percentage atomic element composition was calculated on an ash-free basis. The C 1s and O 1s spectra were resolved into five and three individual component peaks, respectively [17,18]. Results shown in Table 3 are complemented by acid/basic and pH$_{PZC}$ data presented in Table 1.

3.2. Influence of ozonation on textural and chemical properties of activated carbon samples saturated with BT

Table 4 shows the effect of 10 min ozonation on textural properties of activated carbon samples saturated with BT. Ozone

Table 2
Metallic composition of activated carbon ash, by X-ray fluorescence (in w/w% d.b.)

SiO₂	43.19
TiO₂	1.37
Al₂O₃	31.82
Fe₂O₃	18.06
MnO	0.03
MgO	0.81
CaO	2.51
Na₂O	0.84
K₂O	1.32
P₂O₅	0.07

Table 3
XPS results: surface composition for carbon samples

Element	Functional groups	Binding energy (eV)	% Atomic (ash free basis)			
			F	F-60	F-D	F-G
C 1s	Graphitics, aromatics	284.6	55	43.7	55.4	68.3
C 1s	C in hydroxyls, ethers	286.0	16.8	15.2	21.7	17.4
C 1s	C in carbonyls	287.3	5.3	2.4	6.0	n.d.
C 1s	C in COOR (R = H or alkyl)	288.6	3.7	10.7	4.5	n.d.
C 1s	$\pi-\pi^*$ transitions in aromatics	291.0	4.2	3.2	4.6	11.0
O 1s	Hydroxyls, ethers, carbonyls, quinones	532.1	12.9	14.3	3.6	3.3
O 1s	Anhydrides, lactones, carboxylic acids	533.3	2.1	9.8	3.6	n.d.
O 1s	Chemisorbed H_2O and/or O_2	535.3	n.d.	0.7	0.6	n.d.

n.d.: non detected.

Table 4
Textural characterisation of treated activated carbon samples saturated with BT

Sample	S_{N_2} (m^2/g)	V_{mi} (cm^3/g)	S_{meso} (m^2/g)
F-BT	830	0.38	73
F-BT-10	876	0.40	79
F-60-BT-10	659	0.31	66
F-D-BT-10	947	0.44	88
F-G-BT-10	840	0.39	79

treatment led to a significant decrease in BET area, due to extensive oxidation.

Figs. 1 and 2 show thermal desorption profiles of different activated carbon samples, in absence and presence of adsorbed BT, respectively. As the carbonaceous materials were subjected to programmed temperature increase, the surface oxygen complexes desorbed primarily as CO_2 and CO [19,20]. Indeed, results from activated carbon samples (virgin, and ozonated for 10–60 min) reported elsewhere, using TPD-mass spectrometry, showed that CO evolved at temperatures well above 700 K, whereas, CO_2 appeared over a wider temperature range (500–900 K) [13]. CO_2 emissions within 515–640 K came from thermally unstable carboxylic acids and lactone groups, whereas carboxylic acid anhydrides generated both CO_2 (623–673 K) and CO (873–900 K) peaks. Apart from these, other stable surface groups, such as phenols (873–973 K), ethers (973 K), carbonyls, and quinone groups (973–1253 K) were also held responsible for CO evolution at higher temperatures [13].

As seen in Fig. 1, curve (b), untreated activated carbon (F) presented two slight peaks at 590 and 1200 K, thought to correspond to CO_2 and CO, respectively [13]. Moreover, 60 min ozonation of such activated carbon led to a significant increase in gas evolution with peaks at 515–640 and 873–1073 K (see Fig. 1, curve (d)), corresponding to CO_2 and CO, respectively [13]. The increase in the low temperature peak could also be accounted for the thermal condensation of adjacent carboxylic groups during heating, as confirmed by the presence of water at 450 K detected by mass spectrometry [13]. These results indicate that the carbon surface was oxidised by ozone gas, generating acid groups, such as lactones, carboxylic acid anhydrides, and carboxylic acids, as confirmed by XPS data in Table 3.

The deoxygenated carbon (F-G), curve (a), shows a different behaviour. Little gas evolution was detected below 900 K. This was expected since such sample had already been treated at 1273 K in a N_2 atmosphere. Under such conditions, a large fraction of oxygenated acid surface groups were removed, as confirmed by acid/base titration and XPS analysis (see Tables 1 and 3).

On the other hand, demineralised carbon (F-D), curve (c), shows little low temperature gas evolution, presenting a steady increase at temperature above 700 K, suggesting the presence of different groups and/or the same oxygen complex located in
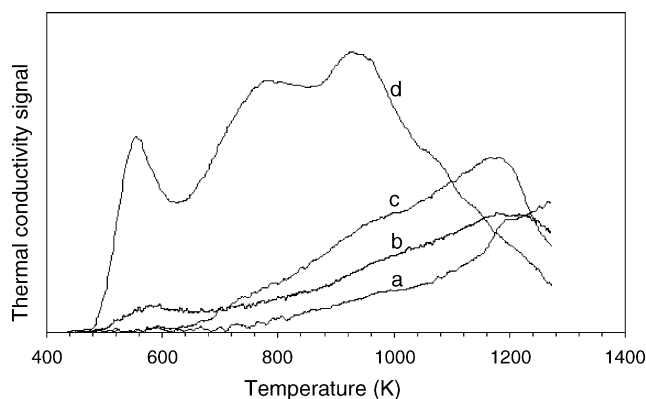

Fig. 1. TPD desorption profiles for activated carbon series without adsorbed BT: (a) F-G, (b) F, (c) F-D, and (d) F-60.
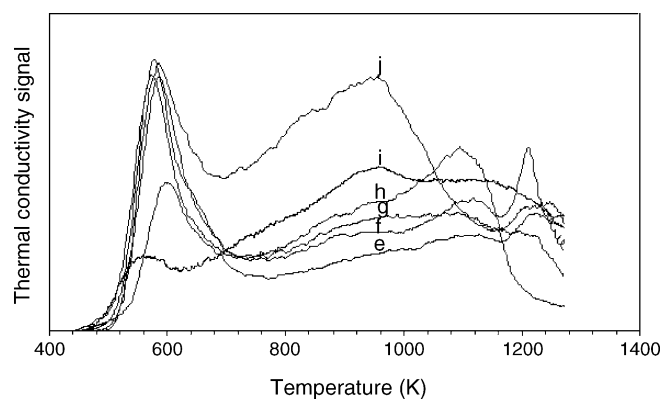

Fig. 2. TPD desorption profiles for activated carbon series with adsorbed BT: (e) F-BT, (f) F-G-BT-10, (g) F-BT-10, (h) F-D-BT-10, (i) F-10, and (j) F-60-BT-10.

energetically different positions. Similar to untreated carbon, a maximum also appeared at elevated temperature (1200 K), and could be related to the presence of carbonyl groups and/or decomposition of pyrone groups. The shoulder around 950 K was the result of the presence of phenol groups [13].

As illustrated in Fig. 2, BT saturated-activated carbon (curve (e)) shows an increase in gas production within 500–700 K, coinciding with the BT boiling point. All BT-saturated carbon samples ozonated for 10 min showed a sharp increase in gas evolution within the 500–700 K temperature range, with a peak around 600 K. Apart from unreacted BT evaporation, CO_2 evolution from unstable oxygenated surface groups such as lactones and carboxylic acids, also contributes to emissions within 500–700 K. Indeed, a blank TPD analysis was carried out with virgin activated carbon ozonated during 10 min, shown as F-10, curve (i) in Fig. 2. A distinctive peak is seen within 515–640 K, related to CO_2 evolution from carboxylic acids and lactones decomposition [13]. Other reported results show that some minor CO and water evolution takes place at 450–600 K, coming from anhydride groups formed by condensation of two carboxylic groups when the sample is heated [13].

Additionally, ozonation of carbon samples with adsorbed BT increased the content of highly stable groups, which decomposed at elevated temperatures. In particular, F-G-BT-10 DTP-profile (curve f), shows two peaks at around 1100 and 1200 K which could be associated with the decomposition of pyrones and quinone groups, respectively [20].

3.3. Effects of chemical surface properties on BT adsorption

Adsorption isotherms of BT on pre-treated activated carbons with increasing concentration of oxygenated surface groups (F-G < F < F-60) are shown in Fig. 3. Data fitted well a Langmuir model in agreement with other studies reported in the literature [21,22]:

$$q_e = q_m \frac{bC_e}{1 + bC_e} \tag{2}$$

Table 5
Parameters of Langmuir model applied to benzothiazole adsorption on activated carbons with increasing concentration of oxygenated surface groups, at pH 5 and 298 K

Sample	q_m (mg BT/g)	b (L/g)
F-G	200	3.57
F	179	1.86
F-60	115	0.16

where q_m and b are parameters related to the maximum BT adsorption monolayer capacity and the affinity constant, respectively, and are reported in Table 5.

A significant reduction in the carbon adsorption capacity of BT was observed in the case of highly oxidised samples (F-60). Furthermore, a reduction in the affinity parameter was detected in this case, indicating a weakening in adsorbate–adsorbent interactions. That reduction could be related to a decrease in π–electron density on graphene layers as a result of carbon extensive oxidation. A high concentration of oxygenated acid surface groups near these π sites, decreased the carbon Lewis basicity due to an electron-withdrawing effect that suppressed electron de-localisation. Weakening π–π dispersive interactions between the π–electron aromatic ring of BT molecules and the π–electron system of the carbon basal planes would be responsible for the reduction in adsorption capacity. These results are in agreement with those reported by others authors [21,23].

3.4. Effects of carbon chemical surface properties on the ozonation of adsorbed BT

Fig. 4 illustrates the reduction in the unreacted BT adsorbed on the activated carbon, as a result of gaseous ozone regenerative treatment in the range 10–120 min. Dimensionless concentrations were calculated as a fraction of concentration of desorbed BT at time zero for each carbon samples.

In all cases, the amount of residual BT decreased with the extent of ozonation, being mostly eliminated after 120 min treatment. However, the initial BT removal rate depended on the carbon chemical surface properties. Indeed, slower BT degrada-
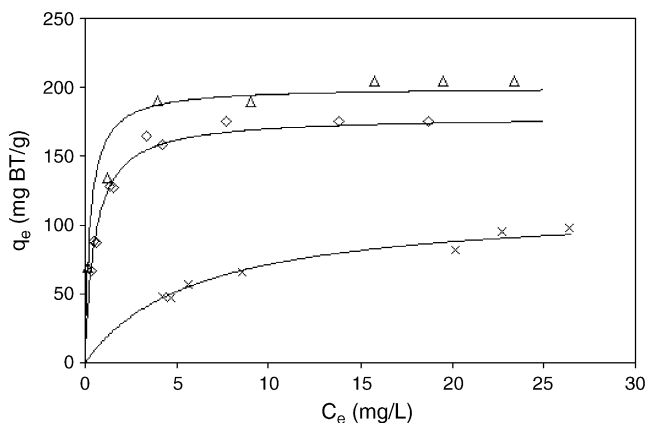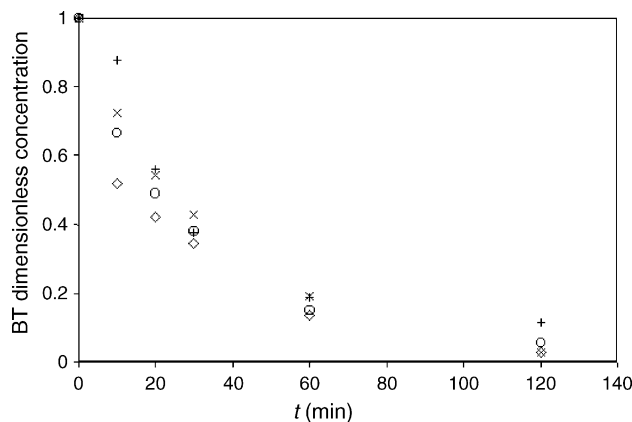

Fig. 3. Adsorption isotherms of benzothiazole on pre-treated activated carbons with increasing concentration of oxygenated surface groups: (△) F-G, (◇) F, (×) F-60 (pH 5; 298 K). Solid lines correspond to simulations using the Langmuir model with parameters shown in Table 5.

Fig. 4. Influence of chemical surface properties of activated carbons on BT ozonation: (+) F-60; (×) F-D; (◯) F-G; (◇) F (pH 2; 2 g activated carbon samples, 5 gO_3/h, 298 K, 1 atm).

tion rates were initially observed in the case of highly oxidised and demineralised carbon surfaces. As seen in Fig. 4, only 12% of initial BT adsorbed on F-60 carbon was oxidised after 10 min ozonation, as compared with nearly 50% BT removal for F samples. Demineralised and deoxigenated carbons showed around 30% BT reduction after 10 min ozone treatment. Moreover, as ozonation progressed, similar BT reduction rates were observed for all samples.

The initial rate of BT removal was clearly affected by the level of oxidation of the carbon matrix. In the case of pre-ozonated activated carbon (F-60), the surface presents a high concentration of oxygenated acid groups such as carboxylic acids, and carboxylic acid anhydrides. As mentioned above, these groups reduce π–electron de-localisation on carbon graphene layers. Ozone is known to present electrophillic interaction with high electron density sites [24,25], and a reduction in π–electron density on carbon basal planes should decrease the ozone reactivity towards the carbon. Moreover, as shown above, the adsorption affinity of BT towards the carbon surface decreases with its oxidation level.

The high π–electron density on the carbon basal planes and the presence of basic surface groups, such as chromene and γ-pyrone type structures, on untreated and deoxygenated activated carbons could be related to the greater ozone reactivity towards adsorbed BT. The increase in electron density on the carbon basal planes would enhance the overall BT removal rate. Similar mechanism had been reported for the activated carbon catalytic effect on ozone degradation of 1,3,6-napthalenetrisulfonic acid [26].

On the other hand, the presence of mineral matter enhances BT oxidation, as shown in the case of untreated carbon samples (F), compared with demineralised (F-D) and deoxygenated samples (F-G). X-ray fluorescent results of major metallic oxides present in the ash of untreated activated carbon showed that iron, silicium and aluminium oxides account for 93% of total mineral content (see Table 2). During the saturation procedure of 2 g of deoxygenated activated carbon sample (F-G) with 150 cm^3 of aqueous BT solution (7 mmol/L), pH 2; a precipitate formation was noticed. The solution was analysed by atomic absorption spectroscopy; results showed the presence of Fe, Al, K and Mg in concentration of 44, 8, 3.1, and 0.6 mg/L, respectively. It must be mentioned that no precipitate was observed in the filtrate from F samples, and the mineral content in such filtrate was less than a tenth of the concentration from deoxygenated carbon samples. Thus, deoxygenation at 1273 K enhanced metal leaching from activated carbon samples. These observations agree with those reported by others authors [27–29]. Metal leached from carbon surface of F-G samples could be associated with the decrease in BT observed removal compared with the result obtained with untreated carbon samples. Both results lead to postulate that mineral matter present on activated carbon surface take part in surface reactions promoting catalytic ozonation of adsorbed BT.

3.5. Mechanistic considerations

The reaction mechanisms involving heterogeneous gas–solid ozonation of carbonaceous materials have been the subject of extensive research [13,15,30–32]. Gaseous ozone has been thought to adsorb on the carbon surface by chemical interaction between one of its terminal atomic oxygen and surface active sites. The nature of those active sites and the presence of adsorbed reactive organic species determine further chemical processes. Indeed, ozone may undergo self-decomposition and participate in oxidation reactions with both surface carbonaceous and/or adsorbed organic structures. Two general pathways have been proposed to explain those chemical processes: (a) catalytic decomposition of adsorbed O_3 leading to radical species and O_2 formation; (b) partial oxidation of carbonaceous and/or organic molecules by direct ozone reactions. Further oxidation may lead to CO_2 formation and carbon weight loss [13,15,30–35].

Catalytic decomposition of ozone is enhanced by the presence of metallic active sites. These sites are responsible for the formation of highly reactive oxygen radicals ($O_2^{\bullet-}$) on the carbon surface. These transfer an electron to another ozone molecule to form an ozonide anion ($O_3^{\bullet-}$), which is the chain reaction promoter on the carbon surface [33–35]. Such radical-driven chain reactions may lead to extensive oxidation of nearby adsorbed organic species and electron-rich carbonaceous sites. Results from demineralised (F-D) carbon confirmed that BT oxidation rate was reduced due to the absence of metals on the carbon surface.

Direct oxidation of carbon surface and adsorbed organics is enhanced by the existence of electron rich structures. Therefore, as the carbon surface oxidation level increases, the rate of ozone reaction is likely to decrease, as shown here. Moreover, in the case of highly oxidised carbon structures such us in the F-60 samples, BT molecules should be less affected by direct oxidation of ozone molecules, due to the weaker interactions between the π–electron aromatic ring of BT molecules and the π–electron system of the carbon basal planes. Here, oxidation of adsorbed BT molecules are likely to be mostly affected by surface generated radicals rather than by direct oxidation of ozone molecules.

4. Conclusions

The interaction between the BT molecule and the activated carbon surface was weakened as the oxidation level of the carbon surface increased, leading to a significant reduction in adsorption capacity when activated carbon was subjected to extensive gaseous ozonation.

In turn, extended gaseous ozonation of activated carbon saturated with BT led to the effective destruction of the adsorbate, by oxidation reactions.

Oxidation of BT adsorbed on virgin activated carbon seemed to occur via direct and indirect ozone reactions. Direct reactions with ozone molecules could be enhanced by high-density electronic sites, which may come from the interactions of the BT aromatic ring molecules and the carbon basal π–electron system. Indirect reactions with oxygen radical species could be promoted by catalytic ozone decomposition on metallic surface sites.

In the case of highly oxidised surface carbon structures, oxidation of adsorbed BT molecules takes place at a lower

rate, as compared with virgin and demineralised activated carbon.

References

[1] T. Reemtsma, Determination of 2-substituted benzothiazoles of industrial use from water by liquid chromatography/electrospray ionization tandem mass spectrometry, Rapid Commun. Mass Spectrom. 14 (2000) 1612–1618.

[2] T. Reemtsma, M. Jekel, Dissolved organics in tannery wastewater and their alteration by a combined anaerobic and aerobic treatment, Water Res. 31 (1997) 1035–1046.

[3] H. de Wever, H. Verachtert, Biodegradation and toxicity of benzothiazoles, Water Res. 31 (1997) 2673–2684.

[4] M.A. Gaja, J.S. Knapp, Removal of 2-mercaptobenzothiazole by activated sludge: a cautionary note, Water Res. 32 (1998) 3786–3789.

[5] O. Fiehn, G. Wegener, J. Jochimsen, M. Jekel, Analysis of the ozonation of 2-mercaptobenzothiazole in water and tannery wastewater using sum parameters, liquid and gas chromtography and capillary electrophoresis, Water Res. 32 (1998) 1075–1084.

[6] H. Valdés, C.A. Zaror, M. Jekel, Kinetic study of reactions between ozone and benzothiazole in water, Wat. Sci. Tech. 48 (2003) 505–510.

[7] H. Valdés, M. Sánchez-Polo, C.A. Zaror, Effect of ozonation on the activated carbon surface chemical properties and on 2-mercaptobenzothiazole adsorption, LAAR 33 (2003) 129–133.

[8] H. Valdés, C.A. Zaror, Effect of activated carbon chemical surface properties on the adsorption mechanism of benzothiazoles, in: P. Lens, R. Stuetz (Eds.), Water and Environment Management Series: Young Researchers 2004, IWA Publishing, London, 2004, pp. 195–202.

[9] F.S. Cannon, J. Dusenbury, P.D. Paulsen, J. Singh, D.W. Mazyck, D.J. Maurer, Advanced oxidation regeneration of granular activated carbon for controlling air-phase VOCs, Ozone: Sci. Eng. 18 (1996) 417–441.

[10] C.A. Zaror, Enhanced oxidation of toxic effluents using simultaneous ozonation and activated carbon treatment, J. Chem. Tech. Biotechnol. 70 (1997) 21–28.

[11] C.A. Zaror, G. Soto, H. Valdés, H. Mansilla, Ozonation of 1,2 dihydroxybenzene in the presence of activated carbon, Wat. Sci. Tech. 44 (2001) 125–130.

[12] H. Valdés, C.A. Zaror, Heterogeneous and homogeneous catalytic ozonation of benzothiazole promoted by activated carbon: kinetic approach, Chemosphere, submitted for publication.

[13] H. Valdés, M. Sánchez-Polo, J. Rivera-Utrilla, C.A. Zaror, Effect of ozone treatment on surface properties of activated carbon, Langmuir 18 (2002) 2111–2116.

[14] F. Rodriguez-Reinoso, J.M. Martin-Martinez, C. Prado-Burguete, B.A. McEnaney, A standard adsorption isotherm for the characterization of activated carbons, J. Phys Chem. 91 (1987) 515–516.

[15] V.R. Deitz, J.L. Bitner, The reaction of ozone with adsorbent charcoal, Carbon 10 (1972) 145–154.

[16] C. Moreno-Castilla, F. Carrasco-Marin, F.J. Maldonado-Hódar, J. Rivera-Utrilla, Effects of non-oxidant and oxidant acid treatments on the surface properties of an activated carbon with very low ash content, Carbon 36 (1998) 145–151.

[17] S. Biniak, G. Szymanski, J. Siedlewski, A. Swiatkowski, The characterization of activated carbons with oxygen and nitrogen surface groups, Carbon 35 (1997) 1799–1810.

[18] U. Zielke, K.J. Hüttinger, W.P. Hoffman, Surface oxidized carbon fibers. I. surface structure and chemistry, Carbon 34 (1996) 983–998.

[19] R.C. Bansal, J.B. Donnet, F. Stoeckli, Active Carbon, Marcel Dekker, New York, 1988.

[20] J.L. Figueiredo, M.F.R. Pereira, M.M.A. Freitas, J.J.M. Órfão, Modification of surface chemistry of activated carbons, Carbon 37 (1999) 1379–1389.

[21] J. Rivera-Utrilla, M. Sánchez-Polo, The role of dispersive and electrostatic interactions in the aqueous phase adsorption of naphthalenesulphonic acids on ozone treated activated carbons, Carbon 40 (2002) 2685–2691.

[22] P.M. Álvarez, F.J. Beltrán, V. Gómez-Serrano, J. Jaramillo, E.M. Rodríguez, Comparison between thermal and ozone regenerations of spent activated carbon exhausted with phenol, Water Res. 38 (2004) 2155–2165.

[23] L.R. Radovic, I.F. Silva, J.I. Ume, J.A. Menéndez, C.A. Leon y Leon, A.W. Scaroni, An experimental and theoretical study of the adsorption of aromatics possessing electron-withdrawing and electron-donation functional groups by chemically modified activated carbon, Carbon 35 (1997) 1339–1348.

[24] P.S. Bailey, Ozonation in Organic Chemistry, Academic Press Inc., New York, 1982.

[25] F.J. Beltrán, G. Ovejero, J.M. Encinar, J. Rivas, Oxidation of polynuclear aromatic hydrocarbons in water. 1. Ozonation, Ind. Eng. Chem. Res. 34 (1995) 1596–1606.

[26] M. Sánchez-Polo, J. Rivera-Utrilla, Effect of the ozone–carbon reaction on the catalytic activity of activated carbon during the degradation of 1,3,6-napthalenetrisulfonic acid with ozone, Carbon 41 (2003) 303–307.

[27] C. Ishizaki, J.T. Cookson, Influence of surface oxides on adsorption and catalysis with activated carbon, in: A.J. Rubin (Ed.), Chemistry of Water Supply Treatment and Distribution, Ann Arbor Science Publishers Inc., Ann Arbor, Michigan, 1974 (Chapter 10).

[28] J.T. Cookson Jr., Adsorption mechanism: the chemistry of organic adsorption on activated carbon, in: P.N. Cheremisinoff, E. Ellerbosch (Eds.), Carbon adsorption handbook, Ann Arbor Science Publishers Inc., Ann Arbor, Michigan, 1978, pp. 241–279.

[29] C.H. Tessmer, R.D. Vidic, L.J. Uranowski, Impact of oxygen-containing surface functional groups on activated carbon adsorption of phenols, Environ. Sci. Technol. 31 (1997) 1872–1878.

[30] V.R. Deitz, J.L. Bitner, The interaction of ozone with adsorbent charcoal, Carbon 11 (1973) 393–401.

[31] L.F. Atyaksheva, G.I. Emel'yanova, Catalytic decomposition of ozone on the surface of an activated carbon fabric, Russ. J. Phys. Chem. 63 (1989) 1432–1434.

[32] V. Gómez-Serrano, P.M. Alvarez, J. Jaramillo, F.J. Beltrán, Formation of oxygen structure by ozonation of carbonaceous materials prepared from cherry stones. I. Thermal effects, Carbon 40 (2002) 513–522.

[33] F.P. Logemann, J.H.J. Anne, Water treatment with a fixed bed catalytic ozonation process, Wat. Sci. Tech. 35 (1997) 353–360.

[34] J.P. Kaptijn, The ecoclear process. Results from full-scale installations, Ozone Sci. Eng. 19 (1997) 297–305.

[35] C.H. Ni, J.N. Chen, Heterogeneous catalytic ozonation of 2-chlorophenol aqueous solution with alumina as a catalyst, Wat. Sci. Tech. 43 (2001) 213–220.