Degradation of Benzothiazole by Ozonation and Adsorptive Ozonation

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The paper deals with the study of the use of ozonation for removal of benzothiazole from model wastewater in order to perform chemical transformation and facilitate consecutive biological mineralization of ozonation products. Adsorption of benzothiazole on active carbon and integrated ozonation of benzothiazole with the addition of active carbon, were also studied. Lab-scale ozonation experiments were performed using ozone prepared from pure oxygen. Concentration values of benzothiazole as well as COD and TOC were measured during experiments. The oxidation intermediates of the processes were also studied. The best efficiency of benzothiazole degradation and transformation was observed when the combined ozonation/activated carbon process was applied. Respirometric measurements were carried out in order to evaluate the impact of ozonation products on the activated sludge microorganisms activity. Enhancement of biodegradability by ozonation was indicated by the increase in oxygen uptake rate with an increase in dosed volume of ozonated sample into respirometric cell.

Key words: activated sludge, benzothiazoles, ozonation, respirometric measurements, toxicity

Introduction

Benzothiazole derivatives are widely used as industrial chemicals; mainly as fungicides in the leather and wood processing industries, herbicides, components in automobile antifreeze, corrosion inhibitor in cooling systems, and in particular as vulcanization accelerators in the rubber industry. Benzothiazole enters the environment from a variety of sources such as the leaching of rubber products, but particularly by routes associated with the manufacture and use of mercaptobenzothiazole (MBT) and MBT-based rubber additives. Benzothiazoles can also be found in the environment as natural products, since these are included in molecular structure of vitamin B1. Their occurrence was observed not only in industrial and municipal wastewater but also in soil, estuarine sediments and surface water.

Several benzothiazole derivatives exhibit high toxicity. MBT shows the highest toxic effects on activated sludge; it is a carcinogenic compound and can cause allergic reactions, dermatitis, and initiate genetic damage in mammalian cells.

According to Knapp et al., 7 mg L⁻¹ BT causes 50 % and 54 mg L⁻¹ BT causes 100 % inhibition of ammonia oxidation, while nitrate utilization is not affected. Contaminants are removed from the environment without being destroyed or transformed in conventional physical treatment at high operating costs, while toxic residues are accumulated. Application of biological process is inadequate when the wastewater contains highly toxic refractory compounds.

Commonly used urban WWT processes, including the removal processes of macronutrients are insufficient to remove specific synthetic substances. It is therefore necessary to search for combined chemical-biological or physicochemical-biological processes that can remove these substances efficiently and effectively. Among others, chemical oxidation with subsequent detoxification on biological sand filter or using granular activated carbon could be considered a perspective solution. Processes, which are widely studied and partially applied in practice include those using ozone, as well.

Ozone is characterized by a high oxidation potential. Its basic disadvantages are, however, high operating costs. It is therefore necessary to explore methods to achieve more efficient ozone use. One possibility of increasing the efficiency of ozone utilisation is by means of the ozonation process parameters (pH, temperature, power generator, etc.). The combined process of ozone with other reactants/processes (UV, H₂O₂, catalytic ozonation, adsorptive ozonation) characterized by radical reaction mechanism, higher reaction rates and thus also higher efficient use of ozone appear more efficient.
Materials and methods

Fig. 1 shows the lab-scale ozonation equipment. Experiments were carried out in a reactor with a volume of 500 mL. Ozone was produced by oxygen laboratory ozone generator. The measurements were performed with a model wastewater containing 130 mg L⁻¹ of BT. A mixture of oxygen and ozone was dosed into the ozonation reactor through a porous frit and mixed with model wastewater by a magnetic stirrer. The reactor was filled with model wastewater to volume of 450 mL. Experiments were carried out at constant oxygen flow of 40 L h⁻¹ and constant ozone generator output of 20 % of its maximum power, which corresponds to the ozone production of 5 g h⁻¹. The constant flow of oxygen was maintained using laboratory flowmeter. Concentration of ozone in the gas phase at the inlet and outlet of the reactor was measured using a laboratory scale ozone UV detector.

Benzothiazole was determined by high-pressure liquid chromatography (HPLC). TOC was measured with analyzer Shimadzu TOC-V(CP)CPN (Japan). Analytical control of model wastewater during the treatment procedures included also COD (chemical oxygen demand) determination.

Kinetic data processing

Experimental data were processed with kinetic models of zero (1), the first (2) and second (3) orders:

\[
\begin{align*}
S_t &= S_0 - k_0 t \\
S_t &= S_0 \exp (-k_1 t) \\
S_t &= S_0/(1 + S_0 k_2 t)
\end{align*}
\]

where

\[S_0 [\text{mg L}^{-1}]\] is the concentration of the substance being studied at time 0, \(S_t [\text{mg L}^{-1}]\) is the concentration of the substance being studied at time \(t\) and \(k_0 [\text{mg L}^{-1} \text{min}^{-1}], k_1 [\text{min}^{-1}]\) and \(k_2 [\text{mg}^{-1} \text{L min}^{-1}]\) are rate constants for kinetic zero, first and second orders.

Results and discussion

The aim of this work was degradation of benzothiazole, which is a toxic and slowly biodegradable substance. Adsorption on activated carbon, ozonation and adsorptive ozonation were investigated as potential BT removal processes. BT removal was monitored through cumulative wastewater quality indicators, i.e. COD and TOC. The oxidation intermediates of the processes were also studied.

Time dependence of BT concentrations measured on activated carbon during adsorption are shown in Fig. 2. Fig. 3 illustrates the time courses

![Fig. 1 – Schematic diagram of the experimental apparatus; 1 – oxygen source, 2 – ozone generator, 3 – ozone and oxygen mixture inlet to the reactor, 4 – reactor with model water, 5 – ozone detector, 6 – magnetic stirrer](image1)

![Fig. 2 – Time dependence of measured BT concentrations](image2)

![Fig. 3 – Time dependence of measured BT and BTS concentration](image3)
of BT and benzothiazolsulfonic acid (BTS) during ozonation and adsorptive ozonation processes.

From Figs. 2 and 3 follows that sufficiently low final BT concentrations were observed with both processes. BT concentration of 0.1 mg L⁻¹ was measured after 24 hours when activated carbon adsorption was applied. BT concentration was below its detection limit after 45 minutes of ozonation process. Adsorptive ozonation resulted in the lowest time (30 min) for detection limit. BTS is produced during BT ozonation, as an intermediate product. Its concentration increases simultaneously with BT concentration decreasing. BTS concentration decreased to value 2.6 mg L⁻¹ in adsorptive ozonation. It follows from these measurements that adsorptive ozonation is the most effective process for BT degradation (Table 1).

<table>
<thead>
<tr>
<th>Table 1 – Values of rate constant and correlation coefficient</th>
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<tr>
<td>0 (mg L⁻¹ min⁻¹)</td>
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<td>1 (min⁻¹)</td>
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<td>2 (mg⁻¹ L min⁻¹)</td>
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Time dependences of COD and TOC values measured during adsorption on activated carbon are shown in Fig. 4. Fig. 5 shows similar dependencies of ozonation and adsorptive ozonation processes performance. Lower residual values of COD and TOC result from adsorption on activated carbon compared to the results of ozonation process, which is thought to be caused by BTS intermediate formation during BT oxidation by ozone, and thus the values of COD and TOC are higher than during separation process. When comparing with the ozonation alone, lower values of COD and TOC resulted from adsorptive ozonation. Low BT and BTS concentrations were observed already after 10 minutes in adsorptive ozonation, and thus also COD and TOC values were lower.

Inhibition effect of benzothiazole and its degradation products on oxygen uptake rate (OUR) by microorganisms of activated sludge was also studied in the course of benzothiazole transformation/degradation. Influence of BT on activated sludge activity is shown in Fig. 6. Influence of BT transformation/degradation products on activated sludge microorganisms is presented in Fig. 7.

It can be concluded from Fig. 6 that BT concentration growth also causes the inhibition effect...
to increase. As presented in Fig. 7, adsorptive ozonation with a reaction time of 20 minutes is the most suitable process for BT oxidation, due to the fact that the lowest inhibition influence resulted from the performance of this process.

The aim of this study was also to examine biodegradability of BT and BT ozonation transformation products. Respirometric measurements were applied for degradability assessment. Dependence of oxygen uptake rate (OUR) using BT and samples of ozonated model wastewater is illustrated in Fig. 8. Initial sample of BT model water and ozonated 30 minutes were used for respirometric measurements. As shown in Fig. 8, BT model water volumetric OUR is close to zero. It could be considered that BT has a toxic effect on activated sludge. From experiments in which BT samples after ozonation were used, it can be concluded that intermediates created by oxidation of BT are biodegradable, which is obvious from OUR growth with an increase in the applied dose of sample volume. Increased respiration rate occurred in samples with model wastewater after adsorptive ozonation.

Conclusions

BT removal experiments were carried out using adsorption on activated carbon, ozonation alone, and adsorptive ozonation processes. Changes in COD, TOC values, as well as concentration changes in BT and BTS as an intermediate of BT oxidation, were compared during experiments. Based on the obtained results, it can be concluded that adsorptive ozonation is the most effective of all examined processes.

Adsorptive ozonation with reaction time of 20 minutes resulted as the most convenient process for BT oxidation, when studying the toxicity of ozonation effect of BT and its oxidation intermediates on activated sludge microorganisms. This conclusion follows from the fact that the products of this process exhibited the lowest inhibition effect on activated sludge microorganisms. Respirometric measurements were carried out to follow biodegradability products of ozonation BT. The respirometric measurement results show an inhibitory effect on the activated sludge activity. BT ozonation, on the other hand, generated biodegradable intermediates, as evidenced by increasing the concentration of ozonated sample, which also increased the volumetric oxygen uptake rate.

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References