Biodegradability of benzothiazole ozonation products

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Abstract: Ozonation experiments were performed with model wastewater containing 100 mg·l^{-1} BT concentration. Ozonation was carried out in air-lift reactor with external recirculation of reaction mixture. BT removal efficiency of 80 % was measured. BT residual concentration and concentration of its degradation products after ozonation were expressed by COD and TOC values. Samples of ozonisated model wastewater were used for respirometric measurements performed with activated sludge microrganisms. Increase in exogenous oxygen uptake rate (OUR) compared to the endogenous phase was recorded in all measurements. Experimental data were fitted by Monod and Haldane equations. The best match of experimental and calculated data was achieved by Haldane kinetic model due to substrate inhibition. The results of respirometric measurements indicate that BT and its decomposition products are biodegradable. However, substrate inhibition was observed with higher COD content. Measurements have shown that ozonated wastewater OUR may increase and decrease over ozonation time. Toxicity test were performed in three organisms (*Sinapis alba*, *Daphnia magna* and *Vibrio fischeri*), and have shown that each studied organism reacts differently on ozonated wastewater.

Keywords: Ozonation, ozonation products, toxicity, oxygen uptake rate

1. Introduction

Benzothiazole (BT) is xenobiotic heterocyclic chemical that contains benzene ring fused with a thiazole-ring (El-Bassi *et al*., 2010). The heterocyclic structure provides multiple functionality and opportunities for derivatization, making it a good starting material for other industrial chemicals (Ginsberg *et al*., 2011). BT and its derivatives are manufactured worldwide for a wide variety of applications; they are mainly used as vulcanizing agents in the rubber industry (De Wever and Verachtert, 1997), fungicides in lumber and leather industry, bio-corrosion inhibitors in antifreeze, and in industrial cooling systems. Benzothiazoles are found in industrial and municipal wastewater, as well as in soils, river sediments and superficial waters posing environmental concern (Valdés and Zaror, 2006). Benzothiazole was selected for the study as one of relevant substances for the Slovak Republic.

Ozonation has been recently recognized as a prospective method for removing POPs. It is well known, that conventional wastewater treatment processes cannot effectively remove BT from wastewater. This substance is resistant to biological degradation and is susceptible to the sorption on membrane cells, resulting in bioaccumulation (De Wever and Verachtert, 1997). Advanced oxidation processes, such as, H2O2/UV, photo assisted Fenton, and ozone have been used to oxidise benzothiazole compounds (Valdés *et al*., 2008).

Respirometric tests were carried out to study the influence of degradation products to the activated sludge microorganisms (Hrdlička *et al*., 2015). Convetional ozonation process was investigated with the aim to decrease the toxicity of selected pollutants to microorganism of activated sludge (Derco *et al*., 2012). All water samples were subjected to toxicity on terrestrial plants (OECD Guidelines 208: „Terrestrial plants, Growth tests"). Then, the most common bacterial bioluminescence test was carried out with marine bacteria *vibrio fishery* (ISO 11348-1; Urminská, 2015). It was considered of critical importance that both a plant and an animal species be selected for testing. *Dafnia magna* represents animal species (Azizian *et al*., 2003).

2. Experimental methods

Among the diverse biological wastewater treatment methods, aerobic processes, especially activated sludge, dominates. Thus, most of the new toxicity assays that have been developed focus on their application to activated sludge (Xiao *et al*., 2015). Samples of ozonized model wastewater were used for respirometric measurements performed with activated sludge microorganisms. Oxygen uptake rate (OUR) was measured. The same simplified procedure was used for each sample. Certain amount of activated sludge was put into oxygen cell of volume 300 ml in order to achieve concentration at least 0,5 mg·l^{-1}. Then, water and ozonized water were added into the cell in a volume that left no space for air. Ozonized water volume was ranging from 0.5 to 200 ml as it was limited by the cell volume and activated sludge concentration. The cell was closed with a nozzle and oxygen probe to prevent entry of air. Magnetic stirrer was turned on and the measurement started. Activated sludge from main waste water treatment plant in Bratislava was also used.

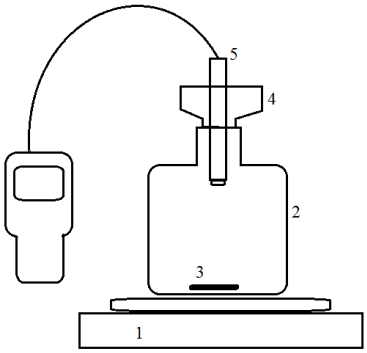

Figure 1. Schematic of respirometric measurement; 1 –- magnetic stirrer, 2 – oxygen jar, 3 – stirrer, 4 – insert the oxygen sensor, 5 – oxygen probe.

Model wastewater with BT concentration 100 $mg \cdot l^{-1}$ was used in experiment. Ozonation was carried out in air lift reactor only. Five ozonation tests were performed. Ozonation time was 5, 10, 20, 30 and 40 minutes.

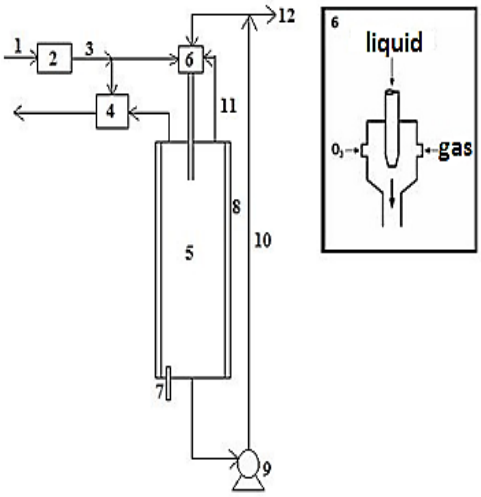

Figure 2. Ozonation air lift reactor; 1 – input of O_2, 2 – O_3 generator, 3 – gas mixture (O_2 + O_3), 4 – detector of ozone concentration in the gaseous phase, 5 – reactor V = 3 l, 6 – venturi ejector, 7 – UV lamp, 8 – reactor tempering, 9 – pump, 10 – external liquid recirculation, 11 – head space gas recirculation, 12 – sampler.

The ozonation reactor size is 0,08 m in diameter and 1,0 m in height. Effective volume of the reactor is 3,5 l. Membrane pump was used for external circulation of the reaction mixture. A diaphragm pulsation damper (SERA 721.1 Seybert & Rahier, Immenhausen, Germany) was used to minimize the external circulation pulsation. Life Tech ozone generator with the maximum ozone production of 5 $g \cdot h^{-1}$ was used. Ozone was prepared from pure oxygen.

BT concentration and COD and total organic carbon (TOC) values were measured in samples, which describe the process of ozonation and were therefore, used to calculate values describing the partial oxidation and mineralization of model wastewater. Oxidized COD, which was completely mineralized αCOD_{miner}, and $\alpha COD_{partoxi}$ is only partially oxidized COD of the synthetic wastewater during the process.

$$\alpha COD_{oxi} = 1 - \frac{COD_t}{COD_0} \quad (1)$$

$$\alpha COD_{min} = 1 - \frac{DOC_t}{DOC_0} \quad (2)$$

$$\alpha COD_{partoxi} = \alpha COD_{oxi} - \alpha COD_{min} \quad (3)$$

$$\mu COD_{oxi} = \frac{\alpha COD_{partoxi}}{\alpha COD_{oxi}} \quad (4)$$

Experimental data were fitted by zero (eq. 5), first (eq. 6), and second (eq. 7) order reaction kinetic models. For a batch reaction system, under the assumption of a constant reaction volume, the following relationships are obtained (Melicher *et al*. 2012).

$$S_t = S_0 - k_0 \cdot t \quad (5)$$

$$S_t = S_0 \exp(-k_1 \cdot t) \quad (6)$$

$$S_t = \frac{S_0}{(1 + S_0 \cdot k_2 \cdot t)} \quad (7)$$

Oxygen uptake rate values were put in dependence with COD values. Experimental data were fitted by Monod (8) and Haldane (9) equations (Kumar *et al*. 2004).

$$r_x = r_{x,max} \cdot \frac{S}{S + K_S} \quad (8)$$

$$r_x = r_{x,max} \cdot \frac{S}{S + K_S \cdot \frac{S}{K_I}} \quad (9)$$

In this experiment, the toxicity was studied on three organisms: *Sinapis alba, Daphnia magna* and *Vibrio fischeri*. Namely the root growth inhibition with *Sinapis alba*, mortality and immobilization with *Daphnia magna*, and inhibition of luminescence of *Vibrio fischeri*.

3. Results and discussion

The experiment was carried out in air lift reactor. BT concentration and COD and total organic carbon (TOC) values were measured in samples. COD removal efficiency of 38,2 % was measured after 40 minutes and TOC removal efficiency of only 21,2 % was measured after same time.

Table 1. BT concentrations and COD, TOC values during ozonisation.

t (min)	BT ($mg \cdot l^{-1}$)	CHSK ($mg \cdot l^{-1}$)	TOC ($mg \cdot l^{-1}$)
0	98	201,5	63,6
5	82	188	63,4

10	63	183	60,4
20	49	169,5	58,6
30	30	144,5	57,0
40	21	124,5	50,1

Approximately 80 % efficiency was achieved in process of BT degradation after 40 minutes. The best match between experimental and calculated data was achieved by the first order of reaction kinetic model. The kinetic rate constant of reaction and correlation coefficient are given in Table 2.

Table 2. Kinetics parameters of BT ozonation process.

k_1 [min^{-1}]	$3{,}8339 \cdot 10^2$
r_{xy}^2	0,9935

Dependance curves of partial oxidation and mineralization of model wastewater with ozonation time are shown in Figure 4. It is obvious that partial oxidation raises simultaneously with COD oxidation at the beginning of ozonation process. Process of mineralization starts to take place after first five minutes. After 30 minutes mineralization is the most significant partial process of ozonation.

OUR was measured in all model wastewater samples after ozonation. Results are shown in Figure 5. The best match between experimental and calculated data was achieved by Haldane kinetic model due to substrate inhibition. The results of respirometric measurements indicate that BT and its decomposition products are biodegradable. Substrate inhibition, though, was observed with higher COD content. In most cases samples Lower values of maximum OUR were observed in the most samples containing higher residual concentration of BT and higher COD value, while higher maximum OUR values were observed in samples with lower residual concentration of BT and the lower COD value. This, however, does not apply to ozonation time of 30 minutes. The highest OUR in ozonated wastewater was measured after 20 minutes and then after 40 minutes.

Measurements have shown that ozonated wastewater OUR may increase and decrease over ozonation time. This fact can affect the next biological wastewater treatment step. Toxicity tests were performed on three organisms and trophic levels of water ecosystem. Results are shown in Figure 6.

Inhibition decreased with ozonation time, from 64,6 % to 27,5 % for *Sinapis alba*. Inhibition has maximum at 10 minutes ozonation time in *Vibrio fischeri* and then it decreased in time. On the other hand, in *Daphnia magna* inhibition lower than 100 % was measured after 10 minutes of ozonation only.

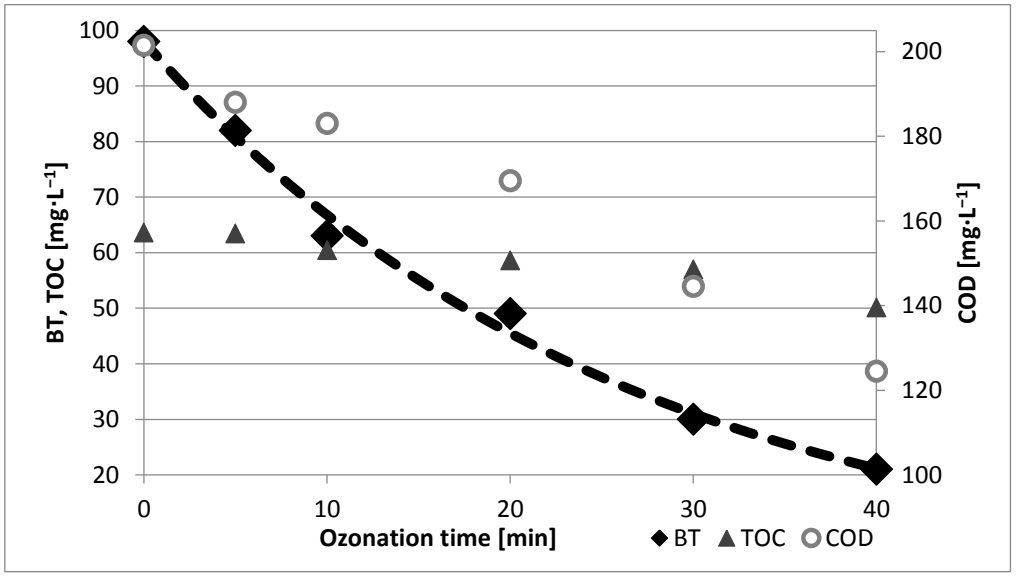

Figure 3. Calculated BT concentration and measured COD, TOC values and BT concentration

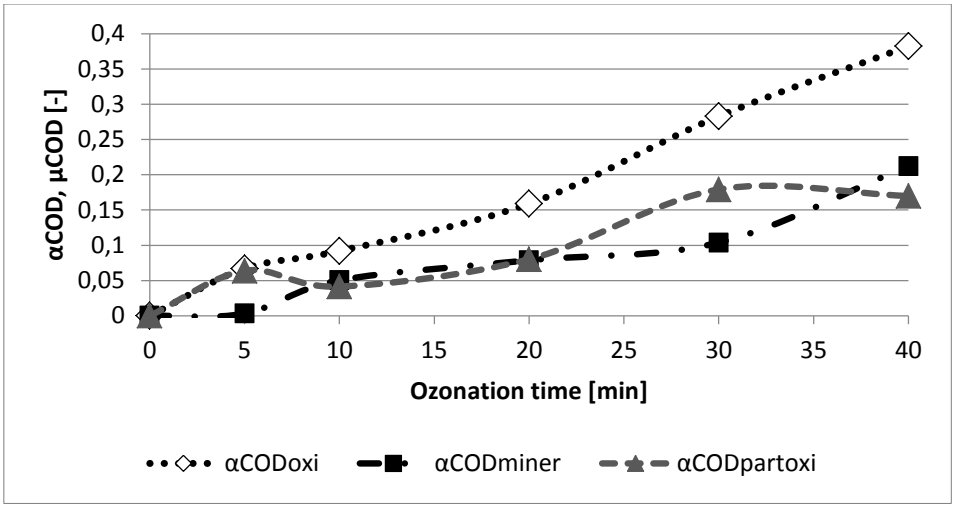

Figure 4. Partial oxidation and mineralization with ozonation time

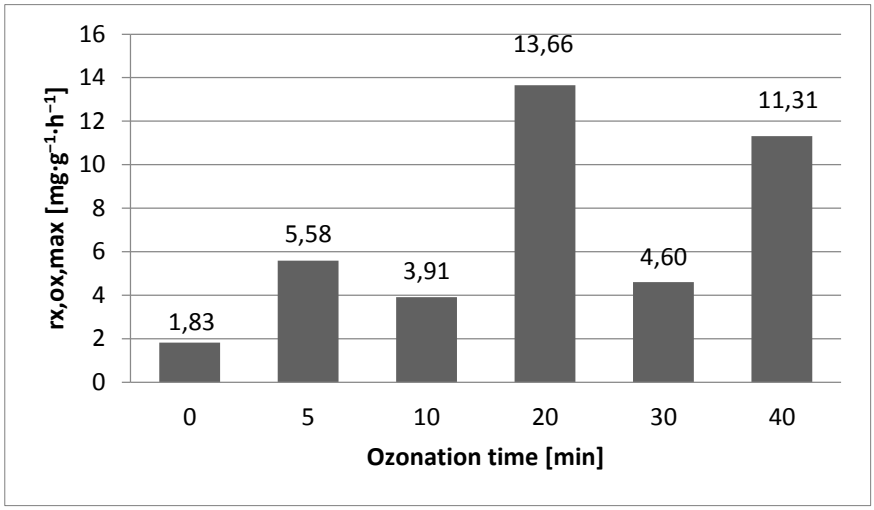

Figure 5. OUR measured with ozonated wastewater after different ozonation time.

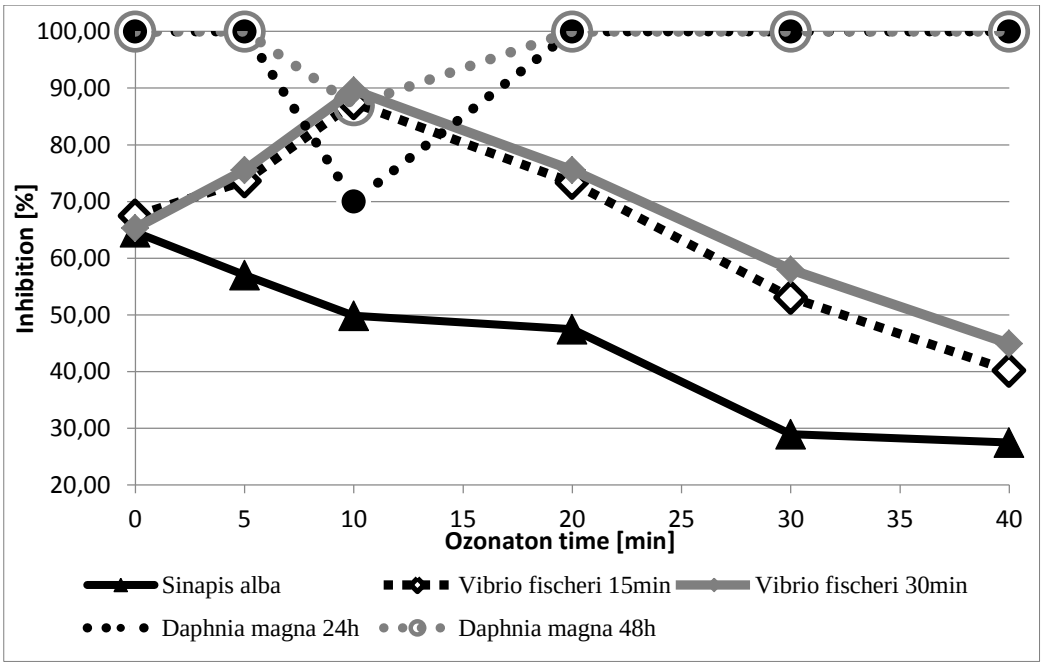

Figure 6. Results of toxicity tests.

4. Summaries

Ozonated wastewater OUR increase and decrease over ozonation time. OUR of 1,83 $mg \cdot g^{-1} \cdot h^{-1}$ was measured with non-ozonised model wastewater, which is a low value. The highest OUR reached the value of 13,66 $mg \cdot g^{-1} \cdot h^{-1}$ after 20 minutes of ozonation time. Strong decrease to 4,6 $mg \cdot g^{-1} \cdot h^{-1}$ recorded after 30 minutes of ozonated, which may be explained by the formation of ozonation product capable of inhibiting the sludge activity. OUR raised again to 11,31 $mg \cdot g^{-1} \cdot h^{-1}$ after longer ozonisation (40 minutes), which means that the unwanted intermediate has been at least partially removed. Various intermediates are both formed and then destroyed during ozonisation that may have adverse effect on sludge activity. It means that ozonated wastewater is more suitable for subsequent biological treatment after certain ozonation. Maybe even good enough to be used as substrate.

Toxicity tests have shown that each studied organism reacts differently on ozonated wastewater. Inhibition of 100 % for *Daphnia magna* and approximately 65 % for *Vibrio fischeri* and *Sinapis alba* was measured in non-ozonated model wastewater. Inhibition measured on *Sinapis alba* simply decreases with ozonation time from 64,6 % to 27,5 %. Response *Vibrio fischeri* and *Daphnia magna* was exactly the opposite. After 10 minutes of ozonation when inhibition of *Vibrio fischeri* reached its maximum at 87,4 % (15 minutes) and 89,6 % (30 minutes), *Daphnia magna* has reached the lowest inhibition at 70 % (24 hours) and 87 % (48 hours). was Measured inhibition reached 100% for *Daphnia magna* again after 10 minutes (20, 30, 40) of ozonation For *Vibrio fischeri*, smooth downward in inhibition was recorded after 10 minutes (20, 30, 40) of ozonation, which ended at the respective values of 40,2 % (15 minutes) or 44,9 % (30 minutes).

Therefore, it is necessary to carry out more experiments. It is important to find ozonization conditions under which it may be applied in practice, in terms of reduced toxicity and the efficacy of the process.

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