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Assessment of toxicity of synthetic specific substances after ozonation process

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Abstract. Wastewater treatment processes have a key role in sustainable development as a tool of protection of surface waters from anthropogenic pollution. Ozonation process is a promising technology for removal of toxic and biologically resistant compounds from wastewater. However, the aim is not only to remove selected pollutants from wastewater but also to minimize any adverse / toxic effects of oxidation processes byproducts. In addition to assessment of physical and chemical indicators of water pollution it is very important to use also ecotoxicological bioassays for direct toxicity evaluation. This approach helps to predict the biological effects caused by wastewater discharges to water ecosystems and to find out whether the treatment process is sufficient to provide a satisfactory decrease of environmental impact (ecotoxicity). This paper documents our results in the field of removal of synthetic specific substances, especially alkylphenols and benzothiazole derivatives. Most of the compounds were efficiently removed by ozonation processes; however, toxicity of the samples remained relatively high. Further research will be focused on detoxification of the samples after ozonation.

Keywords: ecotoxicity, bioassay, ozonation processes, synthetic specific substances

1. Introduction

Ozonation is a perspective technological process of removing toxic and biologically resistant compounds from wastewater. Ozone is very strong oxidant and reacts with most of inorganic and organic pollutants. It is used in water and wastewater treatment and can react directly with a compound or indirectly through reactions of hydroxyl radicals generated in the ozone decomposition. The resulting decomposition products, however, may sometimes be more toxic than the original material. The aim is not only to remove selected pollutants from wastewater but also to eliminate any adverse / toxic effects of oxidation byproducts.

Estimation of toxicity can be based on determination of the physical and chemical parameters; however, this will not provide a complete picture of the toxicity and effects of effluents on organisms living in the aquatic environment. Therefore it is very important to evaluate direct toxicity using ecotoxicological bioassays. The combined assessment of physical and chemical parameters with ecotoxicological effects is to achieve reliable identification of risks, often hidden in the substances with low concentration but high toxicity – micropollutants or degradation and reaction products in wastewater (Urminská, 2013).

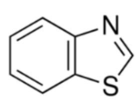
The results of our prior research can be divided into two areas: the removal of benzothiazole and its derivatives and removal of alkylphenols.

2. Materials and methods

2.1. Removal of benzothiazole and benzothiazole derivatives

Benzothiazole derivatives are known as persistent substances that enter the environment from the industry. They are used in various industry sectors: such as rubber vulcanization accelerators in the rubber industry and as a fungicide in leather making, paper and textile industry or for paintwork used for metals finishing (Sumegová *et al.*, 2014).

Benzothiazole (BT) is a specific synthetic compound relevant for the Slovak Republic. Traditional biological treatment processes cannot effectively remove BT from the wastewater as it is resistant to biological degradation (Kecskés *et al.*, 2014). 2-mercaptobenzothiazole (2-MBT) is present particularly in wastewater from the rubber industry where the concentration may be more than 200 mg L^{-1}. It is a strong contact allergen, toxic and resistant to biological degradation and at a concentration of about 100 mg L^{-1} can disrupt the biological processes of wastewater treatment. It also inhibits the nitrification and decomposition of easily degradable organic matter and is also acutely toxic (Derco *et al.*, 2014).



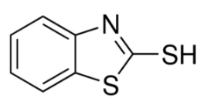


Fig. 1: benzothiazole **Fig. 2**: 2-mercaptobenzothiazole

For the experiments with degradation of benzothiazole the ozonation and combined ozonation processes O_3 / UV, O_3 /

H_2O_2 and O_3 / GAC (granulated activated carbon) were used. During the processes O_3 / UV and O_3 / H_2O_2, 10 minutes were sufficient for almost complete degradation of BT. Inhibition of respiration activity of activated sludge microorganisms reached the lowest value after 20 minutes of the process (Fig. 3 and 4). Toxicity tests on the seeds of white mustard (*Sinapis alba*) and the organisms *Daphnia magna* and *Vibrio fischeri*, however, showed a relatively high toxicity of the samples – especially the test on *Daphnia magna* showed inhibition of almost 100 %. Inhibition of bioluminiscence of *Vibrio fischeri* reached almost 100 % after O_3/H_2O_2; on the contrary, the inhibition after the process O_3 / UV was less than 10%. *Sinapis alba* seemed to be a less sensitive organism and it was not able to clearly distinguish the samples before and after the oxidation processes (Table 1). The study of ozonation of 2-MBT in model wastewater confirmed that the oxidation with ozone is an effective process of removal of benzothiazole derivatives (20 minutes of ozonation was sufficient for total degradation of 2-MBT sufficient). However, the sample after 15 minutes of ozonation still had an inhibitory effect on the respiratory activity of the sludge. After 40 minutes of ozonation the inhibitory effect diminished and respiratory rates were significantly higher, indicating that the inhibitory effect of a toxic substance and its breakdown products can be reduced by a longer ozonation. The ecotoxicity tests were performed with organisms *Daphnia*

Table 1. Average values of root growth inhibition Sinapis alba (72 hours test) and the inhibition of bioluminescent Vibrio fischeri (15 and 30 min test)

	Results of toxicity test (% of inhibition)			
BT sample	***Sinapis alba***	***Daphnia magna***	***Vibrio fischeri***	
	72 h test	**48 h test**	**15 min test**	**30 min test**
before process	16.6	100.0	37.25	27.77
after ozonation	16.1	98.5	20.45	11.02
after O_3/UV	27.0	96.0	8.96	4.98
after O_3/H_2O_2	11.2	100.0	99.01	99.40

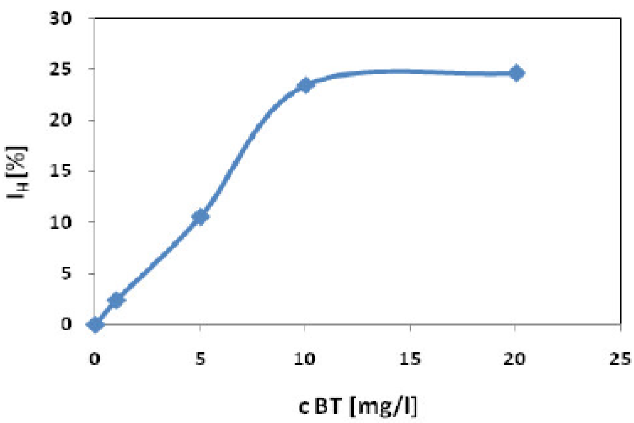


Fig. 3. Inhibition of respiration activity of activated sludge microorganisms by benzothiazole

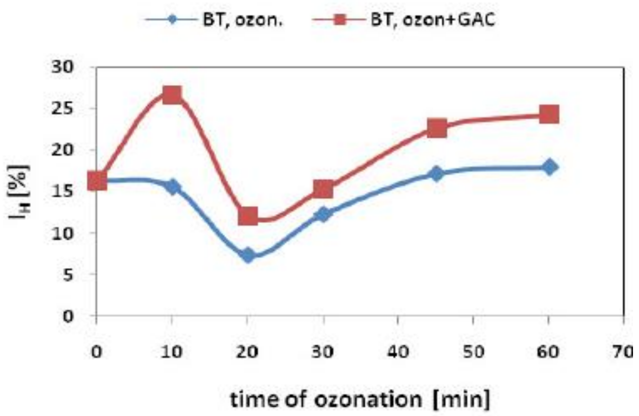


Fig. 4. The effect of benzthiazole and its degradation products after ozonation and combined process O_3 / GAC on the microorganisms of the activated sludge

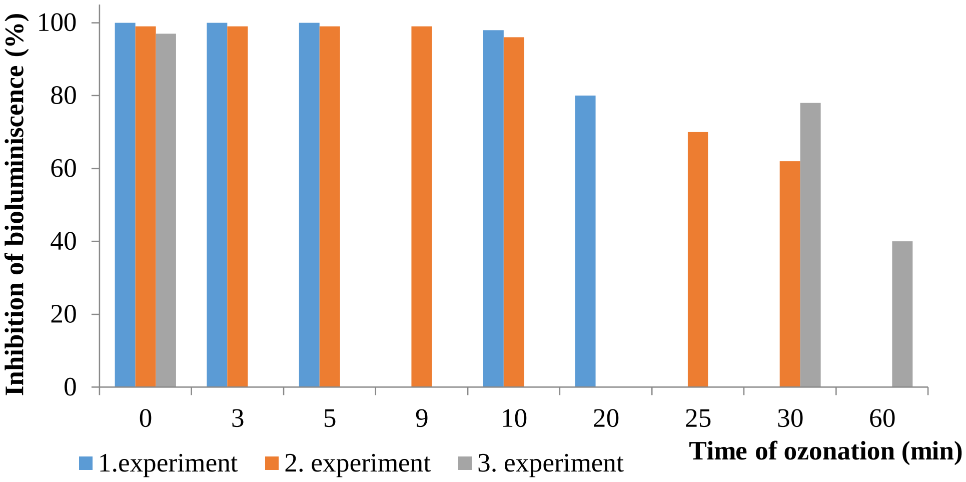
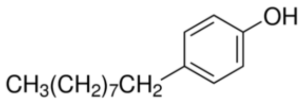


Fig. 5. MBT –Inhibition of bioluminiscence of *Vibrio fischeri* (15 min test) depending on time of ozonation

magna and *Vibrio fischeri*. The results showed that the lowest inhibition of around 40 % on bacteria *Vibrio fischeri* was reached after a 60-minute ozonation (Fig. 5). For *Daphnia*, however, it was 100% mortality of testing organisms regardless of the length of ozonation. Since the sample of the wastewater after ozonation contained a mixture of different benzothiazole derivatives and degradation byproducts, it was not possible to determine which component had the most toxic effects.

2.1. Removal of alkylphenols

Alkylphenols are used as antioxidants and plasticizers, as well as for the production of alkylphenol ethoxylates (APEO). Approximately 80% of APEO production is covered by nonylphenol polyethoxylates (NPEO), which are used for the production of plastics, textile and agricultural chemicals and also as a part of household detergents, dyes, pesticides and cosmetics. Nonylphenol polyethoxylates are degraded primarily to nonylphenols, they are toxic to aquatic ecosystems and exhibit estrogenic activity (Soarez *et al*.; Derco *et al*., 2015). Nonylphenols and nonylphenols ethoxylates are listed as priority hazardous substances in the Water Framework Directive (Directive 2000/60/EC, 2000) and most of their use is currently regulated (Directive 2003/53/EC, Soarez *et al*., 2008).



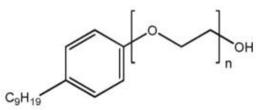


Fig. 6: 4-nonylphenol **Fig. 7.** nonylphenol ethoxylate

For the experiments with removal of 4-nonylphenol (NP), 4-t-octylphenol (OP), nonylphenol ethoxylate (NPEO) and octylphenoletoxylate (OPEO) the ozonation and combined process of ozonation with adsorption on the activated carbon were used. In the case of NP and NPEO the removal efficiencies for both processes were comparable, for OP and OPEO removal the process of ozonation with activated carbon was much more efficient. Ozone selectivity of the examined APs and their ethoxylates depended on wastewater composition. High removal efficiencies of NP and NPEOs were measured during ozonation of industrial wastewater. Mean values of removal efficiency varied from 6.2 % for OP to 93.2 % in case of OPEO. Mean values of treatment efficiencies in the range from 9.2 % for NP to 47.9 % for NPEO were observed during the ozonation of municipal wastewater after receiving and industrial wastewater with AP content.

Toxicity tested on the organism *Vibrio fischeri* was lower after the ozonation than after the combined process of ozonation and activated carbon adsorption. The lowest toxicity impact of intermediates and products of ozonation treatment on Vibrio fischeri was measured after 10 minutes of ozonation which was lower in comparison to products of O_3 / GAC process.

3. Conclusions

Ozonation is an effective and promising technology for the removal of synthetic specific substances from wastewater. In the experiments the controlled substances were removed from the model or the real wastewater with high efficiency. The toxicity tests have shown the reduction of ecotoxicity of the samples towards some of the testing organisms; however, the results of the tests on *Daphnia magna* showed the mortality of 100 % for the most of the samples. It can be concluded that despite the degradation of the monitored pollutants the toxicity of the samples remained high. Further research will be focused on the possibility of detoxification of the samples after ozonation. One of the possibilities is the inclusion of further technological changes (eg. detoxification on the biological sand filters, activated carbon, etc.) to remove residual contaminants and their degradation products. In order to effectively protect the environment the importance of assessment of the toxicity of wastewater should gradually increase.

Acknowledgements.

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