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OZONATION OF BIOLOGICALLY REFRACTORY POLLUTANTS

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Advanced oxidation processes (AOPs) are an effective emerging technology for removal and enhancement of biodegradability of biologically resistant and toxic pollutants of wastewater. One of these AOPs is ozonation carried out at higher pH values. Ozone is a powerful oxidizing agent available for the treatment of industrial wastewaters. The ozonation reactions are accomplished into two pathways: direct ozone oxidation and indirect free hydroxyl radical oxidation.

The industrialization of human society has grown also the risk of environmental problems caused by a diversity of anthropogenic chemicals and substances in wastewater from industry. Wide group of these substances are able to enter into the organism and interrupt with their endocrine systems. They are resistant and bioactive, thus they are able to pass conventional treatment systems, wide-spread with surface and underground water and enter into organisms.

We have studied removal of 2-mercaptobenzothiazole (MBT) contained in synthetic wastewater. This xenobiotic compound is used mainly in the manufacture of rubber additive chemicals but also has other uses, notably as a corrosion inhibitor in cooling water and in antifreeze for automobiles. It is known as a widespread, toxic and poorly biodegradable pollutant. Biological treatment of the wastewaters of rubber chemicals production often seems to be problematic, most probably due to presence of MBT. In fact, MBT is used due to its fungicidal properties, or its antimicrobial effects. Data concerning the biodegradation of MBT are inconclusive. Some authors have suggested it is recalcitrant to biodegradation. MBT was not metabolised by microorganisms, which were non adapted to activated sludge to this pollutant. The feasibility of utilisation of ozonation process for reduction of concentration of MBT was investigated in laboratory scale equipment. The system was operated in batch mode. Synthetic wastewater with MBT was added into ozonation reactor at the beginning of trials. Continuous flow of oxygen 30 l h^{-1} was applied for generation of ozone. Ozonation trials were carried out at different performance of ozone generator in the range from 30 to 90% of the power maximum. Initial concentration of MBT in synthetic wastewater was about 50 mg l^{-1}.

Significant decrease of MBT content was observed after four minutes of ozonation. Correspondent efficiency values for COD and TOC removal were 55 and 16%. Higher removal rates were achieved in the sample with lower initial content of MBT. The highest removal rate values were observed during the first 10 minutes of the process for both COD as well as TOC content. The first order reaction kinetics follows for COD removal. Positive influence of power of ozone generator on COD removal resulted from the work.

Keywords: bubble ozonation column, degradation, 2-mercaptobenzothiazole, ozone, ozonation

Introduction

The industrialization of human society has grown also the risk of environmental problems caused by a diversity of anthropogenic chemicals and substances in wastewater from industry. Wide group of these substances are able to enter into the organism and interrupt with their endocrine systems. They are resistant and bioactive, thus they are able to pass conventional treatment systems, wide-spread with surface and underground water and enter into organisms. Benzothiazoles and their derivatives are manufacture worldwide for a wide variety of applications. They are used, among other things, as slimicides in the paper and pulp industry, as fungicides, as herbicides or as antialgal agents. The main use is as vulcanization accelerators in rubber production, catalyzing the formation of sulfide linkages between unsaturated elastomeric polymers in order to obtain a flexible and elastic cross linked material [1].

2-mercaptobenzothiazole (MBT) is the member of the benzothiazole group of heterocyclic aromatic compounds. It is a pale yellow, crystalline substance with an unpleasant odor and a bitter taste, with molecular weight 167.25 g mol^{-1} and specific density 1.42-1.52. It is easily soluble in ethyl acetone, acetone, dilute solution of sodium hydroxide and sodium carbonate and soluble in ethyl alcohol. It is not easily soluble in benzene. MBT can occur in two tautomeric forms. This xenobiotic compound is used mainly in the manufacture of rubber additive chemicals but also has other uses, notably as a corrosion inhibitor in cooling water and in antifreeze for automobiles. It is known as a widespread, toxic and poorly biodegradable pollutant. Biological treatment of the wastewaters of rubber chemicals production often seems to be problematic, most probably due to presence of MBT. In fact, MBT is used for its fungicidal properties, or its antimicrobial effects. Data concerning of the biodegradation of MBT are inconclusive. Some authors have suggested it is recalcitrant to biodegradation [2]. Epidemiological investigations indicate that workers occupationally exposed to MBT have an increased risk of death from bladder cancer. Genotoxicity investigations in bacterial and mammalian test systems provide some evidence indicating that MBT has the potential to induce mutations and chromosomal aberrations. Toxicity studies in rats and mice chronically exposed to MBT identified increases in various tumors. MBT interfered with the nitrification processes and exhibited biocidal effects. MBT inhibit the degradation of easily degradable organics. MBT was not metabolised by microorganisms, which were non adapted to activated sludge to this pollutant. Decrease of respiration activity of non adapted activated sludge was observed with the increase of MBT concentration.

Utilisation of ozone as possible process for MBT removal from wastewater was studied.

Advanced oxidation processes (AOPs) are an effective emerging technology for removal and enhancement of biodegradability of biologically resistant and toxic pollutants of wastewater. One of these AOPs is ozonation carried out at higher pH values. Ozone (O_3) is a powerful oxidizing agent available for the treatment of industrial wastewaters. O_3 is an unstable gas produced by electric discharge in a gas phase (air or pure oxygen). It is strong disinfectant with high oxidation power, potentially toxic and explosive, requiring on-site generation and caution for use. The ozonation reactions are accomplished into two pathways: direct ozone oxidation and indirect free hydroxyl radical oxidation. The direct ozone oxidation reaction is highly selective but relatively slow by selectively attacking the unsaturated electron-rich bonds contained in specific functional groups, e.g., aromatics, olefins and amines. In comparison, the indirect reaction has a relatively low selectivity but a quick reaction rate by hydroxyl radicals, which are generated by decomposition of ozone molecule. The hydroxyl radicals can oxidize regular organic substrates, micro-organisms and NH_3-nitrogen; the oxidation reaction lead to the formation of different but stronger radicals usually represented by the R symbol. The R radical can further react with ozone molecules to generate more hydroxyl radicals for further oxidation. However, the formation of free radicals from ozone is affected by either the solution pH or the presence of some scavenger chemicals in the water to be treated [3].

Experiments and results

Degradation of MBT with ozone has been studied. The experiments were performed in bubble ozonation column. The ozonation equipment consists of two glass columns, 0.04 m diameter and 1.70 m height. The first column was filled with synthetic wastewater with MBT, the other one was filled with solution of potassium iodide. The role of the second column was to destroy residual ozone in the outlet of the first ozonation column. The effective volume of both columns was 1.0 litre. Schematic diagram of experimental bubble ozonation apparatus is shown in *Fig. 1.*

The system was operated in batch mode. Synthetic wastewater with MBT was added into ozonation reactor at the beginning of trials. Continuous flow of oxygen 30 l h^{-1} was applied for generation of ozone. The Lifetech ozone generator with the maximum ozone production 5 g h^{-1} and Lifetech ozone UV detector were used. Ozonation trials were carried out at different performance of ozone generator in the range from 30 to 90% of the power maximum.

The content of MBT in sampling was measured by High performance liquid chromatography with reverse osmosis (RP-HPLC). Concentration of COD (chemical oxygen demand) was measured by semi micro method and TOC (total organic carbon) by analyser SCHIMADZU TOC$_{VCPH/CPN}$ [4].

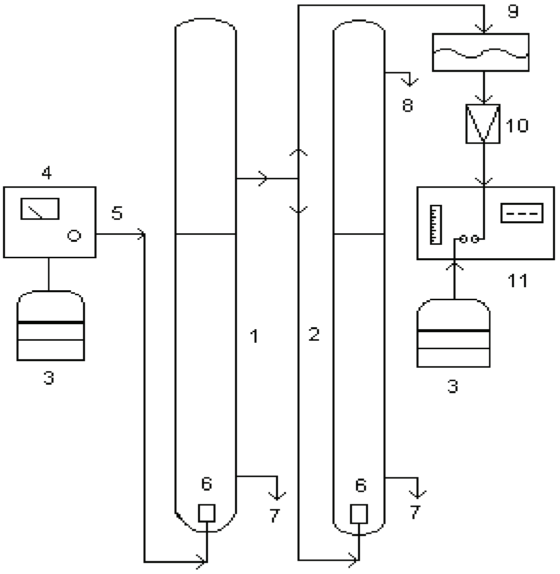

Figure 1: Schematic diagram of experimental column apparatus
1 – ozonation column, 2 – destruction of residual O_3, 3 – oxygen cylinder, 4 – ozone generator, 5 – mixture of O_2 and O_3, 6 – distribution of O_3, 7 – sampling, 8 – residual gas outlet, 9 – moisture catcher, 10 – glass fibre filter, 11 – UV detector of O_3

Ozonation trials were carried out with synthetic wastewater containing MBT in lab-scale ozonation apparatus. Initial concentration of MBT in synthetic water was about 50 mg l^{-1}. Fien et al. [5] shown, that MBT and its breakdown products had a high affinity towards ozone as indicated by the rates for partial oxidation and mineralization. Benzothiazole (BT) was identified as the first ozonation product, reaching up to 60 mol% of the original MBT concentration, followed by low concentration of 2(3-H) benzothiazolone. *Fig. 2a* illustrates the influence of ozonation on variation of concentration COD, TOC and MBT at the ozone generator power 90%. The specific ozone supply was in this case 0.97 g_{O3} g_{COD}^{-1}. According to results shown at the *Table 1* the highest COD removal was observed during the first 10 minutes of ozonation. COD removal rate 5.9 mg l^{-1} min^{-1} was achieved at 90% of maximum ozone generator power. The initial ratio of COD/MBT was 2.2 (exp1, 2). Comparing with the initial COD value the 66% conversion of COD was achieved after 10 min of ozonation (exp 2) and 98% was achieved after 1 h (exp1). The first order reaction kinetics follows for COD removal. Good coincidence in COD and TOC removal follows from the Fig. 2a.

Table 1: Concentration of COD, TOC and MBT at W = 90% and Q_{O2} = 30 l h^{-1}, t = 60 min (exp1)

t [min]	COD [mg l^{-1}]	TOC [mg l^{-1}]	MBT [mg l^{-1}]
0	95.97	24.8	44.6
5	42.59	18.8	0.1
10	13.47	14.0	0.1
15	11.05	12.9	0.008
20	8.62	12.5	0.008
60	1.34	11.5	0.008

Table 2: Concentration of COD, TOC and MBT at W = 90% and Q_{O2} = 30 l h^{-1}, t = 10 min (exp2)

t [min]	COD [mg l^{-1}]	TOC [mg l^{-1}]	MBT [mg l^{-1}]
0	89	20.2	40.7
2	55	18.9	1.71
4	40	16.9	0.086
6	30	14.3	0.008
8	30	12.1	0.008
10	30	10.8	0.008

Table 3: Concentration of COD, TOC and MBT at W = 70% and Q_{O2} = 30 l h^{-1}, t = 50 min (exp3)

t [min]	COD [mg l^{-1}]	TOC [mg l^{-1}]	MBT [mg l^{-1}]
0	168	56.3	54.1
5	-	53.4	2.34
10	116	48.2	0.089
15	-	42.1	0.0189
20	33	36.7	0.008
30	-	29.6	0.008
50	23	25.5	0.008

The efficiency of removal of TOC was 46% after 10 minutes (exp2) and 54% after 1 hour (exp1) of ozonation. Removal (99%) of MBT from the sample was achieved by ozonation after 5 minutes (exp 1, 2). The presence of BT was identified. The amount of BT measured after 60 minutes of ozonation corresponded to 5% of initial MBT concentration in the synthetic wastewater.

Fig. 2b (Table 3) shows the results of ozonation process carried out at 70% of power of ozone generator and the oxygen flow 30 l h^{-1}. The specific ozone supply was 0.59 g_{O3} g_{COD}^{-1}. The initial ratio of COD/MBT was 3.1. The efficiency of removal of COD and TOC were 86% and 54% after 50 minutes (exp3) of ozonation. 95.7% of MBT was removed after 5 minutes of ozonation.

The process efficiency was considerably influenced by duration of ozonation. The content of MBT in synthetic wastewater containing this pollutant decreased closely to zero after first 4 minutes of ozonation performed at 90% of the maximum power of ozone generator. Similar decrease of MBT was achieved after 10 minutes of ozonation carried out at the 70% of the maximum power of ozone generator.

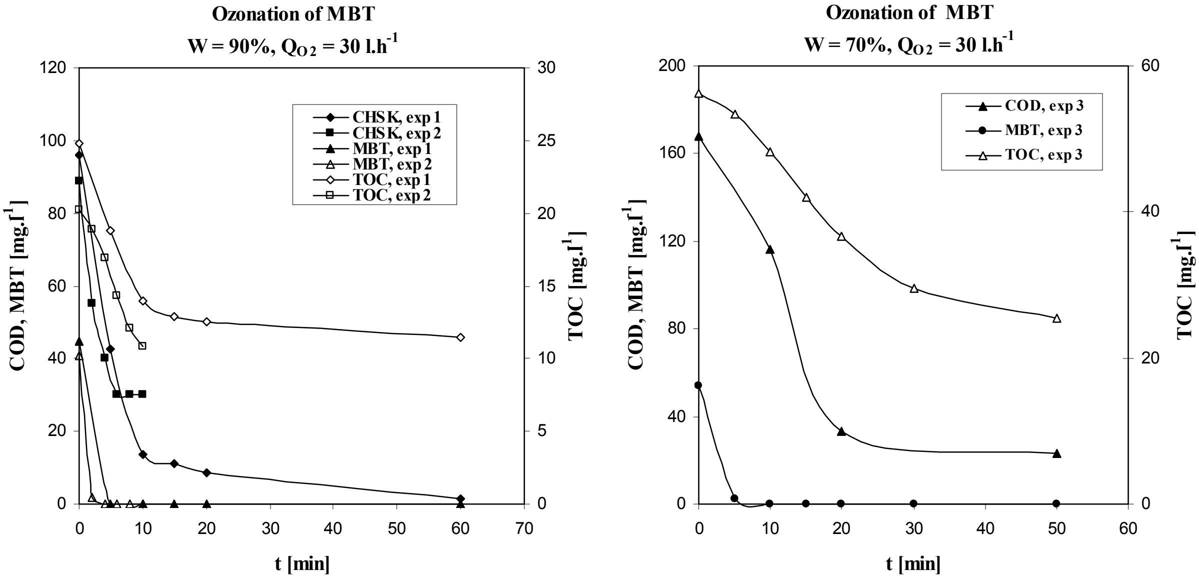

Figure 2: COD, TOC and MBT as a function of ozonation time at oxygen flow rate 30 l h^{-1}
a) W = 90% **b.)** W = 70%

Conclusion

Feasibility of ozone utilisation for MBT removal from wastewater was studied. Significant decrease of MBT content was observed after four minutes of ozonation carried out at 90% of maximum ozone generator power. Corresponded efficiency values for COD and TOC removal were 55 and 16% respectively. The highest removal rate values were observed during the first 10 minutes of the process for both COD as well as TOC content. Related specific ozone supply was 0.97 g_{O3} g_{COD}^{-1}. COD removal follows the first order reaction kinetics.

The removal rate 5.2 mg l^{-1} min^{-1} was observed at ozonation trial carried out at 70% of maximum ozone generator power was maintained. Positive influence of power of ozone generator on COD removal results from the work. The removal rate 5.9 mg l^{-1} min^{-1} was achieved at the 90% of maximum ozone generator power. In conclusion, MBT is readily transformed by ozonation.

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