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OZONATION OF SYNTHETIC WASTEWATER CONTAINING 2-MERCAPTOBENZOTHIAZOLE

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Abstract:
The possibilities of utilisation of ozone for removal of 2-mercaptobenzothiazole (MBT) from wastewater were studied in lab-scale. COD removal efficiency about 85 % was achieved after 6 hours of ozonation of the synthetic wastewater. The best fit of experimental COD data during ozonation was achieved with the zero order reaction kinetic model. Ozonation of MBT had positive influence on increase of biodegradability and respiration activity of activated sludge in the presence of wastewater after ozonation. The increase of BOD values and specific exogenous respiration rate with time of ozonation was observed within the performed measurements.

Keywords: *biologically resistant compounds, biological degradability, industrial wastewater treatment, 2-mercaptobenzotiazole, ozonation, respirometric measurements*

Introduction

Oxidation with ozone represents one of the alternatives for the removal of biologically resistant and toxic compounds from wastewater. According to product of oxidation the process of ozonation can lead to a total degradation of chemical compounds or to transformation of resistant highly hydrophobic organics to more polar biodegradable molecules. Total ozonation can lead to mineralization i.e. complete transformation of organic compounds to CO_2, H_2O and relevant inorganic chemicals. The aim of controlled oxidation is transformation of resistant compounds to more biodegradable molecules. In this case the process of ozonation can be integrated in the wastewater treatment line in front of biological treatment as a pre-ozonation. Other possibility is to use the wastewater after ozonation as a source of organic carbon for post-denitrification[1].

The combinations of the ozonation with hydroperoxide and Fenton reagents (H_2O_2/Fe^{2+}) are also used to treat wastewater with a high content of organic pollutants or industrial wastewater. In these advanced oxidation processes (AOP), highly reactive hydroxyl radicals ($^{\cdot}OH$) are formed, which are strong and nonselective oxidants for organic pollutants in wastewater[2, 3].

2-Mercaptobenzothiazole (MBT) is known as a widespread, toxic and poorly biodegradable compound[4, 5]. The cellular membranes in the activated sludge adsorb MBT; it leads to bioaccumulation of MBT. At 600 μmol.l^{-1} it may hamper wastewater treatment; MBT inhibits degradation of easily degradable organics and process of nitrification in a wastewater treatment process[5, 6].

The results of the study of ozonation treatment of an industrial wastewater containing MBT were presented in[7]. The aim of the work was to study ozonation treatment of a synthetic wastewater containing MBT. Controlled oxidation with the aim to improve biological degradation of ozonation by products was also investigated. Some results of the study were presented at the 16th International Congress of Chemical and Process Engineering CHISA 2004[8].

Experimental

The experimental apparatus is shown in Figure 1. Ozone is produced from oxygen by an ozone generator with the maximum capacity 625 $mg.h^{-1}$. The mixture of oxygen and ozone was injected at the bottom through porous air diffusers with a constant flow rate 40 $l.h^{-1}$. The column was filled with 1 litre of synthetic wastewater containing 1 $g.l^{-1}$ of MBT. The system was operated in batch mode. Measurements of COD and BOD_5 concentrations were carried out according to a standard methods[9]. Respirometric measurements[10] were carried out in order to evaluate an effluence of ozonation products on activated sludge activity.

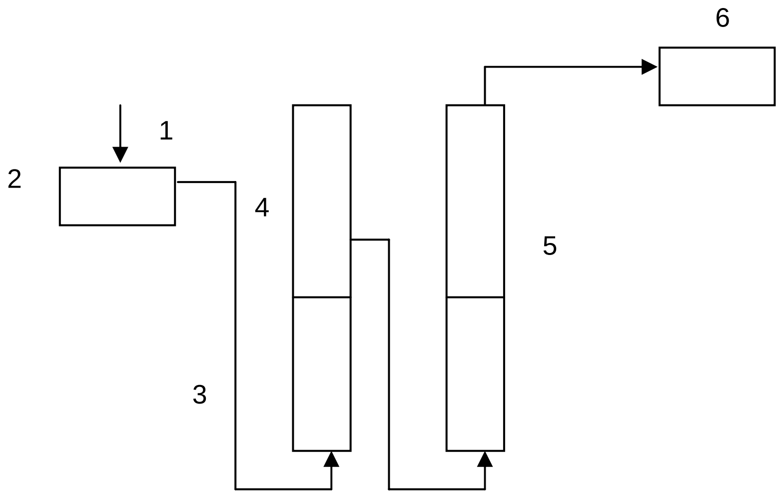

Figure 1. Schematic of experimental apparatus
1 - feed of oxygen, 2 - ozone generator, 3 - feed of ozone, 4 - ozonation column with synthetic wastewater, 5 - ozonation column with KI solution, 6 – destruction of residual ozone

Results and discussion

Figure 1 presents evolution of COD of MBT with the ozonation time. After 6 hours of ozonation COD removal efficiency was achieved about 85 %.

Experimental data were fitted by zero (1), the first (2) and the second (3) order reaction kinetic models.

$$COD_t = COD_0 - k_0 \cdot t \qquad (1)$$
$$COD_t = COD_0 \cdot \exp(-k_1 \cdot t) \qquad (2)$$
$$COD_t = COD_0 / (1 + COD_0 \cdot k_2 \cdot t) \qquad (3)$$

COD_t - concentration of COD in wastewater in the time "t" [$mg.l^{-1}$]
COD_0 - initial concentration of COD in wastewater [$mg.l^{-1}$]
k_0, k_1, k_2 - the rate constants for the kinetics of 0, the 1. and the 2. order [$mg.l^{-1}.h^{-1}$]

Parameter values of applied kinetic models were calculated by grid search optimisation procedure. The residual sum of squares between the observed values and the values given by the model, divided by its number of degrees of freedom ν (the number of observations less the number of parameters estimated) was used as an objective function. The rate constants and values of correlation coefficient are given in Table 1.

The best description of COD removal during ozonation of MBT was achieved by the zero order reaction kinetic models (Fig. 2).

Table 1. Kinetic parameters and statistical characteristics values

n	k_n^*	R^2_{YX}
0	315.76 $g.m^{-3}.h^{-1}$	0.9605
1	0.27 h^{-1}	0.9435
2	$2.20.10^{-4}$ $g^{-1}.m^3.h^{-1}$	0.8699

The time dependence of ln (COD/COD_i) is displayed on Figure 2. From this behaviour results, that organics is removed from the synthetic wastewater during ozonation in three stages by kinetics of the 1. order. Different oxidation speed is characteristic for each stage, the second stage of MBT oxidation is the earliest stage, 530 $mg.l^{-1}.h^{-1}$. Higher resistance of the second stage's by-products to ozonation is probably the reason of the decrease of the oxidation speed during third stage (109 $mg.l^{-1}.h^{-1}$). During ozonation the average specific consumption of ozone (adsorbed amount) to removal of unit amount of COD was 2.42 $mg.g^{-1}$ ($\Delta O_3/\Delta COD$).

Respirometric measurements with activated sludge cultivated in lab-scale activated sludge model operated at 5 days of solid retention time were performed. The aim was to study the influence of intermediate products resulted from controlled ozonation of MBT on the activated sludge respiration activity.

The values of specific exogenous respiration rate and relative exogenous respiration rate are given in Table 2. The values of relative exogenous respiration rate were calculated by the following calculation formula:

$$r = r_{X,ox}/r_{X,end} \quad (4)$$

BOD_5 measurements were also applied to evaluate biodegradability of MBT oxidation products.

Experimental values of COD, BOD_5, specific exogenous respiration rate and relative exogenous respiration rate are presented in Table 2. As it can be seen from Table 2, the values of the specific exogenous respiration rate increased with ozonation time. The about same values of COD ratio were in respirometric cell. The difference between the values of specific exogenous respiration rate at the beginning of ozonation and after 6 hours of ozonation was 32.3 $mg.g^{-1}.h^{-1}$.

Table 2. Monitoring of changes in the biodegradability of MBT during the ozonation

Time of ozonation	COD [$mg.l^{-1}$]	BOD_5 [$mg.l^{-1}$]	$r_{X,ox}$ [$mg.g^{-1}.h^{-1}$]	$r_{X,ox}/r_{X,end}$
0	14.5	0.0	0.20	0.02
1	14.5	-	3.40	0.20
2	14.9	2.3	17.40	0.60
3	14.9	-	19.00	0.50
4	15.0	4.2	19.30	0.80
5	15.0	-	30.60	1.40
6	15.0	6.8	32.50	0.90

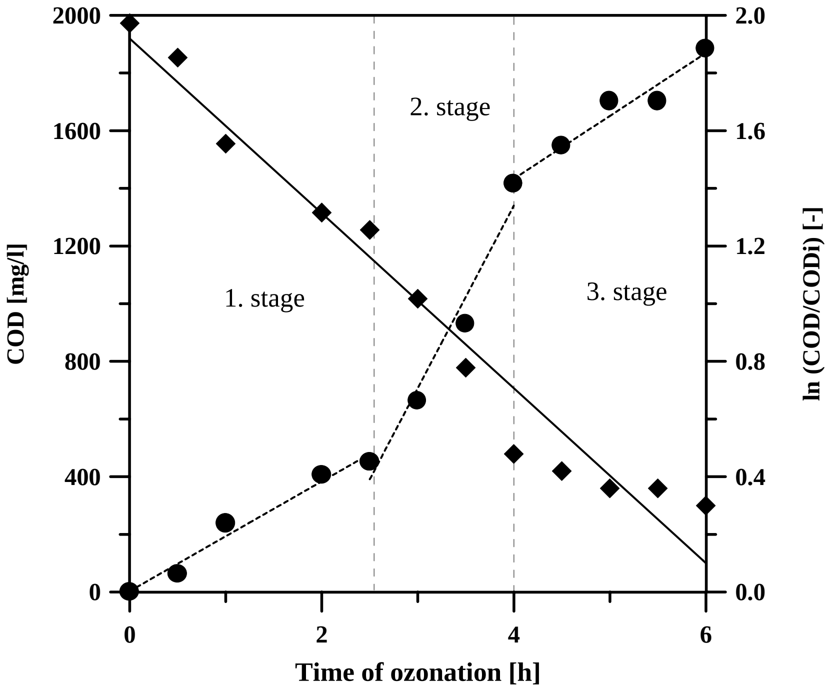

Figure 2. Experimental (♦) and calculated (solid line) time dependencies of COD during ozonation

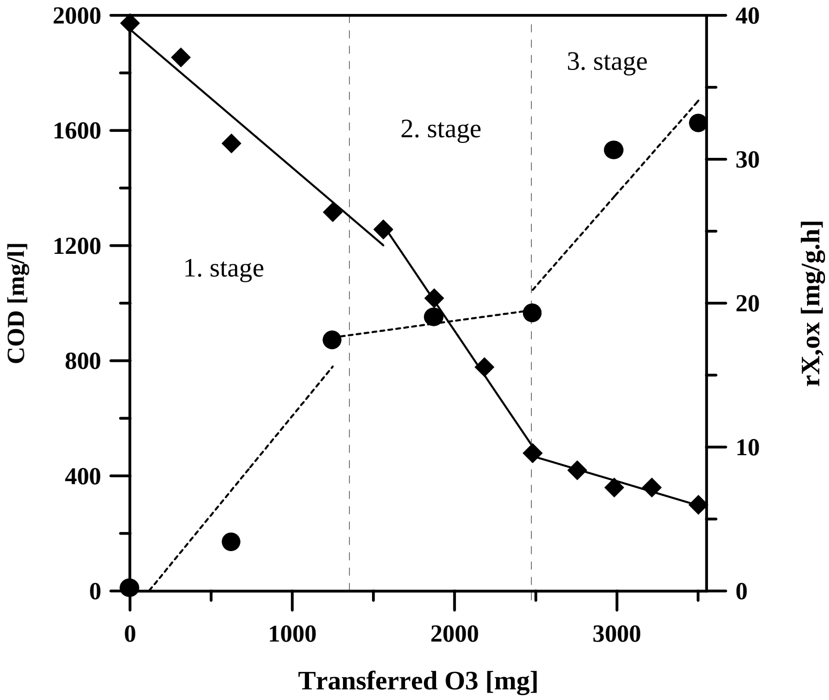

Figure 3. Modification of respiration activity of activated sludge (●) during ozonation of MBT solution in comparison with decrease of COD values (♦)

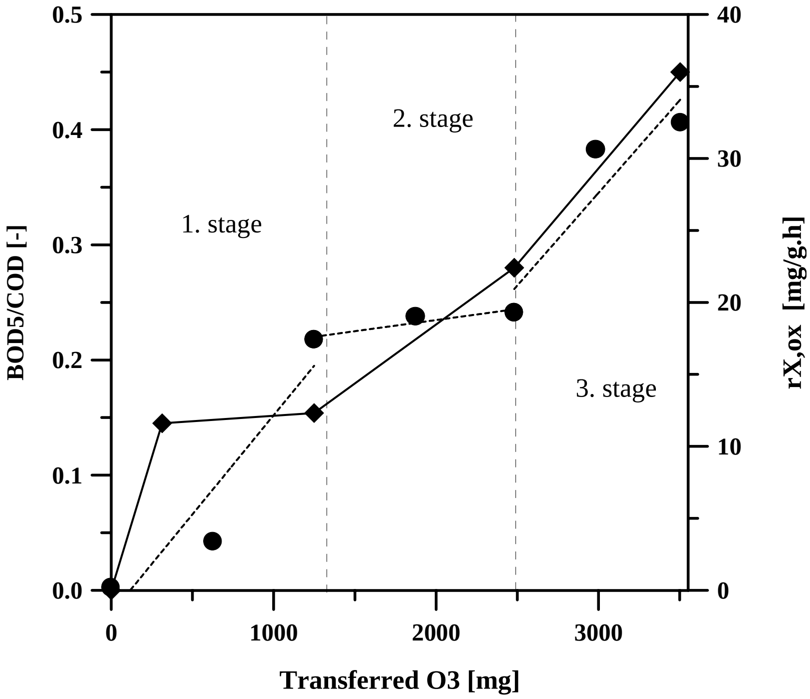

Figure 4. Relation of BOD_5/COD (♦) and specific exogenous respiration rate (●) from transferred O_3 during MBT ozonation

Increased biodegradability (BOD_5 values) during ozonation of synthetic wastewater was observed. The values of both indicators of biodegradation, i.e. specific exogenous respiration rate and BOD_5/COD ratio increased during 6 hours of ozonation (Fig. 4). Similarly to decrease of COD values during the ozonation also three stages in changes of immediate biodegradation of ozonation products were observed (Fig. 3 and 4). Unlike behaviour of COD decreasing the highest values of specific exogenous respiration rate were measured in the first and the third stages of MBT ozonation.

Conclusion

Ozonation treatment of synthetic wastewater with the content of 2-mercaptobenzothiazole was studied.

COD removal efficiency about 85 % was achieved after 6 hours of ozonation of the synthetic wastewater.

The zero order reaction kinetic model achieved the best description of experimental COD data. Organics were removed from the synthetic wastewater during ozonation in three stages by the 1. order kinetics.

Increased biodegradability during ozonation of synthetic wastewater was observed. The values of both indicators of biodegradation, specific exogenous respiration rate and BOD_5/COD ratio increased during 6 hours of ozonation.

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