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## ADVANCED OXIDATION OF SOLUTIONS CONTAINING FORMALDEHYDE PART 2. CATALYTIC OZONATION

The combined effect of ozonation and catalysts on the oxidation of aqueous solutions of formaldehyde was investigated. The catalysts tested were oxides of transition metals: NiO, CuO, TiO<sub>2</sub>, WO<sub>3</sub>, CoO<sub>2</sub>, V<sub>2</sub>O<sub>5</sub>, MnO<sub>2</sub> and MoO<sub>3</sub>. Of all the catalysts tested only MnO<sub>2</sub> and MoO<sub>3</sub> showed catalytic activity. The effects of a catalyst dose, pH of the medium and the ratio of the catalysts on the effectiveness of the process were examined. It was observed that catalytic ozonation increased the yield of the oxidation process at both working acid and alkaline reactions. The efficiency of catalytic ozonation increased with an increase in the dose of the catalyst. At pH 10 the results obtained showed that an increase in the ratio of MnO<sub>2</sub> to MoO<sub>3</sub> resulted in an increase in the process effectiveness. The effectiveness of catalytic ozonation of formaldehyde was compared with the effectiveness of ozonation alone under the same operating conditions. It was found that at pH 10 the effect of the catalyst on the degree of conversion of formaldehyde led to an increase in the degree of conversion from 28% to 88% at the end of the process. At pH 3.5 an increase in the degree of conversion at the end of the process ranged from 58% to 85%. A comparison of the COD reduction for catalytic ozonation and ozonation alone under the same operating conditions suggests that catalytic ozonation is a more effective method for formaldehyde removal from its aqueous solutions.

### 1. INTRODUCTION

In the first part of our paper [13], we described the application of AOTs, namely ozone combined with hydrogen peroxide, in the removal of formaldehyde from model aqueous solutions. Another alternative treatment is catalytic ozonation, which combines the action of ozone with the absorptive and oxidative properties of solid phase [2] which results in a more powerful degradation of organic-inorganic content.

#### 1.1. OZONE APPLICATIONS

Ozone oxidation has been widely employed for treating wastewaters from electroplating, textile, pulp and paper and petroleum industries [1]. Ozone reacts in aqueous

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solutions with various organic and inorganic compounds, either by direct reaction of molecular ozone or through a radical type reaction involving the hydroxyl radical induced by the ozone decomposition in water. The advantages of ozone oxidation process are the ability to apply ozone directly in the gaseous phase and a short reaction time of the ozone with effluent. Ozone application neither increases the effluent volume nor results in sludge formation. In addition, ozone reacts preferably with refractory substances. The disadvantages of ozone oxidation include a relatively high energy cost of producing ozone and insignificant TOC (total organic carbon) reduction. Ozonation alone has been shown to bring about a limited reduction in COD (chemical oxygen demand) in industrial effluent. Consequently, advanced oxidation processes have been investigated as potential methods for degradation of organic compounds.

### 1.2. CATALYTIC OZONATION

Recently, alternative ozonation processes catalysed by transition metals have been investigated for degradation of organics. Investigations conducted by HEWES and DAVINSON [3] have shown an increase of TOC removal in the presence of iron(II), manganese(III), nickel or cobaltous sulphates compared to ozonation alone. GRASIA et al. [4], [5] reported a significant reduction in the content of humic substances in the presence of manganese and silver. More recent investigations by ABDO et al. [6] showed the effect of the catalyst in the form of metal salts on ozonation of dye effluent. ANDREOZZI et al. [7] reported an improvement of oxilic acid ozonation at acidic reaction induced by the presence of  $MnO_2$ . NAYDENOV and MEHANDJIEV [8] observed mineralization of benzene obtained by its ozonation in the presence of  $MnO_2$ . AL-HAYEK et al. [9] have shown that ozonation of phenol in the presence of the  $Fe(III)-Al_2O_3$  catalyst leads to a significant increase of the TOC removal compared to ozonation alone. The authors suggested either the formation of free radicals or an increase of nucleophilic sites of adsorbed molecules.

In our previous work [10], the results for catalytic ozonation of reactive dye Blue-1 were reported. It was established that catalytic ozonation yielded a significant improvement in dye removal.

This paper discusses the combined effect of ozonation in the presence of catalysts, i.e. oxides of transition metals on the removal of formaldehyde from aqueous model solutions, compared to ozonation alone.

## 2. MATERIALS AND METHODS

The experiments were carried out using model solutions of formaldehyde (FA) with initial concentration of  $100 \text{ mg}\cdot\text{dm}^{-3}$  at  $20^\circ\text{C}$ . The working pH values were 3.5 and 10. The pH of the samples was adjusted to the desired value by the addition of either sulfuric acid or sodium hydroxide to the medium. The concentration of formaldehyde before and during the ozonation was determined spectrophotometrically. The

determination was based on the reaction of formaldehyde with chromotropic acid, which leads to the formation of a coloured compound. The absorbance maximum of the product obtained was at  $\lambda_{\text{max}} = 575$  nm. The absorbance was measured with a Perkin-Elmer  $\lambda$  uv/vis. The relative standard deviation of the method is  $\pm 6\%$ .

Ozone was produced with a laboratory ozonizer described elsewhere [11]. The ozone concentration acquired from the generator was  $5 \text{ mg}\cdot\text{dm}^{-3}$ . The pre-treatment of the air for ozonation consisted in passing it through silicagel. A constant ozone-air flow was applied to the solution of the volume of  $0.05 \text{ dm}^3$  through a porous glass plate of  $20\text{--}30 \mu\text{m}$  pore diameter. All the experiments were carried out at the ozone-air rate of  $20 \text{ cm}^{-3}\cdot\text{min}^{-1}$ . In catalytic ozonation experiment, a catalyst comes into contact only with the solution containing dissolved ozone and formaldehyde. The catalysts tested were oxides of transition metals: NiO, CuO, TiO<sub>2</sub>, WO<sub>3</sub>, CoO<sub>2</sub>, V<sub>2</sub>O<sub>5</sub>, MnO<sub>2</sub> and MoO<sub>3</sub>. These catalysts have been chosen because, on the one hand, there is no information about formaldehyde oxidation with ozone in their presence and, on the other hand, it is known that they are active in the oxidation with molecular oxygen. Catalysts were added to ozonated solution and stirred permanently. The dose of the catalyst applied to solution ranged between  $3 \text{ g}\cdot\text{dm}^{-3}$  and  $18 \text{ g}\cdot\text{dm}^{-3}$ . The dose of ozone was determined iodometrically in a liquid phase [12]. The effectiveness of the process was estimated based on the degree of conversion  $\alpha$  [%] calculated from the formula:

$$100 \cdot (C_0 - C)/C_0,$$

where  $C_0$  and  $C$  are the initial and current concentrations of formaldehyde, respectively.

### 3. RESULTS AND DISCUSSION

pH is an important operating parameter influencing significantly the treatment performance of the ozonation process, affecting ozone decomposition to the highly reactive free radicals  $\text{OH}^\bullet$ . For testing the ability of the selected catalyst to enhance the efficiency of ozone oxidation at different pH, the effect of pH on the medium was studied. In the presence of catalyst (metal ions), the ozone decomposition was initiated according to radical chain mechanism [14]. For an  $\text{OH}^\bullet$  radical chain to occur requires both (1) an initiator that transfers an electron to  $\text{O}_3$ , producing ozonide anion  $\text{O}_3^-$  and eventually  $\text{OH}^\bullet$  radicals and (2) a promoter that converts  $\text{OH}^\bullet$  to  $\text{O}_2^-$ , which selectively reacts with  $\text{O}_3$  to form ozonide anion  $\text{O}_3^-$ . This anion is immediately broken down into  $\text{OH}^\bullet$  radicals. Consequently, it is interesting to investigate the effect of pH on the ozonation in the presence of the catalyst. The working pH values were the same as these reported in the first part of our paper on the oxidation of model solution of formaldehyde [13]. At pH 3.5 of all the catalyst tested only MnO<sub>2</sub> and MoO<sub>3</sub> showed catalytic activity. The results obtained in the case catalytic ozona-

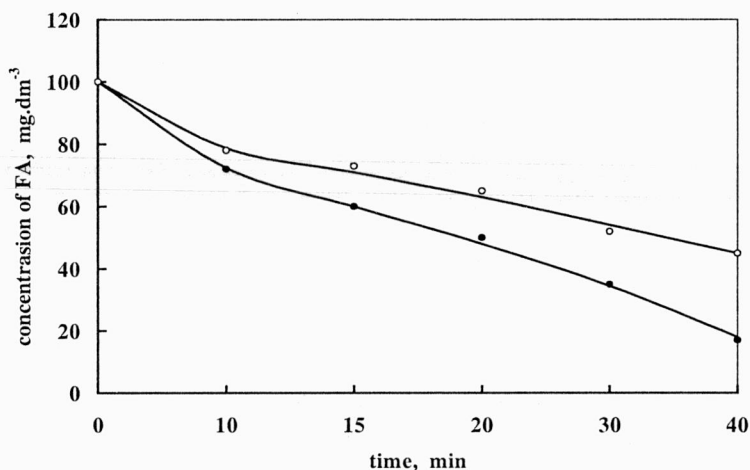


Fig. 1. Concentration of formaldehyde in the solutions tested versus time of catalytic ozonation: pH 3.5; the dose of the catalysts,  $12 \text{ g}\cdot\text{dm}^{-3}$ ; -●-  $\text{MnO}_2$ ; -○-  $\text{MoO}_3$

tion of formaldehyde at pH 3.5 are shown in figure 1. It can be seen that under the same experimental conditions  $\text{MnO}_2$  is more active than  $\text{MoO}_3$ . The effect of all selected catalysts on the formaldehyde degradation was tested at pH 10. In this case, the effect of  $\text{MnO}_2$  was lesser than the effect of  $\text{MoO}_3$  at pH 3.5, and the other catalysts showed no effect, but the mixture of  $\text{MnO}_2$  and  $\text{MoO}_3$  in the proportion 1:1 showed some catalytic activity. Figure 2 presents the results of catalytic ozonation at pH 10 in

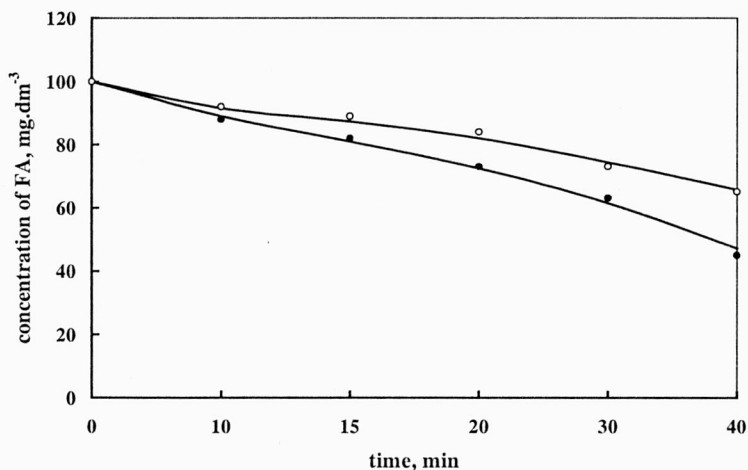


Fig. 2. Concentration of formaldehyde in the solutions tested versus time of catalytic ozonation: pH 10; catalysts: -●-  $\text{MnO}_2$ ,  $12 \text{ g}\cdot\text{dm}^{-3}$ ; -○-  $\text{MnO}_2$ :  $\text{MoO}_3$ ,  $6 \text{ g}\cdot\text{dm}^{-3}$ :  $6 \text{ g}\cdot\text{dm}^{-3}$

the presence of catalyst  $\text{MnO}_2$  and the mixture of  $\text{MnO}_2$  and  $\text{MoO}_3$  in the proportion one to one. The results obtained for catalytic ozonation of formaldehyde at two different pH values indicate that formaldehyde can be degraded in the presence of only two metal oxides:  $\text{MnO}_2$ ,  $\text{MoO}_3$  and their mixture. In order to find out conditions for the complete degradation of formaldehyde at pH 3.5, the dose of the selected catalysts was varied in the range from  $3 \text{ g}\cdot\text{dm}^{-3}$  to  $18 \text{ g}\cdot\text{dm}^{-3}$ . Figure 3 illustrates the degradation of formaldehyde at pH 3.5 in the presence of different doses of the catalysts. The

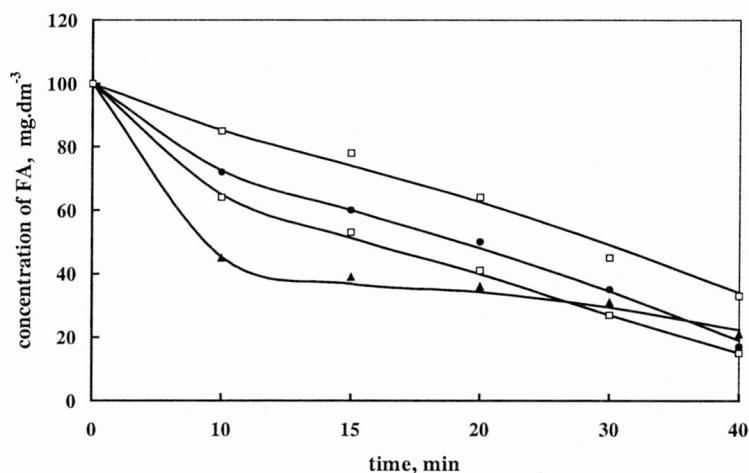


Fig. 3. Effect of the dose of the catalyst on catalytic ozonation at pH 3.5:

-▲-  $\text{MoO}_3$ ,  $3 \text{ g}\cdot\text{dm}^{-3}$ ; -◻-  $\text{MoO}_3$ ,  $6 \text{ g}\cdot\text{dm}^{-3}$ ; -●-  $\text{MnO}_2$ ,  $12 \text{ g}\cdot\text{dm}^{-3}$ ; -◻-  $\text{MnO}_2$ ,  $18 \text{ g}\cdot\text{dm}^{-3}$

highest degree of conversion at pH 3.5 was achieved for catalytic ozonation with  $18 \text{ g}\cdot\text{dm}^{-3}$   $\text{MnO}_2$ . The dose of  $\text{MoO}_3$  used was smaller than that of  $\text{MnO}_2$  because at the dose exceeding  $6 \text{ g}\cdot\text{dm}^{-3}$   $\text{MoO}_3$  showed no catalytic activity. As previously mentioned at pH 10 the mixture of  $\text{MnO}_2$  and  $\text{MoO}_3$  in the proportion one to one shows a relatively weak catalytic activity. In order to find out the influence of the proportion of the two oxides on the catalytic activity of the mixture, some experiments were carried out with increased quantity of  $\text{MnO}_2$ . The kinetic curves at pH 10 for different proportions of the catalysts are shown in figure 4. The results obtained showed that with an increase in the ratio of  $\text{MnO}_2$  to  $\text{MoO}_3$  the effectiveness of the process raises. The effectiveness of catalytic ozonation in the removal of formaldehyde from its aqueous solutions was compared with the effectiveness of ozonation alone. The achieved values of the degree of conversion for catalytic ozonation and ozonation at pH 3.5 and pH 10 are presented in figures 5 and 6. It can be seen that at both pH values catalytic ozonation increases the yield of the oxidation process. For pH 10 the combined effect of ozone and catalyst on the degree of conversion of formaldehyde is considerable.

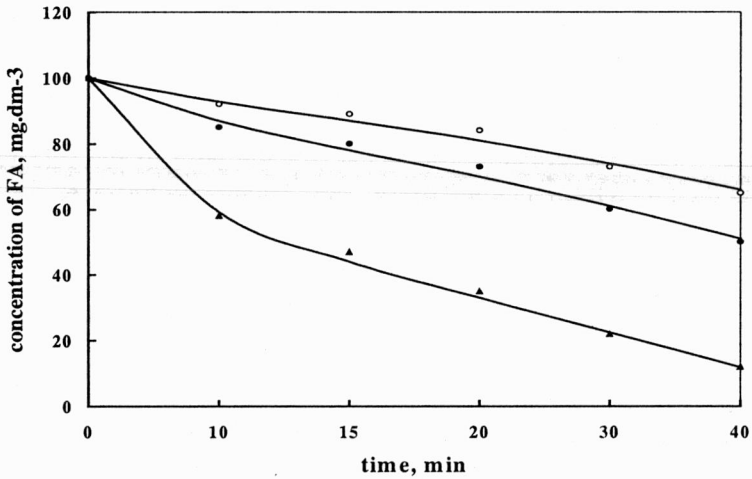


Fig. 4. Catalytic ozonation at pH 10 – effect of the  $\text{MnO}_2$  to  $\text{MoO}_3$  ratio:  
 -○- 1; -●- 2; -▲- 5 ( $6 \text{ g-dm}^{-3} \text{ MnO}_2$ ;  $6 \text{ g-dm}^{-3} \text{ MoO}_3$ ;  
 $8 \text{ g-dm}^{-3} \text{ MnO}_2$ ;  $4 \text{ g-dm}^{-3} \text{ MoO}_3$ ;  $10 \text{ g-dm}^{-3} \text{ MnO}_2$ ;  $2 \text{ g-dm}^{-3} \text{ MoO}_3$ , respectively)

In this case, the degree of conversion increases from 28% to 88% at the end of the process. For pH 3.5 an increase in the degree of conversion at the end of the process ranges from 58% to 85%.

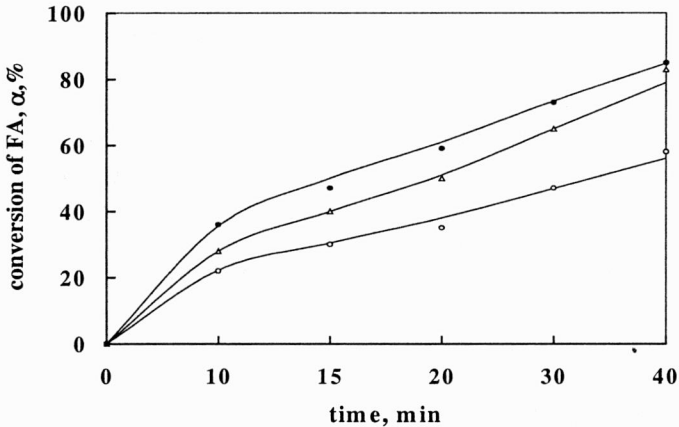


Fig. 5. Efficiency of catalytic ozonation compared to efficiency of ozonation alone:  
 pH 3.5;  $\text{MnO}_2$  catalyst; -▲- catalytic ozonation,  $12 \text{ g-dm}^{-3}$ ;  
 -●- catalytic ozonation,  $18 \text{ g-dm}^{-3}$ ; -○- ozonation

The effectiveness of catalytic ozonation compared to ozonation alone could be confirmed by the COD reductions in presence of the catalyst. For this purpose COD

reductions during ozonation alone and catalytic ozonation at the two working pH values were compared. The results obtained are shown in figure 7. The COD reductions at the end of the process equal 40% for ozonation alone, 69% for catalytic ozonation at pH 3.5 and 72% for catalytic ozonation at pH 10.

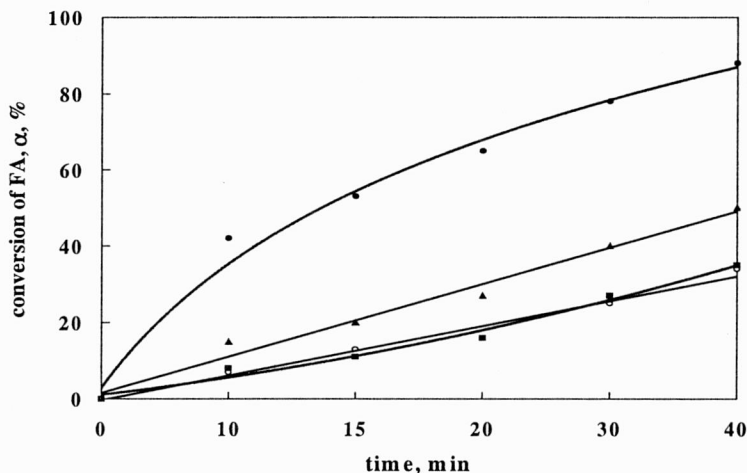


Fig. 6. Efficiency of catalytic ozonation compared to efficiency of ozonation alone: pH 10; catalytic ozonation, -■- MnO<sub>2</sub> to MoO<sub>3</sub> ratio 1; -▲- MnO<sub>2</sub> to MoO<sub>3</sub> ratio 2; -●- MnO<sub>2</sub> to MoO<sub>3</sub> ratio 5; -○- ozonation

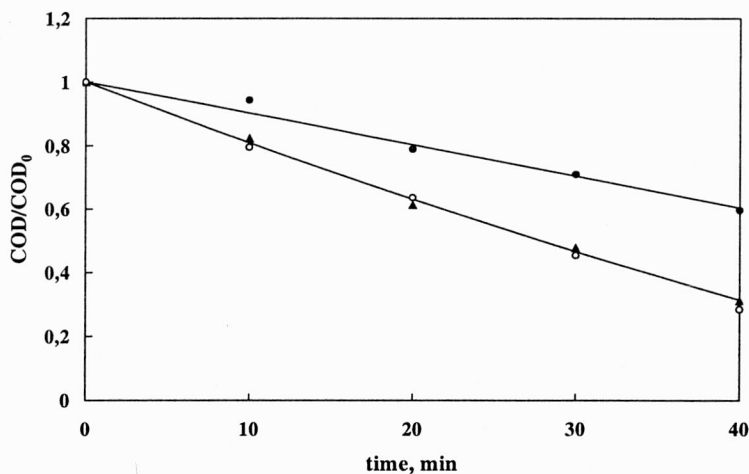


Fig. 7. COD elimination for ozonation and catalytic ozonation: COD<sub>0</sub> = 176 mg O<sub>2</sub>·dm<sup>-3</sup>; -●- ozonation; -▲- catalytic ozonation at pH 3.5 (MnO<sub>2</sub> - 18 g·dm<sup>-3</sup>); -○- catalytic ozonation at pH 10 (MnO<sub>2</sub> : MoO<sub>3</sub> - 5 : 1)

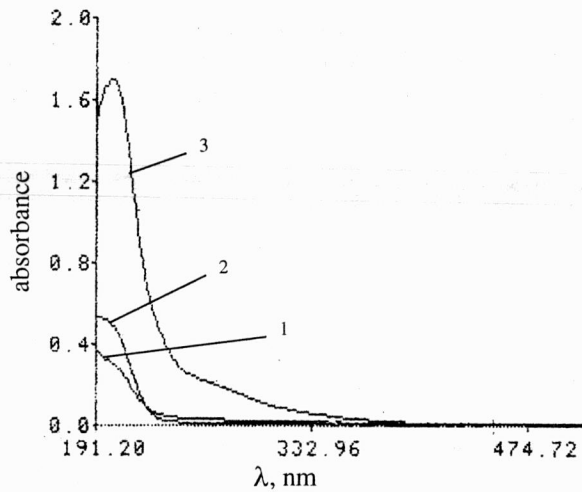


Fig. 8. UV spectra of: 1 – unoxidized formaldehyde; 2 – formaldehyde ozonated for 15 min at pH 3.5; 3 – formaldehyde after catalytic ozonation for 15 min at pH 3.5 ( $\text{MnO}_2 - 18 \text{ g}\cdot\text{dm}^{-3}$ )

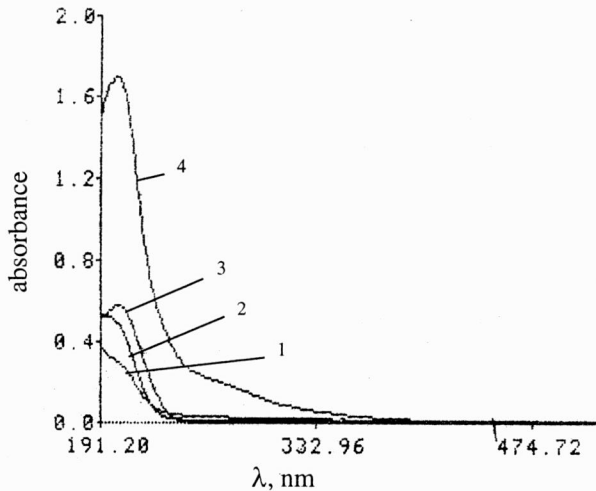


Fig. 9. UV spectra of: 1 – unoxidized formaldehyde; 2 – formaldehyde ozonated for 15 min at pH 3.5; 3 – reference compound (formic acid); 4 – formaldehyde after catalytic ozonation for 15 min at pH 3.5 ( $\text{MnO}_2 - 18 \text{ g}\cdot\text{dm}^{-3}$ )

Typically, ozonation rarely produces complete mineralization to  $\text{CO}_2$  and  $\text{H}_2\text{O}_2$ , but leads to partial oxidation products as organic acids, aldehydes and ketones [15]. In [13], we identified formic acid as by-product of formaldehyde ozonation in the presence of hydrogen peroxide. In order to compare the oxidation process enhanced by



hydrogen peroxide to that enhanced by catalysts and the by-product formed, the absorption spectra of formaldehyde ozonated in the presence of catalyst were recorded. Figure 8 presents the absorption spectra of non-oxidized formaldehyde, formaldehyde ozonated at pH 3.5 and formaldehyde ozonated in the presence of  $\text{MnO}_2$  at the same pH. It can be seen that catalytic ozonation increases formaldehyde degradation compared to ozonation alone under the same experimental conditions. The same spectra were recorded in the presence of a reference compound, i.e. formic acid (figure 9). On comparing the absorbance of the by-product obtained with that of the reference compound it is evident that catalytic ozonation of formaldehyde runs through by-product (formic acid).

#### 4. CONCLUSIONS

The results of the present study as well as the results of Part 1 of this paper clearly reveal that oxidation of aqueous solutions for formaldehyde abatement is more effective when oxidative power of ozone is combined with ozone decomposers, which produce the highly reactive  $\text{OH}^\bullet$  radicals. In view of these experimental results it can be concluded that:

- The efficiency of catalytic ozonation of formaldehyde in the presence of  $\text{MnO}_2$  catalyst depends on pH of the medium. The degree of formaldehyde conversion at pH 3.5 in the presence of 600 mg of  $\text{MnO}_2$  is 83% compared to 55% at pH 10 for the same dose of the catalyst.
- The effectiveness of catalytic ozonation at pH 3.5 in the presence of  $\text{MnO}_2$  increases with an increase in the dose of the catalyst.
- From the results obtained for catalytic ozonation at pH 10 it can be concluded that with an increase in the ratio of  $\text{MnO}_2$  to  $\text{MoO}_3$  the effectiveness of the process raises.
- COD reduction obtained due to catalytic ozonation suggests an improvement of formaldehyde degradation.
- Catalytic ozonation of formaldehyde as well as its ozonation in the presence of  $\text{H}_2\text{O}_2$  produce by-product, i.e. formic acid.

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## ZAAWANSOWANE UTLENIANIE ROZTWORÓW ZAWIERAJĄCYCH FORMALDEHYD CZĘŚĆ 2. OZONOWANIE KATALITYCZNE

Zbadano łączny wpływ ozonowania i katalizatorów na proces utleniania wodnych roztworów formaldehydu. Testowanymi katalizatorami były tlenki metali przejściowych: NiO, CuO, TiO<sub>2</sub>, WO<sub>3</sub>, CoO<sub>2</sub>, V<sub>2</sub>O<sub>5</sub>, MnO<sub>2</sub> i MoO<sub>3</sub>. Z przebadanych katalizatorów tylko MnO<sub>2</sub> i MoO<sub>3</sub> wykazały aktywność katalityczną. Przeanalizowano wpływ dawki, pH roztworów oraz proporcji katalizatorów na efektywność procesu. Zaobserwowano, że katalityczne ozonowanie zwiększa skuteczność utleniania zarówno w środowisku kwaśnym, jak i alkalicznym. Stwierdzono, że skuteczność katalitycznego ozonowania zwiększa się wraz ze wzrostem dawki katalizatora. Badania wykazały, że przy pH 10 zwiększenie stosunku MnO<sub>2</sub> do MoO<sub>3</sub> powoduje zwiększenie efektywności procesu. Porównano efektywność katalitycznego ozonowania formaldehydu z efektywnością ozonowania w tych samych warunkach. Stwierdzono, że przy pH 10 katalizator powoduje zwiększenie stopnia konwersji formaldehydu z 28% do 88%, a przy pH 3,5 – z 58% do 85%. Porównanie stopnia obniżenia ChZT wskazuje, że ozonowanie katalityczne jest bardziej skuteczną metodą usuwania formaldehydu z wodnych roztworów niż ozonowanie.