Environment Protection Engineering

Vol. 30 2004 No. 3

Z. PARISHEVA*, L. NUSHEVA*, P. LICHEVA*

COMPARISON OF THE EFFECT OF OZONE, OZONE–HYDROGEN PEROXIDE SYSTEM AND CATALYTIC OZONATION ON FORMALDEHYDE REMOVAL FROM AQUEOUS MODEL SOLUTIONS

The effect of three oxidizing systems, i.e. ozone, ozone–H_2O_2 and catalytic ozonation in the presence of MnO_2 and MoO_3, on formaldehyde removal from aqueous solutions has been investigated. The effectiveness of the process has been estimated based on the degree of formaldehyde conversion. The influence of pH, the amount of hydrogen peroxide and catalysts and the effect of the proportion of the catalysts on the effectiveness of the process have been examined. It has been established that hydrogen peroxide and catalysts are able to enhance the ozone capability of oxidizing aqueous solutions of formaldehyde. An increase in the reactivity of the ozone–H_2O_2 system at pH 3.5 and pH 10 was higher than that in catalytic ozonation under the same experimental conditions. The highest degree of conversion for catalytic ozonation was achieved at pH 10 and at the ratio of MnO_2 to MnO_3 equal to 5.

1. INTRODUCTION

Ozone oxidation is widely employed for the removal of water pollutants of different nature [1]. Ozonation of organic compounds in water usually produces organic products that are more biodegradable [2]. Ozone is often applied prior to a biological granular activated carbon filter to improve the removal of organic materials and chemical pollutants [3]. However, some compounds are only partially oxidized by ozone or are refractory. Consequently, the combined action of ozone and systems capable of enhancing its reactivity should be considered. Advanced oxidation processes make use of ozone decomposers like hydrogen peroxide, UV radiation and catalysts to promote radical chain mechanism, thus allowing the destruction of even more stable organic pollutants [4]. Ozonation combined with hydrogen peroxide or UV radiation was investigated by BELTRAN et al. [5]. It has been proved that the reactivity of the wasterwaters towards the oxidation system applied improved significantly. BALCIOGLY and ARSIAN [6] studied

* Department of Chemistry, Technical University of Plovdiv, 8 Dustabanov St., Plovdiv, 4000, Bulgaria.

oxidation of reactive dyestuff with ozone and O_3–H_2O_2 system. They found a considerable improvement in COD (chemical oxygen demand) and colour removal rates at pH 11. The efficiency of ozonation could be improved by catalysts, which are able to initiate the chain of ozone decomposition. Many researches were led to further improvement of the efficiency of ozonation process catalysed by transition metals. ANDREOZZI et al. [7] found that Mn(II) accelerates the oxidation of oxalic acid in acidic medium. According to PINES et al. [9] the combination of O_3–metal–TiO_2 is particularly interesting in the oxidation of hydrophilic compounds. Studying fulvic acid oxidation with ozone, O_3–H_2O_2 and O_3–TiO_2, VOLK et al. [8] found that catalytic ozonation resulted in a smaller amount of BDOC (biodegradable dissolved organic carbon) than the other two processes and deduced that carbolic acids (ozonation by-products) could be oxidized preferably in catalytic ozonation.

In our previous works [13], [14], we investigated the influence of hydrogen peroxide and catalysts on the effectiveness of formaldehyde degradation by ozonation.

The present study compares the effect of three different oxidation processes: oxidation with ozone, catalytic ozonation and oxidation with ozone–H_2O_2 on formaldehyde removal from aqueous model solutions.

2. MATERIALS AND METHODS

The experiments were carried out using model solutions of formaldehyde (FA) with initial concentration of 100 mg·dm^{-3} at 20 °C. The working pH values were 3.5 and 10. The concentrations of formaldehyde before and during the ozonation were determined spectrophotometrically. The determination was based on the reaction of formaldehyde with chromotropic acid, which leads to formation of a coloured compound. The absorbance maximum of the product obtained was at λ_{max} = 575 nm. The absorbance was measured with a Perkin-Elmer λ uv/vis. The relative standard deviation of the method is ±6%.

Two oxides of transition metals, MnO_2 and MoO_3, were the catalysts tested. They have been chosen because, on the one hand, there is no literature 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 and hydrogen peroxide with the concentration of 10^{-2} M and 10^{-1} M, respectively, were added to ozonated solution and stirred permanently. The amount of the catalyst applied to solution was between 6 g·dm^{-3} and 18 g·dm^{-3}. The effectiveness of the process was estimated by the degree of conversion α(%) calculated from the formula:

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

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

The experimental procedures were previously described in [12].

3. RESULTS AND DISCUSSION

Ozonation treatment of wasterwater for organic pollutants' abatement is more effective when oxidative power of ozone is combined with ozone decomposers, which produce the highly reactive $OH^{\bullet}$ radicals. These radicals are generated in the direct reaction of ozone with an ionic form of hydrogen peroxide, which initiates a radical mechanism [11]. Another way of generating $OH^{\bullet}$ radicals is initiating ozone decomposition by metal ions in the process of catalytic ozonation. The ozone–hydrogen peroxide system and catalytic ozonation in the presence of different transition metals increase the oxidation level of a wider spectrum of organic compound [10]. Consequently, it is interesting to compare the effect of these two advanced oxidation processes with ozonation alone under the same operating conditions. The oxidation effectiveness of the three oxidizing systems were assessed by monitoring the changes of the formaldehyde concentration in acid and alkaline media. Figure 1 presents the reduction in formaldehyde concentration at pH 3.5 for ozonation, O_3–H_2O_2 and catalytic

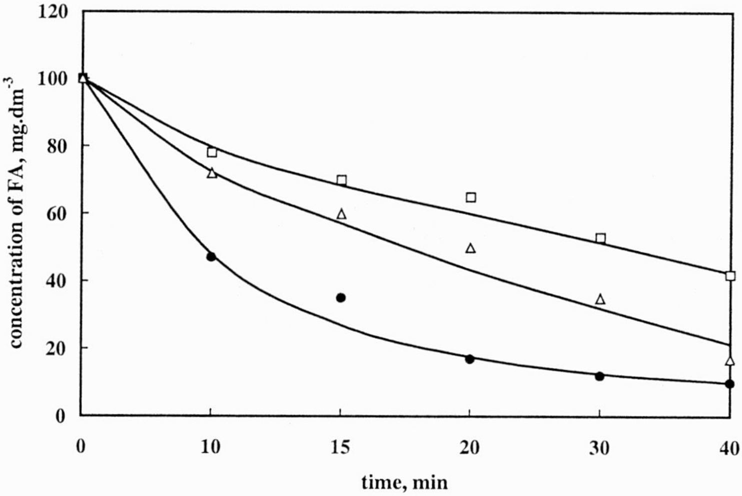

Fig. 1. Concentration of formaldehyde versus operation time for various oxidizing systems and pH 3.5: -□- O_3, alone; -Δ- catalytic ozonation–catalyst–MnO_2, 12 g·dm^{-3}; -●- O_3–H_2O_2, 10^{-2} M H_2O_2

ozonation at the presence of MnO_2. In order to assess the influence of the dose of the catalyst and hydrogen peroxide, the same experiment was carried out with increased doses of catalyst and hydrogen peroxide. The results obtained are shown in figure 2. In both cases, the effect of the hydrogen peroxide on formaldehyde elimination is higher than that of the catalyst. In our previous work [14], we observed that at pH 10 the effect of MnO_2 was lesser than at pH 3.5, and MoO_3 showed no effect, but the mixture of MnO_2 and MoO_3 in different proportion showed catalytic activity. The reduction in formaldehyde concentration at pH 10 is shown in figures 3 and 4. The results presented in figure 3 confirm a higher effectiveness of the O_3–H_2O_2 system. The catalytic activity of the mixture of MnO_2 and MoO_3 increased with an increase in the ratio of the two oxides [14]. The results in figure 4 indicate that the effect of the mixture of the two oxides, which corresponds to a ratio of 5, is similar to that of the hydrogen peroxide.

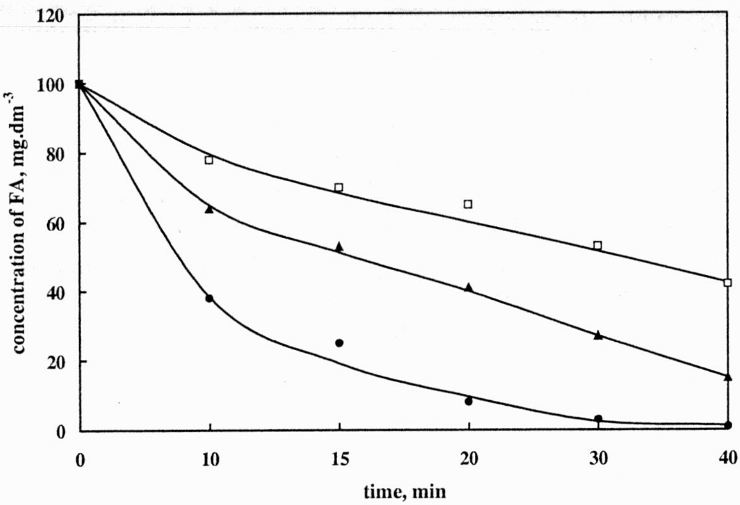

Fig. 2. Effect of the high doses of the catalyst and H_2O_2 on the reduction in formaldehyde concentration at pH 3.5:
-□- O_3, alone; -▲- catalytic ozonation–MnO_2 catalyst, 18 $g \cdot dm^{-3}$; -●- O_3–H_2O_2, 10^{-1} M H_2O_2

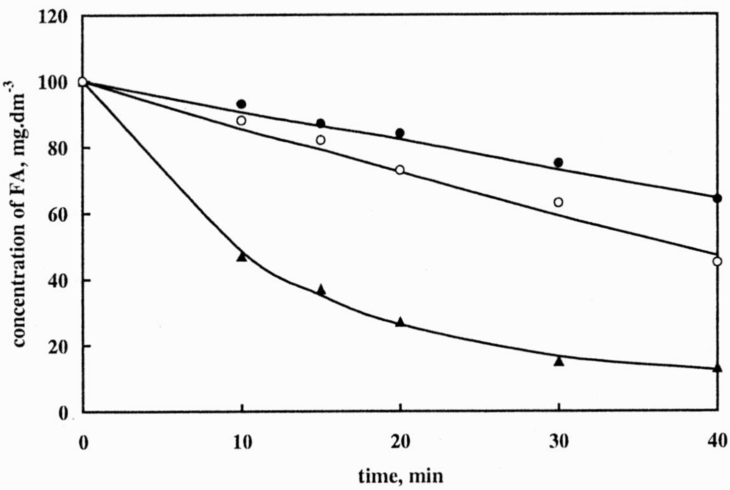

Fig. 3. Concentration of formaldehyde versus operation time for various concentrations of oxidizing systems at pH 10:
-●- O_3, alone; -○- catalytic ozonation–MnO_2 catalyst, 12 $g \cdot dm^{-3}$; -▲- O_3–H_2O_2, 10^{-2} M H_2O_2

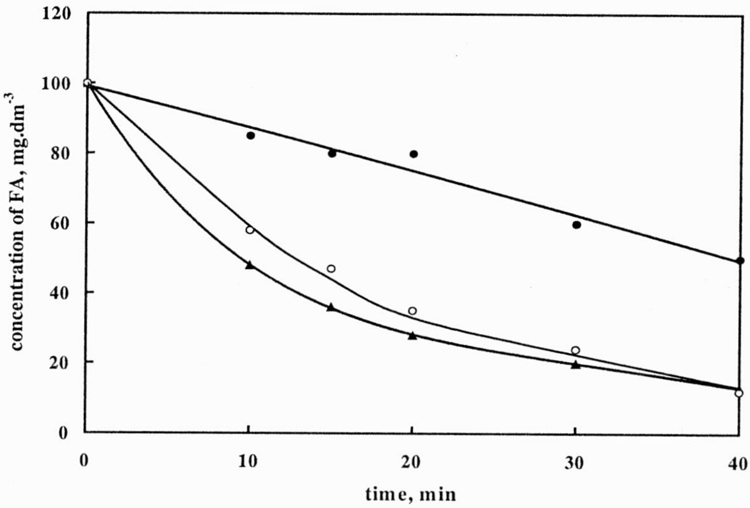

Fig. 4. Effect of the different proportions of catalysts on the reduction in formaldehyde concentration compared to the O_3–H_2O_2 system at pH 10:
-●- catalytic ozonation–MnO_2:MoO_3 catalysts (8 g:4 g);
-○- catalytic ozonation–MnO_2:MoO_3 catalysts (10 g:2 g); -▲- O_3–H_2O_2, 10^{-2} M H_2O_2

The achieved degrees of formaldehyde conversion in the three oxidizing systems are shown in the table. The comparison of the effect of these systems, i.e. ozone, ozone–hydrogen peroxide and catalytic ozonation, shows that combined effect of ozone and hydrogen peroxide or catalysts enhances the removal of formaldehyde from aqueous solutions.

Table

Comparison of the achieved degree of conversion α (%) for the three oxidizing systems

t (min)	pH 3.5					pH 10					
	O_3	O_3–MnO_2		O_3–H_2O_2		O_3	O_3–MnO_2:MoO_3			O_3–H_2O_2	
		12 g·dm^{-3}	18 g·dm^{-3}	10^{-2}M	10^{-1}M		1:1	4:2	5:1	10^{-2}M	10^{-1}M
10	22	28	36	54	62	7	8	15	42	52	56
15	30	40	47	66	75	13	11	20	53	64	70
20	35	50	59	84	92	16	14	20	65	72	78
30	47	65	73	88	97	25	27	40	76	78	88
40	58	83	85	90	99	28	34	50	88	87	89

4. CONCLUSIONS

On the basis of the results obtained it can be concluded that O_3–H_2O_2 and catalytic ozonation could improve formaldehyde degradation. The O_3–H_2O_2 system is effective in acid and alkaline media and the degrees of conversion when 10^{-1}M H_2O_2 is added are 99% for pH 3.5 and 89% for pH 10. The highest degree of conversion for catalytic ozonation corresponds to 18 g·dm^{-3} MnO_2 at pH 3.5 and the ratio of MnO_2 to MoO_3 of 5 (10 g:2 g per dm^{-3}) for pH 10.

REFERENCES

[1] RICE, *Application of ozone for industrial waster water treatment: a review*, Ozone Science Engineering, 1997, 18, 477.

[2] GILBERT E., *Biodegradability of ozonation products as a function of COD and DOC elimination by example of substituted aromatic substances*, Wat. Res., 1987, 21, 1273.

[3] LANGLAIS B., RECKHOW D., BRINK D., *Ozone in water treatment. Application and engineering*, AWWA Res. Found., Lewis Publisher, 1991, 569.

[4] GLAZE W., KANG J., *Evaluation the ozone-hydrogen peroxide process in a semi-batch reactor using tetrachloroethylene as a model compound*, Proceedings of the Ninth Ozone World Congress, New York, 1989, 596.

[5] BELTRAN F., ENCINAR J., GONZALES J., *Industrial waster water advanced oxidation*. Part 2. *Ozone combined with hydrogen peroxide or UV radiation*, Wat. Res., 1997, 31, 2415.

[6] BALCIOGLU I., ARSIAN I., *Partial oxidation of reactive dyestuff and synthetic textile dye bath by the O_3 and O_3/H_2O_2 processes*, Water Science and Technology, 2001, 43, 221.

[7] ANDREOZZI R., INSOLA A., CAPRIO V., MARROTA R., TUFANO V., *The use of manganese dioxide as a heterogeneous catalyst for oxalic ozonation in aqueous solutions*, App. Catal. A: General, 1996, 138, 75.

[8] VOLK C., ROCHE P., JORET J., PAILLARD H., *Comparison of the effect of ozone, ozone–hydrogen peroxide system and catalytic ozone on the biodegradable organic matter of a fulvic acid solution*, Wat. Res., 1997, 31, 650.

[9] PINES D., HUMAYAN R., RECKHOW D., SPANGEBERG C., *A catalytic ozonation process for removal of ozone by-products*, Water Quality Technology Conference, San Francisco, CA, U.S.A., November 1994, part II, 1493.

[10] HOIGNE J., BADER H., *The role of hydroxyl radical reactions in ozonation processes in aqueous solutions*, Wat. Res., 1976, 10, 377.

[11] STAEHELIN, HOIGNE J., *Decomposition of ozone in water in the presence of organic solutes acting as promoters and inhibitors of radical chain reactions*, Environ. Sci. Technol., 1985, 19, 1203.

[12] PARISHEVA Z., DEMIREV A., *Ozonation of ethanolamine in aqueous medium*, Wat. Res., 2000, 34, 1340.

[13] PARISHEVA Z., NUSHEVA L., DANOVA N., *Advanced oxidation of solutions containing formaldehyde.* Part 1. *Combined effect of ozone and hydrogen peroxide*, Environment Protection Engineering, 2003, Vol. 29, No. 3–4, pp. 5–14.

[14] PARISHEVA Z., NUSHEVA L., DANOVA N., *Advanced oxidation of solutions containing formaldehyde.* Part 2. *Catalytic ozonation*, Environment Protection Engineering, 2004, Vol. 30, No. 3, pp. 13–22.

PORÓWNANIE WPŁYWU OZONU, OZONU WRAZ Z NADTLENKIEM WODORU I KATALITYCZNEGO OZONOWANIA NA EFEKTYWNOŚĆ USUWANIA FORMALDEHYDU Z MODELOWYCH ROZTWORÓW WODNYCH

Zbadano wpływ trzech metod utleniania (ozonem, ozonem wraz z nadtlenkiem wodoru i za pomocą katalitycznego ozonowania w obecności MnO_2 i MoO_3) na efektywność usuwania formaldehydu z roztworów wodnych. Sprawność procesu oceniano na podstawie stopnia transformacji formaldehydu. Przeanalizowano wpływ odczynu oraz dawek nadtlenku wodoru i katalizatorów, a także proporcji katalizatorów na sprawność procesu. Stwierdzono, że nadtlenek wodoru i katalizatory zwiększają skuteczność utleniania ozonem formaldehydu w roztworach wodnych. Zwiększenie stopnia konwersji dla układu ozon–H_2O_2 przy pH 3,5 i pH 10 było większe niż wypadku katalitycznego ozonowania w tych samych warunkach doświadczalnych. Najwyższy stopień konwersji dla katalitycznego ozonowania został osiągnięty przy pH 10 i stosunku testowanych katalizatorów wynoszącym 5.