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ADVANCED OXIDATION OF SOLUTIONS CONTAINING FORMALDEHYDE PART 1. COMBINED EFFECT OF OZONE AND HYDROGEN PEROXIDE

Oxidation of model aqueous solutions of formaldehyde, which is a pollutant contained in numerous industrial wastewaters, was studied. The stringent legal requirements for the content of this toxic substance in wastewater require an appropriate method for its degradation. Oxidation with ozone combined with hydrogen peroxide, which is a more powerful method for degradation, has been studied. The influence of pH of the medium and temperature was investigated. It has been found that the effectiveness of oxidation estimated by the degree of conversion α [%] in the presence of hydrogen peroxide is higher compared to ozonation alone. For pH 3.5 and T = 293 K the degree of conversion at the end of the process in the presence of hydrogen peroxide increases to 99% compared to 58% for ozonation alone. The effectiveness of oxidation was observed to depend on hydrogen peroxide concentration and increased with its concentration. It has been proved that the oxidation process runs through formic acid as by-product, which is identified spectrophotometrically.

1. INTRODUCTION

Formaldehyde is a key precursor in the industrial manufacture of phenol-formaldehyde or urea-formaldehyde resins. Many industrial activities utilize formaldehyde in organic synthesis, such as synthesis of pentaerythritol, ethylene glycol, drugs and others. Therefore, effluents arising from these applications may contain significant amounts of formaldehyde.

Wastewaters from various manufactures, such as compounds in aqueous solutions, can be treated in different ways in order to improve biodegradability or reduce their organic and inorganic content. Advanced oxidation technologies (AOTs) are currently being studied as a practical way of achieving these objectives. Oxidation of wastewater with ozone combined with hydrogen peroxide or UV radiation was studied by BELTRAN

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et al. [1]–[3]. It was found that O_3/H_2O_2 adds to a significant increase in COD degradation rate. The effect of O_3/UV radiation on both COD and TOC disappearance was investigated. A combination of ozone and biological oxidation has been reported by GILBERT [4] to give positive results. It has been found that ozone pretreatment of non-biodegradable aromatic compounds leads to biodegradable products. GARRIDO et al. [5] investigated ozonation of wastewaters containing formaldehyde and observed that ozonation enhances biodegradability of the effluents. A method for converting formaldehyde to an easily biodegradable substance was reported by LOFTY et al. [8].

The aim of this paper is to examine the combined effect of ozone and hydrogen peroxide on the removal of formaldehyde from model aqueous solutions, compared to ozonation alone, and to confirm a synergistic effect between ozone and hydrogen peroxide.

2. MATERIALS AND METHODS

The experiments were carried out using aqueous model solutions of formaldehyde with initial concentration of 100 mg·dm^{-3}. The pH values were in the range of 3.5–10 and the selected working temperatures were T = 283 K and T = 293 K. The reaction time between 0 and 40 min was selected considering the fact that at all working pH values further increase of reaction time up to 60 min led to an insignificant decrease of formaldehyde concentration (about 2%). The concentration of formaldehyde before and during the ozonation was determined by spectrophotometry. 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 on a Perkin-Elmer λ UV/vis. The relative standard deviation of the method is ±6%. Ozone was obtained from a laboratory ozonizer described elsewhere [11]. The ozone concentration acquired from the generator was 5 mg·dm^{-3}. The pretreatment of the air for ozonation consisted in passing it through silicagel. The constant ozone–air flow was applied to the solution through a porous glass plate of 20–30 μm pore diameter. All the experiments were executed at ozone–air rate of 20 cm^3·min^{-1}. The amount of ozone was determined in liquid phase by iodometry [7]. The whole amount of hydrogen peroxide was added to the solution at the beginning of the process and stirred permanently. The effectiveness of ozonation was estimated by the degree of conversion α [%], which was calculated from the formula: 100 $(C_0 - C)/C_0$.

The rate constant k [min^{-1}] was calculated from the following first-order kinetic equation

$$k = \frac{1}{t} \ln \frac{C_0}{C}.$$

The activation energy of the process was calculated from the rate constant versus temperature relationship according to the Arrehenius equation:

$$E = \frac{RT_1T_2}{\Delta T} \ln \frac{k_1}{k_2},$$

where k_1 and k_2 are the rate constants for the selected working temperature.

3. RESULTS AND DISCUSSION

3.1. EFFECT OF pH AND TEMPERATURE

In order to find the optimum conditions for complete degradation of formaldehyde, the effect of the pH of the medium and the temperature was studied. The results showing the influence of pH are given in figure 1. It can be seen that the highest degree of conversion is achieved at pH 3.5 and T = 293 K, whereas at pH 8.5 and 10 the effectiveness of ozonation is lower, especially at the beginning of the process. This is probably due to the tendency of formaldehyde to polymerize in alkaline range, associating up to 6 molecules [9], which makes its degradation more difficult.

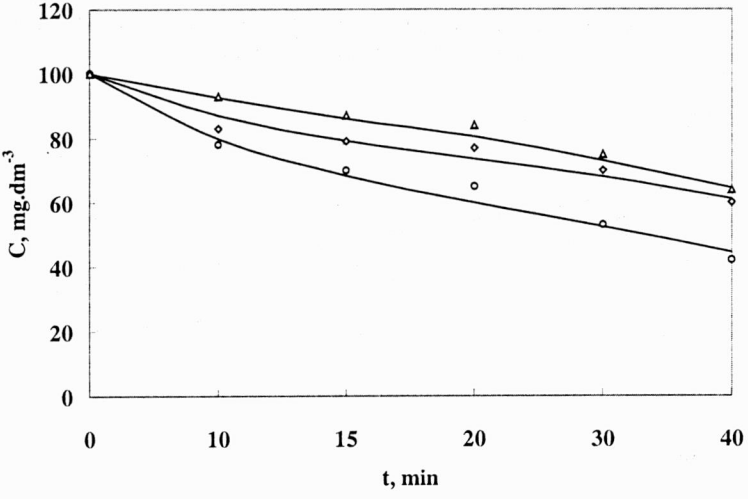

Fig. 1. The effect of the time of ozonation on formaldehyde concentration for different pH: T = 293 K; ○ pH 3.5; ◇ pH 8.5; △ pH 10

The effect of temperature on formaldehyde ozonation for pH 3.5 and pH 10 is presented in figures 2 and 3. For both pH values the degree of conversion achieved under the same conditions is higher at T = 283 K. This can be explained by an increased

solubility of ozone at lower temperatures, which brings about an increases of the amount of dissolved ozone. It can be observed that at pH 10 and time of treatment 20 min, the drop of temperature from 293 K to 283 K leads to a significant increase of the degree of conversion α from 16% to 38% (see the table).

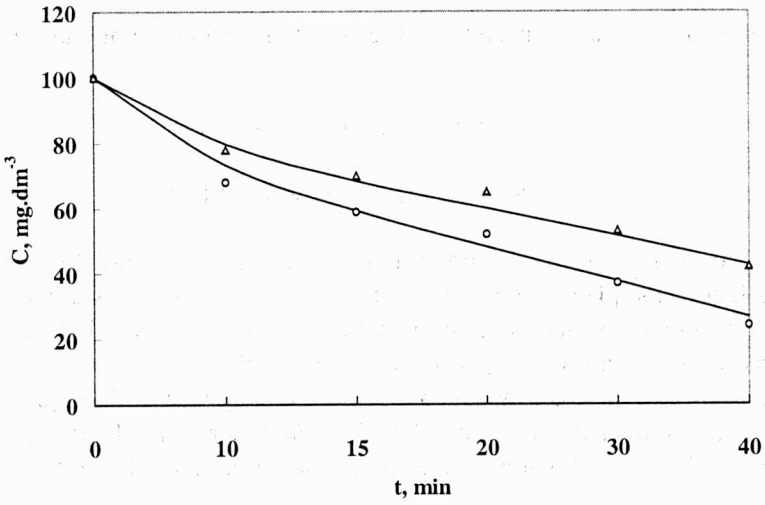

Fig. 2. The effect of the time of ozonation on formaldehyde concentration for different temperatures: pH 3.5; $\circ T = 283$ K; $\Delta T = 293$ K

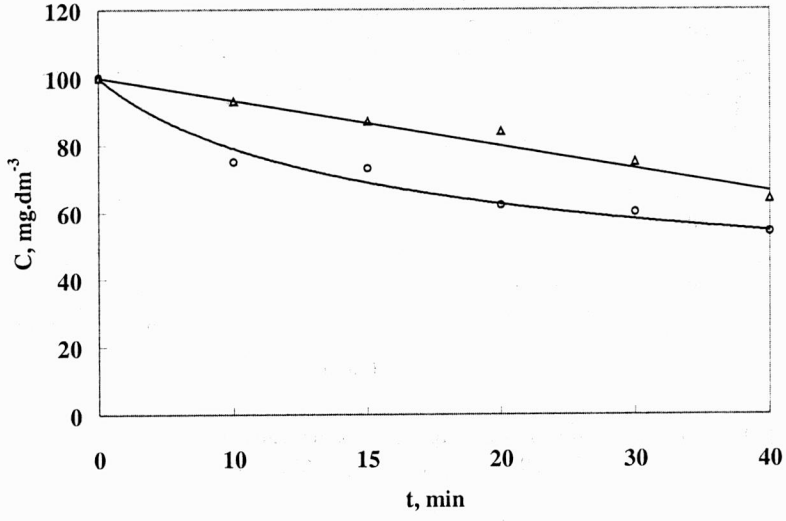

Fig. 3. The effect of the time of ozonation on formaldehyde concentration for different temperatures: pH 10; $\circ T = 283$ K; $\Delta T = 293$ K

Table

Kinetic parameters and efficiency of ozonation

pH	t [min]	$T = 283$ K			$T = 293$ K			E [kJ·mol^{-1}]
		C [mg·dm^{-3}]	α [%]	k^* [min^{-1}]	C [mg·dm^{-3}]	α [%]	k^* [min^{-1}]	
	0	100	0		100	0		
	10	65	35		78	22		
3.5	15	62	38		70	30		
	20	55	45	0.036	65	35	0.023	37.14
	30	37	63		53	47		
	40	17	83		42	58		
	0	100	0		100	0		
	10	75	25		93	7		
10	15	73	27		87	13		
	20	62	38	0.021	84	16	0.0095	60.93
	30	60	40		75	25		
	40	54	46		66	34		

*Average value of the rate constant.

Formaldehyde oxidation proceeds according to the first-order reaction with respect to formaldehyde. This is in agreement with the linear course of the ln C_0/C versus time plot shown in figure 4. For testing the first-order rate equation with respect to formaldehyde the experiments were carried out with an excess of ozone. Our preliminary experiments showed that 1 mmol of ozone oxidized 1.5 mmol of formaldehyde.

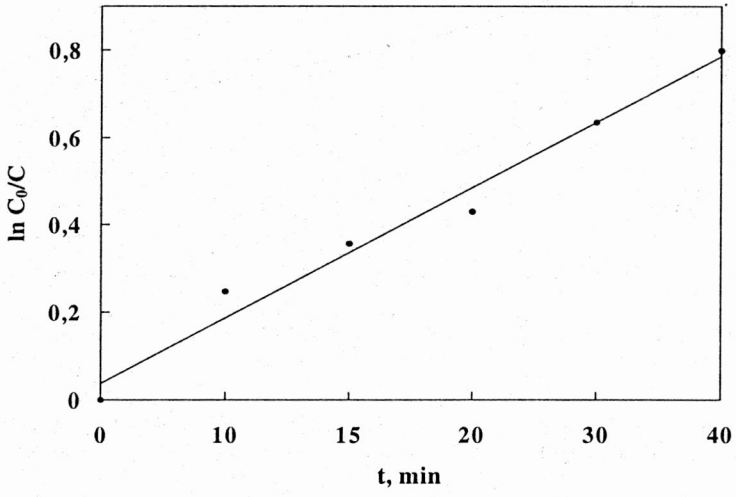

Fig. 4. The relationship $\ln C_0/C = f(t)$: pH – 3.5; $T = 293$ K

The results obtained for the rate constant and activation energy are presented in the table.

3.2. EFFECT OF OZONATION IN THE PRESENCE OF HYDROGEN PEROXIDE

Ozonation is an effective process for reducing the content of pollutants in wastewater, but the aim of AOTs is to confirm an improvement using a combination of ozone and hydrogen peroxide. Oxidizing power of ozone in indirect reaction with pollutants is due to its decomposition to highly reactive hydroxyl radicals ($OH^{\bullet}$). A common objective of AOTs is to produce a larger amount of $OH^{\bullet}$ to oxidize the organic matter. Indeed, hydroxyl radical is a less selective and more powerful oxidant than molecular ozone. Hydrogen peroxide is unable to oxidize formaldehyde. Formaldehyde degradation under the same experimental conditions estimated by the degree of conversion was about 20% at the beginning of the process and remained constant with the change of the hydrogen peroxide and the contact time. Therefore, the action of AOTs should be due to radical reactions. These radicals are generated from the direct reaction between ozone and the ionic form of hydrogen peroxide, which is the initiating step of the radical mechanism [6]:

$$O_3 + HO_2^- \rightarrow HO_2^{\bullet} + O_3^- \ldots \rightarrow OH^{\bullet}.$$

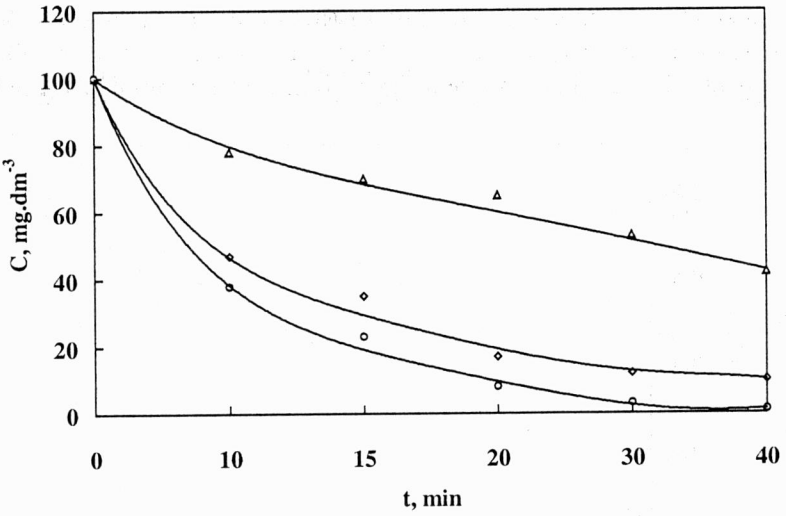

Fig. 5. Oxidation of formaldehyde in the presence of hydrogen peroxide; influence of the amount of H_2O_2: pH 3.5, $T = 293$ K; △ ozonation alone; ◇ $C = 10^{-2}$ M H_2O_2, ○ $C = 10^{-1}$ M H_2O_2

The effect of hydrogen peroxide concentration and pH was investigated. Figure 5 shows the combined effect of ozone and hydrogen peroxide on formaldehyde removal

at pH 3.5 and $T = 293$ K. It can be observed that the yield of oxidation increases with an increase in hydrogen peroxide concentration. Comparing the degree of conversion for ozonation alone and ozonation in the presence of hydrogen peroxide at pH 3.5 presented in figure 7, a synergistic effect of ozone and hydrogen peroxide can be confirmed. For example, the degree of conversion α for ozonation alone at the end of the process is 58% compared to 99% in the presence of 10^{-1}M hydrogen peroxide. The same trend can be seen in figures 6 and 8, presenting the results for ozonation in the presence of hydrogen peroxide at pH 10.

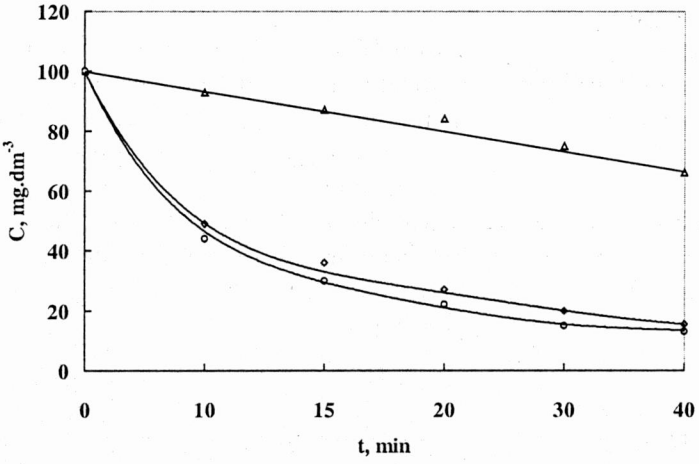

Fig. 6. Oxidation of formaldehyde in the presence of hydrogen peroxide; influence of the amount of H_2O_2: pH 10, $T = 293$ K; △ ozonation alone; ◇ $C = 10^{-2}$ M H_2O_2; ○ $C = 10^{-1}$ M H_2O_2

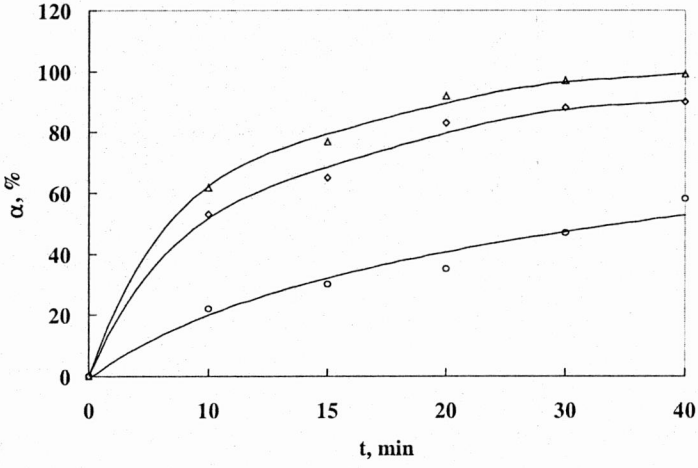

Fig. 7. Dependence of the degree of conversion α on the time of ozonation: pH 3.5, $T = 293$ K; ○ ozonation alone; ◇ $C = 10^{-2}$ M H_2O_2; △ $C = 10^{-1}$ M H_2O_2

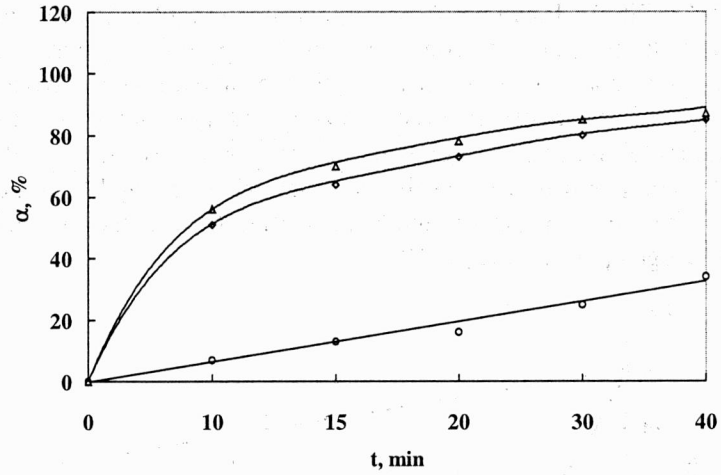

Fig. 8. Dependence of the degree of conversion α on the time of ozonation: pH 10, $T = 293$ K; ○ ozonation alone; ◇ $C = 10^{-2}$ M H_2O_2; △ $C = 10^{-1}$ M H_2O_2

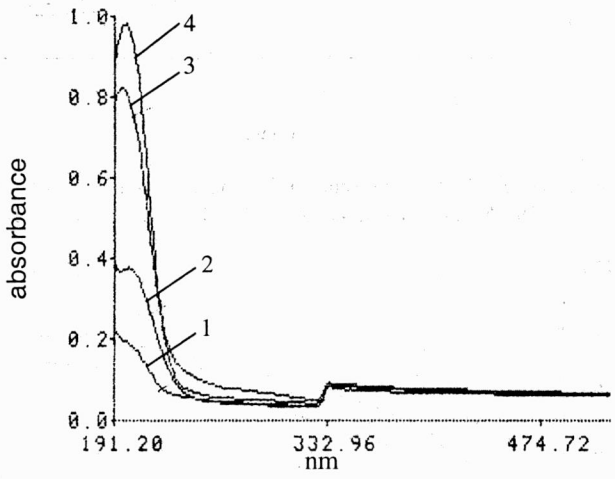

Fig. 9. UV spectra of: 1 – unoxidized formaldehyde; 2 – reference compound, i.e. formic acid; 3 – ozonation at pH 3.5 for 20 min; 4 – ozonation at pH 3.5 for 30 min

According to MCELROY et al. [10], formaldehyde ozonation in the presence of hydrogen peroxide proceeds as a chain mechanism involving $OH^{\bullet}$ radicals and produces formic acid as by-product. In order to confirm this degradation pathway, the spectra of oxidized formaldehyde in the presence of a reference compound (formic acid) were recorded. Figure 9 presents absorption spectra of non-oxidized formaldehyde and formaldehyde oxidized for different times in the presence of formic acid, with absorbance

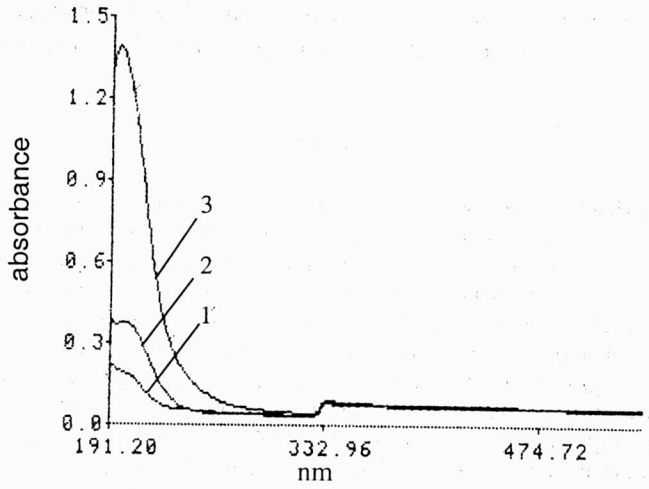

Fig. 10. UV spectra of: 1 – unoxidized formaldehyde; 2 – reference compound , i.e. formic acid; 3 – formaldehyde oxidized at pH 3.5 for 15 min in the presence of hydrogen peroxide ($C = 10^{-1}$M H_2O_2)

at $\lambda_{max} = 200.6$ nm. To confirm an improvement of formaldehyde oxidation during the combined action of ozone and hydrogen peroxide, UV spectrum was recorded for 15 min of oxidation in the presence of 10^{-1}M H_2O_2 (figure 10). On comparing these spectra it becomes evident that O_3/H_2O_2 oxidation increases formaldehyde degradation. In both cases, the only by-product is formic acid.

4. CONCLUSIONS

On the basis of experimental results it can be concluded that ozonation in the presence of hydrogen peroxide enhances the effectiveness of formaldehyde degradation. The main conclusions reached in this work are as follows:

- In the absence of hydrogen peroxide, the effectiveness of ozonation estimated by the degree of conversion α [%] and rate constant k [min^{-1}] is the highest at pH 3.5 and $T = 283$ K.
- Combined effect of ozone and hydrogen peroxide leads to a significant improvement in formaldehyde degradation; for pH 3.5 and $T = 293$ K in the presence of 10^{-1}M H_2O_2 the highest degree of conversion at the end of the process is 99% and for pH 10 is 89%, compared to 58% and 34%, respectively, for ozonation alone.
- The degree of conversion α [%] of formaldehyde depends on hydrogen peroxide concentration and increases with an increase of concentration from 10^{-2}M to 10^{-1}M.
- Synergistic effect of ozone and hydrogen peroxide can be confirmed, which results in a more powerful method for degradation of formaldehyde.

• In the oxidation process, formic acid is produced as by-product, which is identified by recording the absorbance spectra in the presence of a reference compound.

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ZAAWANSOWANE PROCESY UTLENIANIA ROZTWORÓW ZAWIERAJĄCYCH FORMALDEHYD CZĘŚĆ 1. WPŁYW OZONU I NADTLENKU WODORU

Zbadano proces utleniania modelowych roztworów formaldehydu w wodzie. Formaldehyd jest zanieczyszczeniem występującym w ściekach przemysłowych. Ze względu na surowe normy prawne, ustalające dopuszczalne stężenia tej toksycznej substancji w odprowadzanych ściekach, konieczne jest opracowanie skutecznej metody degradacji formaldehydu. Zbadano proces jego utleniania ozonem w połączeniu z nadtlenkiem wodoru. Metoda ta daje lepsze efekty niż proces utleniania samym tylko ozonem. Określono wpływ pH roztworu i temperatury na skuteczność utleniania. Stwierdzono, że efektywność utleniania formaldehydu określana za pomocą współczynnika konwersji α [%] jest większa w obecności nadtlenku wodoru w porównaniu ze skutecznością utleniania tylko ozonem. Stopień konwersji na końcu procesu dla pH roztworu 3,5 oraz w temperaturze 293 K w obecności nadtlenku wodoru wzrósł do 99%, podczas gdy dla samego ozonu wynosił 58%. Zaobserwowano, że skuteczność utleniania zależy od stężenia nadtlenku wodoru i zwiększa się wraz ze wzrostem stężenia tego utleniacza. Wykazano, że w procesie utleniania formaldehydu produktem ubocznym jest kwas mrówkowy identyfikowany metodą spektrofotometryczną.