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OZONATION OF AQUEOUS SOLUTIONS OF SALICYLIC ACID

In the present paper, ozonation of aqueous solutions of salicylic acid is studied. The influence of the main reaction parameters, i.e., pH of the medium and temperature, on the process efficiency was investigated. The effectiveness of the process was estimated based on the degree of conversion α [%]. It was observed that ozonation is more effective at alkaline reaction of medium, which can be explained by higher concentration of $OH^{\bullet}$ radicals in such a medium. The degree of conversion achieved at the end of the process at pH 10 was 91% compared to 55% at pH 6. Another parameter used to quantify the reactivity of salicylic acid during ozonation was the rate constant k [min^{-1}], being calculated from the first-order kinetic equation. The rate constant of the process was two times higher at the temperature rise from 283 K to 303 K. A considerable improvement in chemical oxygen demand (COD) removal was observed at pH above 7. At pH 10 the reduction in COD at the end of the process reached 40%, whereas at pH 6 the reduction in COD under the same conditions was only 8%. It was found that ozonation of salicylic acid produced intermediate oxalic acid, which was identified spectrophotometrically.

1. INTRODUCTION

A greater and greater use of pharmaceutical products is becoming a new environmental problem. Pharmaceutical products in high concentrations reach wastewater treatment plants via human excretion and via pharmaceutical industry discharges. Pharmaceuticals are not totally removed in wastewater treatment plants and therefore can be found in surface water and groundwater.

During the last few years the interest in assessing the presence of pharmaceuticals in the environment has been growing [6], [8], [14]. Anti-inflammatory drugs, analgesic products and their metabolites were detected in wastewater [5], [15], surface water and groundwater [3], [4], [8].

In order to determine pharmaceuticals in water samples, different methods have been applied. FERRE et al. [7] developed a combined analytical method involving toxicity and liquid chromatography. Recently, TERNES [16] has developed several methods for the determination of a wide spectrum of drugs and their metabolites in the range of concen-

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tration lower than ng·dm^{-3}. ANDREOZZI et al. [1] reported positive results for paracetamol oxidation in aqueous solutions by means of ozonation and H_2O_2 photolysis. TERNES et al. [17] have shown that after ozonation of the pharmaceutical-containing effluent from sewage treatment plant, all these compounds were no longer detected. The removal of phenol and salicylic acid as the model compounds and the main components of aquatic humic matter by the means of ultraviolet radiation/hydrogen peroxide/oxygen was studied by SCHECK et al. [13]. LEITHER et al. [10], who removed salicylic acid, peptides and humic substances from aqueous solutions by their catalytic ozonation, have shown that the catalysts used allow these substances to be removed at the rate approximately the same as that of ozonation alone.

The aim of this work was to investigate the operating conditions for degradation of aqueous solutions of salicylic acid and the associated by-product by ozonation.

2. MATERIALS AND METHODS

The experiments were carried out using model solutions of salicylic acid of an initial concentration of 200 mg·dm^{-3} and COD_0 = 345mg O_2·dm^{-3}.The pH values chosen ranged from 3 to 10. The pH of the samples was adjusted to a desired value by either sulfuric acid or sodium hydroxide added to the medium. The reaction temperature was in the interval of 283–303 K. Ozone was synthesized in a glass generator at a voltage of 14 kV and dispersed into solution through a porous glass disc. The amount of ozone was determined iodometrically in liquid phase [9].

The concentration of salicylic acid measured with a Perkin-Elmer UV/VIS spectrophotometer in a 1-cm^3 cell was estimated based on the absorbance at λ_{max} = 530 nm. The relative standard deviation of the method reached ±6%. COD measurements were conducted according to standard methods [2].

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 of salicylic acid, respectively.

The experimental procedures were similar to those described in [11].

3. RESULTS AND DISCUSSION

In general, ozonation of organic matter in aqueous medium is affected by the following factors: reagent and ozone concentration, pH value, temperature and presence of reaction inhibitors.

In our study, the experiments were carried out at varying pH value, temperature and the amount of ozone expressed in terms of the time of ozonation (contact time). As is well-known, ozone reacts with pollutants in aqueous solutions in two ways: by direct ozonation and by a radical mechanism. In the indirect reaction, ozone decomposes to secondary oxidants such as $OH^{\bullet}$ radicals, which may then lead to a series of radical chain reactions accompanied by further ozone consumption [12].

The influence of pH on the effectiveness of salicylic acid degradation by ozonation is shown in figure 1. The results obtained indicate that the process effectiveness increases significantly at pH above 7, which is a result of an enhanced ozone decomposition and the shift towards radical type reaction at pH > 7.

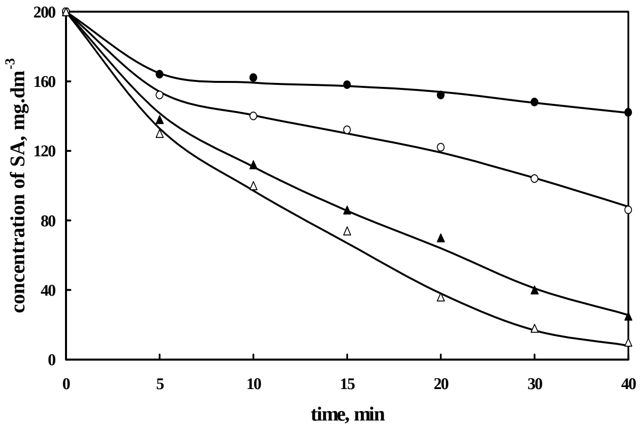

Fig. 1. The effect of the time of ozonation on salicylic acid (SA) concentration at different pH: T = 293 K; -●- pH 3.0; -○- pH 6.0; -▲- pH 8.0; -△- pH 10

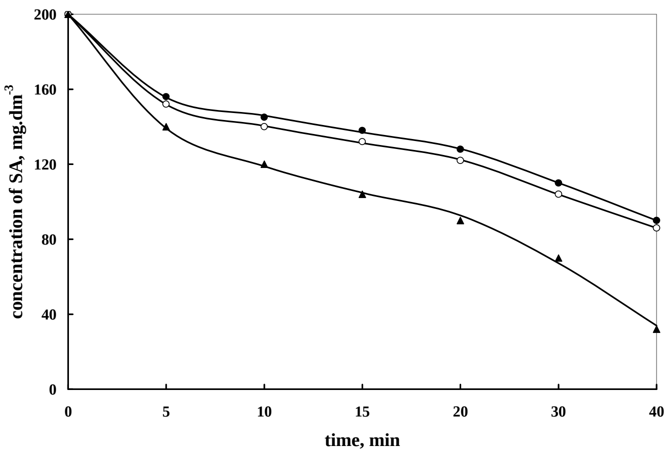

Fig. 2. The effect of the time of ozonation on salicylic acid (SA) concentration at different temperatures: pH 6; -●- T = 283 K; -○- T = 293 K; -▲- T = 303 K

Our preliminary studies showed that at pH 3 the temperature change from 283 to 303 K had negligible effect on the effectiveness of salicylic acid ozonation. With this in mind we investigated the effect of temperature at pH 6, and at alkaline reaction we chose pH 10. The results obtained are presented in figures 2 and 3. It can be seen that for both pH values the removal of salicylic acid increases with an increase in the temperature. However, the achieved degree of conversion at pH 10 is higher than that at pH 6 (see the table 1). This can be explained by a higher concentration of $OH^{\bullet}$ radicals in alkaline medium.

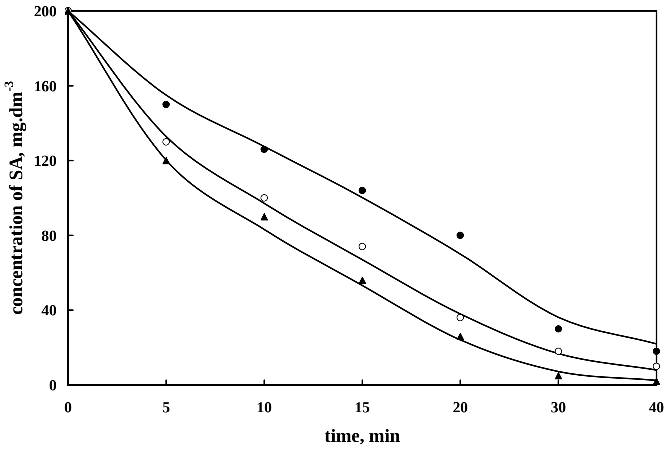

Fig. 3. The effect of the time of ozonation on salicylic acid (SA) concentration at different temperatures: pH 10; -●- T = 283 K; -○- T = 293 K; -▲- T = 303 K

Table

Kinetic parameters of salicylic acid ozonation

pH	t [min]	T = 283 K			T = 303 K			E [kJ.mol^{-1}]
		C [mg.dm^{-3}]	α [%]	k^* [min^{-1}]	C [mg.dm^{-3}]	α [%]	k^* [min^{-1}]	
	0	200	0		200	0		
	5	156	22		140	30		
	10	145	27,5		120	40		
6.0	15	138	31	0.0241	104	48	0.0408	18.77
	20	128	36		90	55		
	30	110	45		70	65		
	40	90	55		32	84		
	0	200	0		200	0		
	5	150	25		120	40		
	10	126	37		90	55		
10.0	15	104	48	0.0452	56	72	0.0867	23.23
	20	80	60		26	87		
	30	30	85		5	97,5		
	40	18	91		2	99		

[*] Average value of the rate constant.

In order to determine the rate constants of the process, a kinetic study was carried out. The linear character of the plot of $\ln C_0/C$ versus time shown in figure 4 proves that ozonation proceeds according to the first-order reaction with respect to salicylic acid. The rate constant k [min^{-1}] was calculated from the first-order kinetic equation. The activation energy of the process was calculated from the dependence of the rate constant on temperature according to the Arrhenius equation:

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

where k_1 and k_2 are the rate constants at the selected working temperatures.

The data on kinetics of salicylic acid ozonation are collected in the table.

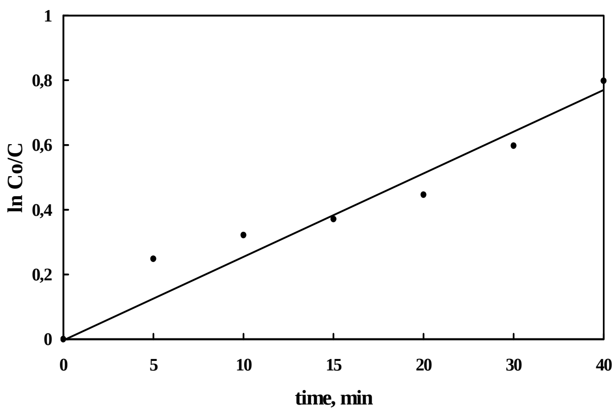

Fig. 4. $\ln C_0/C = f(t)$ versus time at pH 10 and $T = 293$ K

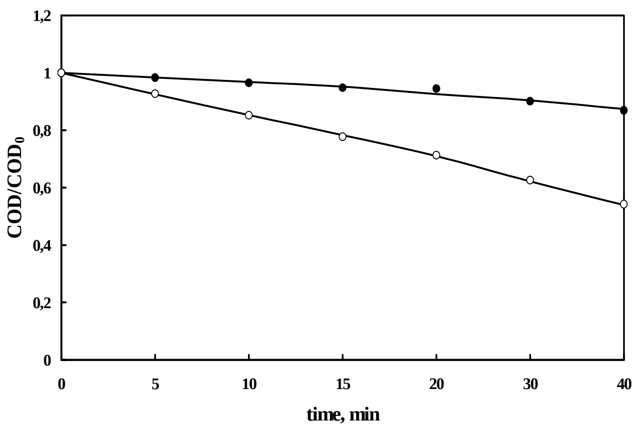

Fig. 5. The effect of the time of ozonation on COD abatement:
$T = 293$ K; $COD_0 = 345$ mg $O_2 \cdot dm^{-3}$; -●- pH 6; -○- pH 10

Figure 5 presents COD removal at pH 6 and pH 10. It can be observed that at pH 6 COD/COD_0 reaches 0.92 which means as low as 8% removal at the end of the process, while at pH 10 under the same conditions the achieved COD reduction amounts to 40%. From the results obtained for COD reduction it is evident that the removal of salicylic acid from its aqueous solutions is more effective in alkaline solutions.

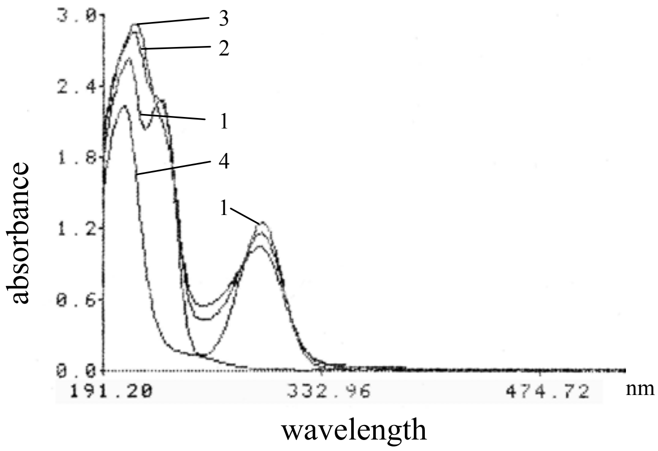

Fig. 6. UV spectra of unoxidized salicylic acid (1), ozonation for 10 min (2), ozonation for 20 min (3), reference compound, i.e. oxalic acid, (4), pH 6

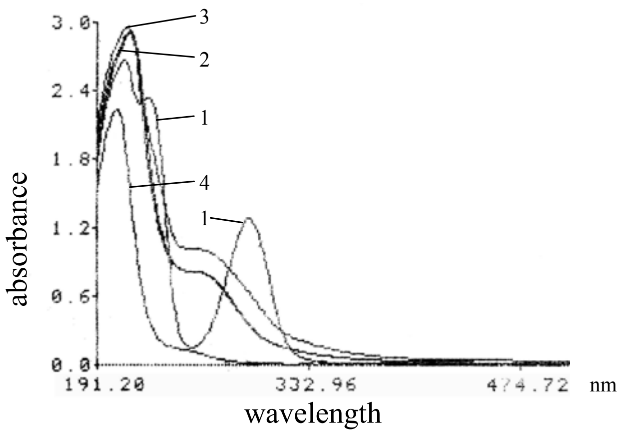

Fig. 7. UV spectra of unoxidized salicylic acid (1), ozonation for 10 min (2), ozonation for 20 min (3), reference compound, i.e. oxalic acid (4), pH 10

According to [10] the main by-product of the catalytic ozonation of salicylic acid is oxalic acid. Our experiments proved that its concentration at the end of ozonation represented about 50% of the remaining TOC. In order to confirm a similar degradation pathway, the UV spectra of unoxidized salicylic acid and salicylic acid ozonized in acid and alkaline media were recorded. The spectra were recorded after 10 min and 20 min oxidation of the acid in the presence of a reference compound, i.e., oxalic acid. Figure 6 presents the spectra recorded at pH 6, and figure 7 – the spectra recorded under the same conditions at pH 10. On comparing these spectra is obvious that the removal of salicylic acid in alkaline medium is significantly more effective.

4. CONCLUSIONS

The results of ozonation of aqueous solutions of salicylic acid (the precursor of aspirin, one of most commonly used drugs, and other structurally related molecules) have revealed the efficiency of ozone application to the removal of salicylic acid when ozonation proceeds in alkaline medium and at elevated temperature. Under these conditions COD reduction at the end of the process reaches 40%. Ozone attack on aromatic ring results in producing intermediates, i.e., carboxylic acids. By recording the absorbance spectra of ozonized solutions of salicylic acid the formation of a by-product, i.e., oxalic acid, is confirmed. In view of these experimental results, we can conclude that ozonation could be an appropriate method for the removal of salicylic acid from its aqueous solutions.

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OZONOWANIE WODNYCH ROZTWORÓW KWASU SALICYLOWEGO

Przedstawiono wpływ odczynu i temperatury wodnych roztworów kwasu salicylowego na skuteczność ich ozonowania. Zaobserwowano, że proces przebiegał efektywniej w roztworach o odczynie zasadowym ze względu na wyższe stężenie rodników $OH^{\bullet}$. Uzyskany stopień konwersji (α) na końcu procesu ozonowania wynosił 91% dla pH = 10 i 55% dla pH = 6. Wzrost temperatury z 283 K do 303 K skutkował dwukrotnym zwiększeniem stałej szybkości reakcji k [min^{-1}] obliczonej na podstawie reakcji pierwszego rzędu. Uzyskano znaczne obniżenie wartości ChZT badanych roztworów w zakresie zasadowego odczynu – 40% dla pH = 10 i tylko 8% dla pH = 6. Na podstawie identyfikacji spektrofotometrycznej stwierdzono, że w procesie ozonowania kwasu salicylowego następuje wytworzenie produktu pośredniego, jakim jest kwas szczawiowy.