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OZONATION OF AQUEOUS SOLUTIONS OF RESORCINOL AND CATECHOL

Ozonation of resorcinol and catechol, which are pollutants contained in numerous industrial wastewaters, was studied. The influence of pH of the medium and a temperature on the effectiveness of ozonation of model solutions of resorcinol and catechol was investigated. It was observed that the ozonation of both phenols is more effective in alkaline range (pH 11.8–13.6), which can be explained by a higher concentration of ·OH radicals at high pH values. The highest reduction in COD (53%) was achieved at pH 11.8. The effectiveness of ozonation was estimated by the degree of conversion α [%]. Another parameter used to quantify the reactivity of the phenols tested towards ozone was the rate constant k [min^{-1}], which was calculated from the first-order kinetic equation. It was established that the drop in temperature from 293 K to 283 K increased the effectiveness of resorcinol ozonation. Under these conditions α [%] increased by about 30% for the same time of ozonation and the rate constant doubled. For catechol the influence of temperature under the same conditions was negligible.

1. INTRODUCTION

The high oxidizing power of ozone and its capacity to generate hydroxyl radicals are used to oxidize wastewaters containing organic and inorganic compounds of different nature [1]–[3]. Phenols are pollutants contained in numerous industrial wastewaters, including wastes from oil refining, petrochemical and cooking plants [4], [5].

Ozonation is appropriate to oxidation of phenols because as a rule these compounds easily react with ozone [6]. Ozone reacts with pollutants via ozonolysis and through radical chain reactions. The reaction of ozone with OH⁻ ions to intermediate radicals and finally to hydroxyl radicals is important in the oxidation of saturated organic compounds where no molecular ozonolysis is possible. The concentration of ·OH radicals increases with the increase of pH. However, high pH values promote decomposition of ozone to oxygen. Therefore, an optimum of the reaction of free radicals with phenols must be established.

The aim of this paper was to examine the dependence of the oxidation conditions of resorcinol and catechol on pH values, as well as the formation of ozonation prod-

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ucts. Chemical oxidation rates and rate constants of the oxidation of the phenols tested were also determined.

2. MATERIALS AND METHODS

The experiments were carried out using a model solution whose initial concentration reached 200 mg · dm^{-3}.

Ozone was produced using a laboratory ozonizer described elsewhere [7]. The concentration of ozone produced by a generator was 5 mg · dm^{-3}. The pre-treatment of the air necessary for ozonation consisted in passing it through silica gel. 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 conducted at the ozone–air rate of 20 cm^3 · min^{-1}. The amount of ozone was determined in liquid phase making use of iodometry [8].

The concentration of phenols was determined spectrophotometrically [9]. The absorption was measured by means of a Perkin–Elmer λ vis/uv. The relative standard deviation of the method is ±6.0%. UV spectra were recorded using a Perkin–Elmer λ vis/uv.

3. RESULTS AND DISCUSSION

In order to find optimum conditions for destruction of resorcinol and catechol, the experiments were carried out at pH values in the range of 6.5–13.6. The effectiveness of ozonation was estimated based on the degree of conversion α [%], which was calculated from the formula 100 · $(C_0 - C)/C_0$ (see the table).
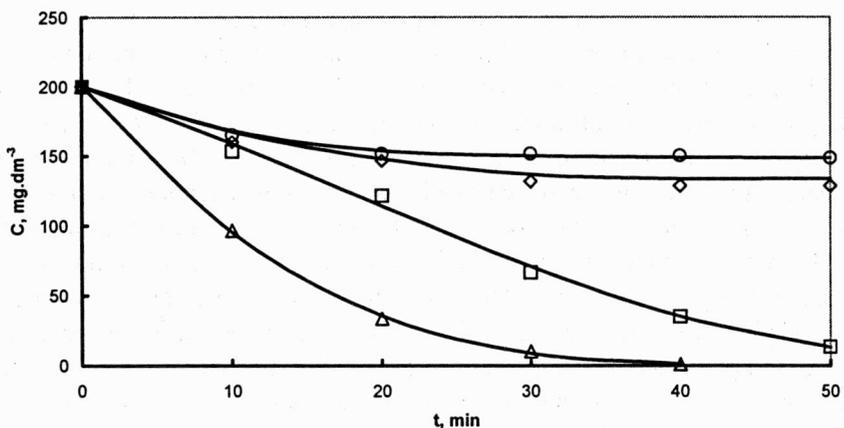
Fig. 1. Dependence of the concentration of resorcinol on the time of ozonation: solution volume 50 cm^3; $t = 293$ K; ○ pH 6.5, ◊ pH 9.0, □ pH 11.8, Δ pH 13.6

The influence of a temperature on the concentration C [mg · dm^{-3}];
degree of conversion α [%], rate constant k [min^{-1}] and activation energy E [kJ · mol^{-1}] at pH 11.8

Phenol	t	$t = 283$ K			$t = 293$ K			E
		C	α	k^*	C	α	k^*	
	[min]	[mg · dm^{-3}]	[%]	[min^{-1}]	[mg · dm^{-3}]	[%]	[min^{-1}]	[kJ · mol^{-1}]
	0	200	0		200	0		
	10	103.5	48.25		153.5	23.25		
Resorcinol	20	41.5	79.25		121.5	39.25		
	30	14.0	93.0	0.080	66.5	66.75	0.037	53.16
	40	5.5	97.25		35.0	82.5		
	50	–	–		13.5	93.25		
	0	200	0		200	0		
	10	146.5	26.75		170	15.0		
Catechol	20	118.5	40.75		123.5	38.25		
	30	98.5	50.75	0.035	105.0	47.5	0.029	12.97
	40	45.0	77.5		50.0	75.0		
	50	21.0	89.5		27.0	86.5		
	60	14.0	93.0		21.0	89.5		

*Average value of the rate constant.

Figure 1 presents the influence of pH on the resorcinol ozonation. It can be seen that the elimination rate of resorcinol is the highest at pH 13.6. At pH 6.5 the destruction of resorcinol is negligible. This is probably caused not only by the lower concentration of ·OH radicals, but also by the lower degree of dissociation of resorcinol at pH 6.5. Ozonation of phenols depends on nucleophilic character of ortho and para
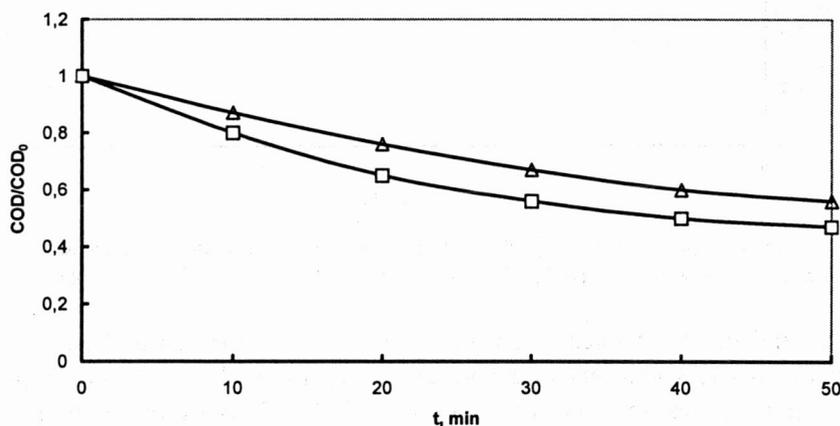
Fig. 2. Dependence of COD elimination on the time of ozonation for resorcinol:
solution volume 50 cm^3; $t = 293$ K; COD$_0$ = 350 mg O$_2$ · dm^{-3}; □ pH 11.8; Δ pH 13.6

positions in an aromatic ring. If pH increases, then the ortho position corresponding to the hydroxyl dissociated group has a higher electronic density, which means that this position is more prone to the electrophilic substitution of ozone, because the substituting O^- is more activating than OH^- [10].
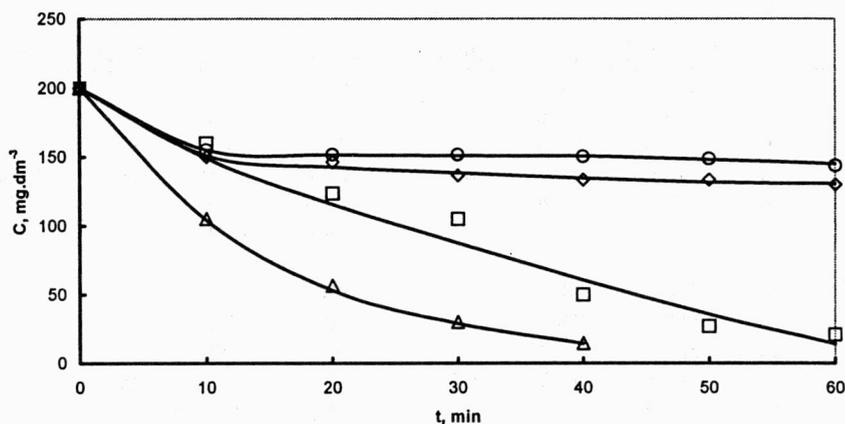
Fig. 3. Dependence of the concentration of catechol on the time of ozonation: solution volume 50 cm^3; t = 293 K; ○ pH 6.5, ◊ pH 9.0, □ pH 11.8, Δ pH 13.6
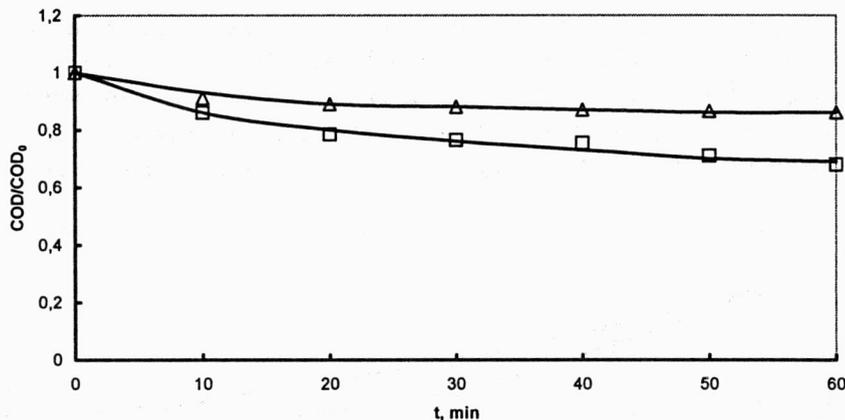
Fig. 4. Dependence of COD elimination on the time of ozonation for catechol: solution volume 50 cm^3; t = 293 K; COD$_0$ = 358 mg O$_2$ · dm^{-3}; □ pH 11.8; Δ pH 13.6

The dependence of chemical oxidation rate on pH for resorcinol is shown in figure 2. The reduction in COD at the end of the process is 53% for pH 11.8 and 44% for pH 13.6.

The kinetic curves obtained for catechol at pH 6.5–13.6 are presented in figure 3. In this case as well, the elimination rate in the alkaline range is higher than at pH 6.5. It can be observed that for the same time of oxidation and at pH 11.8 the oxidation

rate of catechol is lower. This is probably due to the position of the second hydroxyl group. Resorcinol is more reactive than catechol because of the reinforcing action of the second hydroxyl group. Resorcinol's aromatic ring is more prone to cleavage at 4-position, which is para to the one hydroxyl group and ortho to the other.
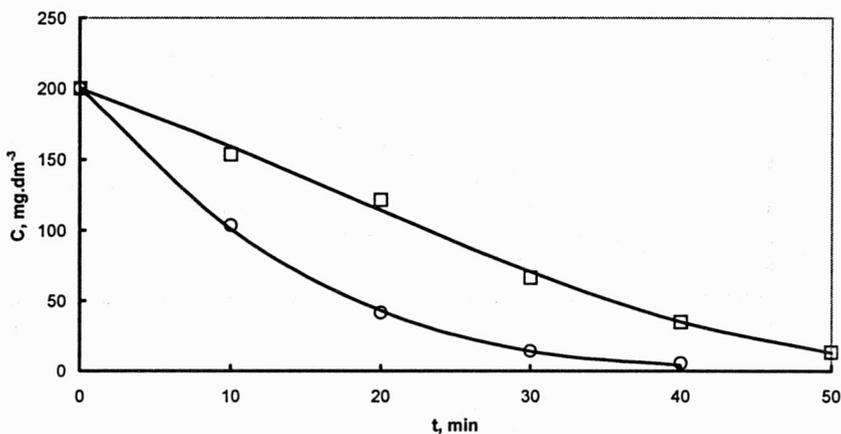
Fig. 5. Dependence of the concentration of resorcinol on the time of ozonation: pH 11.8; solution volume 50 cm³; ○ t = 283 K; □ t = 293 K
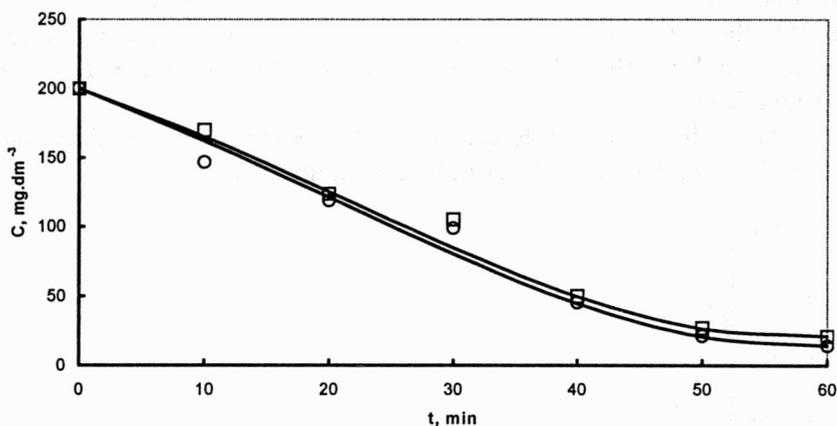
Fig. 6. Dependence of the concentration of catechol on the time of ozonation: pH 11.8; solution volume 50 cm³; ○ t = 283 K; □ t = 293 K

Chemical oxidation rate of catechol in alkaline range (figure 4) is lower compared to that of resorcinol – 31% reduction in COD at the end of the process and at pH 11.8.

In order to find the conditions for the complete oxidation of resorcinol, ozonation was carried out at t = 283 K. Figure 5 shows the kinetic curves obtained at pH 11.8 for both temperatures. The data in figure 5 indicate that ozonation of resorcinol at t = 283 K is more

effective, which is due to the higher solubility of ozone at lower temperature. In the case of catechol (see figure 6), a drop in temperature has a negligible effect.
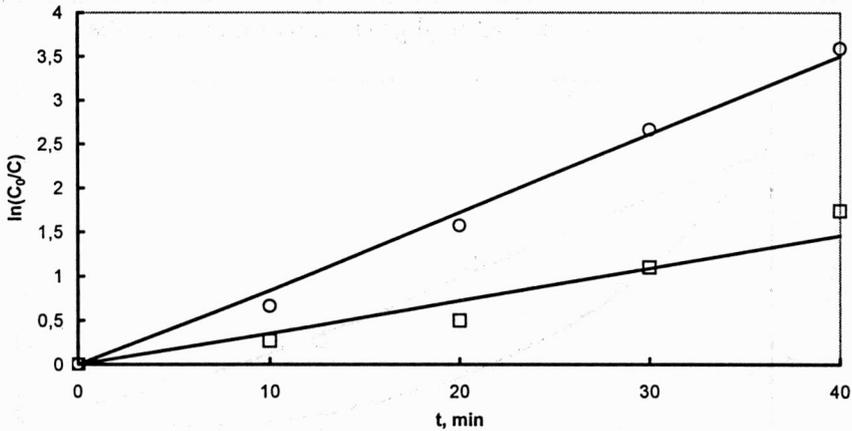
Fig. 7. $\ln (C_0/C) = f(t)$ relationship for resorcinol:
pH 11.8; ○ $t = 283$ K; □ $t = 293$ K

To determine rate constants of ozonation of resorcinol and catechol a kinetic study was carried out. The linear character of the ln (C_0/C) vs. time plot shown in figure 7 evidences that the oxidation runs according to the first-order reaction with respect to both resorcinol and catechol. The rate constants k [min^{-1}] were calculated from the first-order kinetic equation.

The results obtained for the rate constant and activation energy of the ozonation of resorcinol and catechol at pH 11.8 are presented in the table.
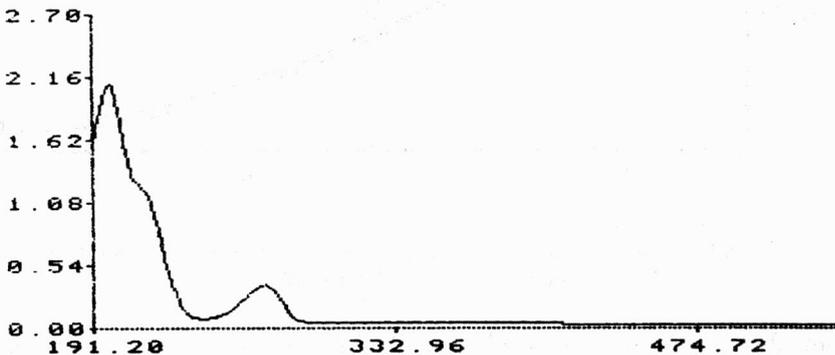
Fig. 8. Absorption spectrum of resorcinol

The activation energy was calculated from the rate constant vs. temperature relationship according to the Arrhenius equation:

$$E = \frac{Rt_1t_2}{\Delta t} \ln \frac{k_{t_1}}{k_{t_2}}.$$

According to the reaction mechanism proposed in [11] ozonation of phenol leads to intermediate products, unsaturated and saturated carboxylic acids. In order to confirm similar degradation pathway, the spectra of non-oxidized and oxidized phenol were recorded.
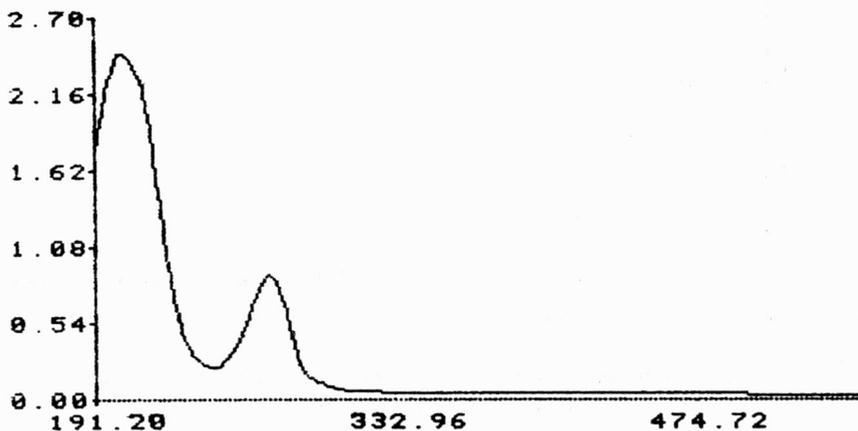
Fig. 9. Absorption spectrum of catechol
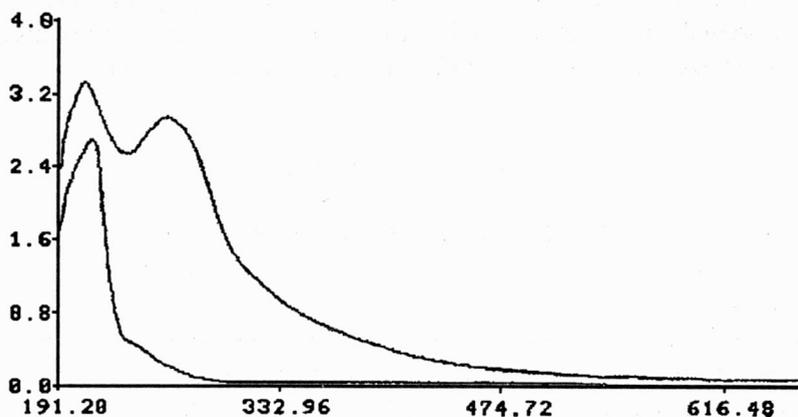
Fig. 10. Absorption spectrum of the resorcinol oxidized
in the presence of reference compound – oxalic acid

It is obvious that in an aqueous medium, resorcinol and catechol absorb at $\lambda_{max} = 219$ nm ($E = 45\ 600$) and $\lambda_{max} = 274$ nm ($E = 36\ 500$) (figures 8 and 9).
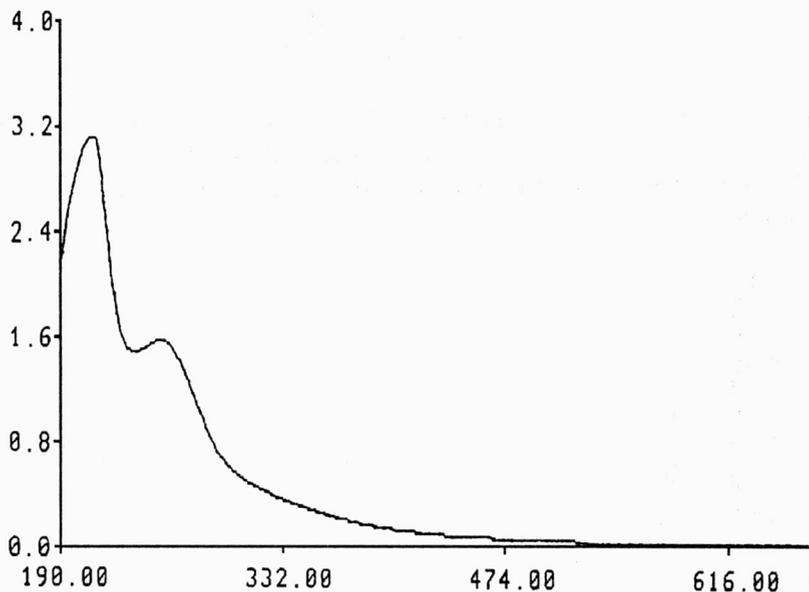
Fig. 11. Absorption spectrum of resorcinol oxidized with oxalic acid
– an reference compound being added

It was established that after oxidation in the reaction mixture besides resorcinol and catechol there was a compound with an absorbtion band at $\lambda_{max} = 250$ nm ($E = 63$) which we assigned to oxalic acid. It becomes evident on comparing UV spectrum of oxidized resorcinol with reference oxalic acid (figure 10). Figure 11 presents absorption spectrum of oxidized resorcinol with reference oxalic acid being added.

4. CONCLUSIONS

Resorcinol and catechol can be oxidized by ozone because of the electrophilic character of this agent. The results obtained for ozonation of these phenols lead to the following conclusions:

• The effectiveness of ozonation estimated based on the degree of the conversion α [%] and rate constant k [min^{-1}] is higher in alkaline range.

• At pH 11.8 and a 40 min time of ozonation the reduction in COD for resorcinol and catechol are 53% and 31%, respectively.

• The drop in temperature increases the effectiveness of ozonation for resorcinol, whereas in the case of catechol the effect of temperature is negligible.

• The oxidation process runs through intermediate oxalic acid, which is identified spectrophotometrically.

REFERENCES

[1] ZWIENER C., FRIMMEL F.H., *Oxidative treatment of pharmaceuticals in water*, Water Res., 2000, Vol. 34, No. 6, 1881–1885.
[2] BELTRAN F., ENCINAR J., GONZALEZ J., *Industrial wastewater advanced oxidation*. Part 2, Water Res., 1997, Vol. 31, No. 10, 2415–2428.
[3] ALBORZFAR M., ESCANDE K., ALLEN S. *Removal of 3,4-dichlorobut-1-ene using ozone oxidation*, Water Res., 2000, Vol. 34, No. 11, 2963–2970.
[4] WURM H.J., *Extraction of phenols from coking plant effluents*, Chem. Ing. Tech., 1976, 48, 840–845.
[5] RISE R.G., *Application of ozone for industrial waste waters treatment: a review*, Ozone Science Engineering, 1997, 18, 477–315.
[6] HOIGNE J., BADER H., *Rate constants of direct reactions of ozone with organic and inorganic compounds in water*. II, Water Res., 1983, b, 17, 184–194.
[7] PARISHEVA Z., DEMIREV A., *Ozonation of ethanolamine in aqueous medium*, Water Res., 2000, Vol. 34, No. 4, 1340–1344.
[8] HERCH P., DENKINGER K., *Galvanic monitoring of ozone in air*, Anal. Chem., 1963, 35, 897–902.
[9] LURIE M., RIBNIKOVA A., *Chemical analysis of natural waters*, Himia, Moscow, 1977.
[10] MORRISON T., BOYD N., *Organic Chemistry*, Boston, 1983.
[11] SOTELO J., BELTRAN F., GONZALES M., *Ozonation of aqueous solutions of resorcinol and phloroglucinol*, Ind. Eng. Chem. Res., 1990, 29, 2358–2367.

OZONOWANIE WODNYCH ROZTWORÓW REZORCYNOLU I KATECHINY

Zbadano ozonowanie rezorcynolu i katechiny, które zanieczyszczają wiele ścieków przemysłowych. Określono wpływ pH i temperatury środowiska na efektywność ozonowania modelowych roztworów obu fenoli. Stwierdzono, że ozonowanie wspomnianych związków jest bardziej efektywne w środowisku alkalicznym (pH od 11,8 do 13,6), co można wyjaśnić większym stężeniem w nim rodników ·OH. Największą redukcję w ChZT (53%) otrzymano dla pH = 11,8. Efektywność ozonowania oszacowano na podstawie wartości współczynnika konwersji α [%]. Innym parametrem, który służy do określenia reaktywności badanych fenoli w stosunku do ozonu, jest stała szybkości reakcji k [min^{-1}], obliczona z kinetycznej reakcji pierwszego rzędu. Stwierdzono, że spadek temperatury z 293 K do 283 K poprawia efektywność ozonowania rezorcynolu. W tych samych warunkach, tym samym czasie ozonowania, a dwukrotnie zwiększonej szybkości reakcji wartość współczynnika α zwiększała się o 30%. Okazało się też, że wpływ temperatury na ozonowanie katechiny w tych samych warunkach był pomijalnie mały.