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DANUTA LESZCZYŃSKA*

THE ULTRASONIC WAVE EFFECT ON OXIDATION OF PHENOL BY OZONE AND HYDROGEN PEROXIDE

In order to accelerate the oxidation of phenol in model solution with hydrogen peroxide and ozone the ultrasonic waves were applied. Decomposition of phenol was analyzed versus the oxidizing agent doses, methods of dosing, pH of the solution, and the power input of the ultrasonic wave generator. The ultrasonic waves improved the efficiency of oxidation by hydrogen peroxide, the best oxidizing agent being ozone.

1. INTRODUCTION

Chemical oxidation is an essential treatment technique for removal of organic pollutants introduced into the rivers due to the activities of many different industries. Among the oxidizing agents which now are applied in this method ozone and hydrogen peroxide deserve special attention, owing to their high redox potential. The efficiency of oxidation with ozone depends on the type of organic compound to be removed, on pH of the wastewater, as well as on the reaction time and the ozone dosage being applied. The mechanism governing the oxidation process is pH-dependent [5, 6]. Like ozone, hydrogen peroxide is a good oxidizing agent, but it has also the ability to act as reducing factor [1]. The effect of ozone and hydrogen peroxide on aromatic compounds is determined by the destruction of the aromatic ring [3, 4, 7, 9] which may also result from application of ultrasounds [2]. Chemical reactions induced by ultrasonic waves were first described in 1927 [11]. The application of ultrasounds gives predominantly oxidation reactions. Years ago, this phenomenon was believed to be due to the influence of ultrasonic vibration on the particle bonds, but now it is being attributed to cavitation [11]. As yet, the mechanism by which the ultrasonic wave acts upon a given compound is still far from being sufficiently well understood [11].

The study reported in this paper aimed at determining the effect of ozone and hydrogen peroxide on the transformations of phenol in the aqueous solution including the study of ultrasonic irradiation effect on the process course. The influence of ultrasonic irradiation alone on the transformations of phenol was also studied.

* Institute of Environment Protection Engineering, Technical University of Wrocław, pl. Grunwaldzki 9, 50-377 Wrocław, Poland.

2. EXPERIMENTAL

The experiments were run for model aqueous solutions of phenol at concentration of 200 mg/dm^3. Phenol was analysed by spectrophotometry at a wavelength of 450 nm in the p-nitro-aniline at an alkaline pH [8]. Ozone was produced on a laboratory scale from the ambient air. Hydrogen peroxide was applied in the form of 30% aqueous solutions (perhydrol). Both ozone and hydrogen peroxide concentrations were determined by the iodometric method [10, 12]. An ultrasonic generator ($f = 20.840$ to 20.700 Hz, 400 Ω) was used to produce ultrasonic waves.

3. RESULTS

3.1. OZONATION OF PHENOL SOLUTION

Aqueous phenol solutions were ozonated at pH 3.0, 5.2, and 9.8. Both the transformation of phenol and the ozone consumption were found to be pH-dependent (tab. 1). An ozone dose of 0.87 g O_3/dm^3 yields a phenol removal of 98.5% at the ozone consumption of 71.8%.

Table 1

Ozonation of phenol solution without ultrasonic irradiation

Ozonowanie roztworu fenolu bez napromieniowania ultradźwiękowego

Phenol concentration		Ozone concentration		pH		Permanganate
initial	final	initial	final	initial	final	COD
mg/dm^3		mg O_3/dm^3		—		mg O_2/dm^3
	91.3	44.6	23.8		3.6	266.7
	77.8	74.3	41.6		3.3	263.3
	70.3	121.8	65.3		3.1	256.7
200	62.5	178.2	71.3	5.2	2.9	280.0
	60.0	231.7	57.3		2.9	223.3
	50.8	398.0	85.4		2.7	220.0
	139.0	23.8	11.7		2.9	305.0
	129.5	71.3	12.3		2.9	310.0
200	110.0	121.8	14.9	3.0	2.8	310.0
	91.2	163.4	25.5		2.7	310.0
	80.5	261.4	40.4		2.6	266.0
	73.5	374.2	71.3		2.6	260.0
	100.0	36.0	35.4		7.3	335.0
	75.3	84.0	77.6		5.4	315.0
	46.8	131.1	121.2		5.1	275.0
200	28.5	222.1	168.7	9.8	4.0	250.0
	22.5	225.5	198.0		3.9	233.3
	17.5	360.2	220.5		3.8	233.0
	3.0	873.0	246.0		3.5	172.5

3.2. OXIDATION OF PHENOL BY HYDROGEN PEROXIDE

Aqueous solutions of phenol were treated continuously for 90 min with hydrogen peroxide without any pH adjustments (fig. 1). The phenol removal obtained with the dose of 15.71 g H_2O_2/dm^3 was as low as 45% at the oxidizing agent consumption of 60%.

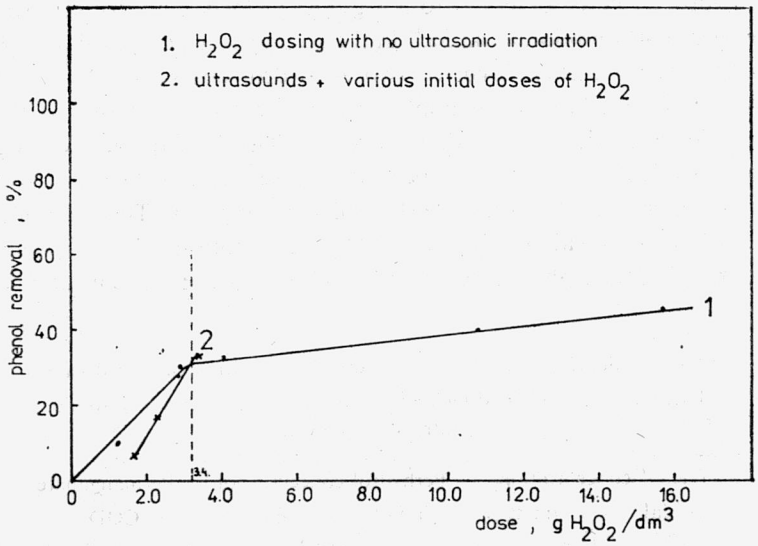

Fig. 1. Phenol removal vs. dose of oxidizing agent and treatment methods

Rys. 1. Usuwanie fenolu w zależności od dawki oksydanta i metod oczyszczania

3.3. ULTRASONIC IRRADIATION OF AQUEOUS PHENOL SOLUTION

The model solution was treated for 20 min with ultrasonic waves at various anode voltages (tab. 2). Applying the specific ultrasonic generator and an anode voltage of 0.45 V the removal of phenol obtained via this route amounted to 37.5%.

Table 2

Phenol solution ultrasonic irradiation at various anode voltage

Ultradźwiękowe napromieniowanie roztworu fenolu przy różnych napięciach anodowych

Phenol concentration initial	Phenol concentration final	Anode voltage	Permanganate COD
	mg/dm³	V	mg/dm³
	176	0.20	440
	160	0.31	380
200	136	0.40	320
	125	0.45	300

3.4. THE EFFECT OF ULTRASONIC IRRADIATION ON THE OXIDATION OF PHENOL WITH HYDROGEN PEROXIDE

Oxidation and ultrasonic irradiation were carried out at the same time (tab. 3). In the first run the aqueous phenol solution was treated with a given perhydrol dose, and then subjected, alternately, to mixing and ultrasonic irradiation for a period of 20 min. The dose of hydrogen peroxide equal to 3.4 g/dm³ yielded a phenol removal of 34% at the oxidizing agent consumption of 42.3%. In the second run perhydrol was dosed during ultrasonic irradiation (fig. 2). It involved two perhydrol doses — 2.27 g H_2O_2/dm³ and 3.4 g H_2O_2/dm³; either of them was applied in one, two, three or four portions throughout the ultrasonic irradiation and mixing processes. The four-portion dosing was found to be the most effective. The increase of perhydrol dose has no substantial influence either on the degree of phenol conversion or perhydrol consumption. The dose of 2.27 g H_2O_2 /dm³ gave a phenol removal of 87% (at H_2O_2 consumption of 77%), whereas that of 3.4 g H_2O_2/dm³ yielded a phenol degradation of 81% (at H_2O_2 consumption of 60%).

Table 3

Phenol oxidation with hydrogen peroxide at ultrasonic irradiation
Utlenianie fenolu nadtlenkiem wodoru przy napromieniowaniu ultra dźwiękowym

Phenol concentration		Perhydrol concentration		Permanganate
initial	final	initial	final	COD
mg/dm³		g/dm³		mg O_2/dm³
200	132	3.40	1.45	210
	144	2.83	1.28	230
	164	2.27	1.02	310
	186	1.70	0.64	350

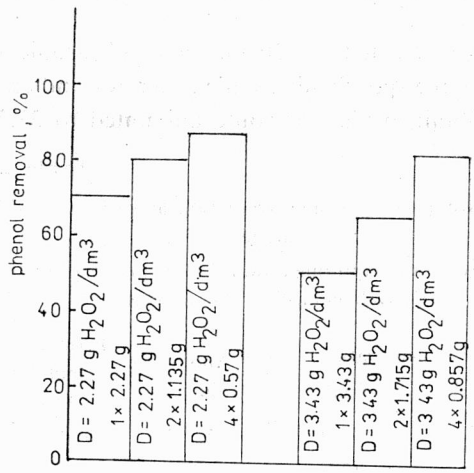

Fig. 2. Phenol removal vs. H_2O_2 dosing

Rys. 2. Usuwanie fenolu w zależności od dawki H_2O_2

4. DISCUSSION

The decrease in phenol concentration depends on the type of oxidizing agent and the degradation method employed (fig. 3). The highest degree of the degradation was obtained when the phenol solution was treated with ozone. Residual phenol concentrations persisting in the solution are pH-dependent. The level of pH is responsible for the course and the mechanism of ozonation reaction owing to which phenol is converted, and the intermediate reaction products are oxidized.

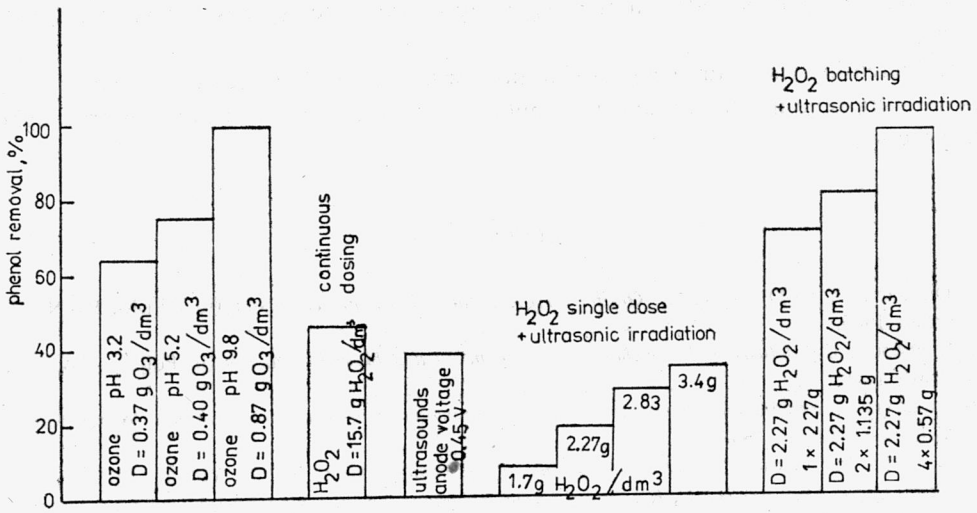

Fig. 3. Relations among phenol removal, treatment method, and process parameters

Rys. 3. Zależności między usuwaniem fenolu, metodą oczyszczania i parametrami procesu

Phenol oxidation in perhydrol treatment is not so pronounced. A perhydrol dose of 3.0 g H_2O_2/dm^3 gives phenol removals of about 30% (fig. 1), whereas the further increase of the oxidizing agent dose (even up to a fivefold one) improves the removal of phenol by 15% only.

Ultrasonic irradiation increases phenol conversion if certain requirements are fulfilled: irradiation combined with hydrogen peroxide treatment (in which the perhydrol dose has been applied at the beginning of the process) does not influence the conversion of phenol; the same holds for the oxidation of phenol with perhydrol alone (supplied continuously) (fig. 1). Phenol degradation with H_2O_2 can be considerably improved by ultrasonic irradiation if a perhydrol dose is supplied in portions throughout the process (fig. 2).

It is interesting to note that the increase in phenol conversion has been achieved with some reduced perhydrol dosage; its further increase does not exert any effect.

5. CONCLUSIONS

1. Ozonation provides the highest phenol removals. An ozone dose which is 1.7 times the theoretical one yields phenol removal of 98.5% at pH 9.8.

2. Good phenol removals (up to 87%) can be achieved by hydrogen peroxide treatment combined with ultrasonic irradiation in which the oxidizing agent dose (twice as high as the theoretical one) is applied in four portions throughout the process.

3. Application of hydrogen peroxide alone yields a poor conversion of phenol (up to 45%) although the oxidizing agent dose is 16 times the theoretical dose.

4. Ultrasonic irradiation in conjuction with hydrogen peroxide treatment in which the oxidizing agent is added at the beginning of the process does not yield interesting results.

5. Increasing the hydrogen peroxide dose will not improve the conversion of phenol despite ultrasonic irradiation and the application of the oxidant in portions trhroughout the process.

REFERENCES

[1] DURRANT P. J., DURRANT B., *Outline of the modern inorganic chemistry* (in Polish), PWN, Warszawa 1965.

[2] ELPINER I. E., *Ultrasounds — their physicochemical and biological action* (in Polish), PWN, Warszawa 1968.

[3] GILBERT E., *Reaction of ozone with transtrans muconic acid in aqueous solution*, Water Research, Vol. 14 (1980), p. 1637.

[4] GOULD J. P., WEBER W. J., *Oxidation of phenols by ozone*, Journal WPCF, Vol. 48 (1976), p. 47.

[5] HEVES C. G., DAVISON R. R., *Kinetics of ozone decomposition and reaction with organics in water*, Am. Inst. Chem. Engrs. Journ., Vol. 17 (1971), p. 141.

[6] HOIGNE J., BADER H., *The role of hydroxyl radical reactions in ozonation processes in aqueous solutions*, Water Research, Vol. 10 (1976), p. 377.

[7] KLOBEI H., RALEIGH C. W., *Hydrogen peroxide industrial pollution control*, Industrial Waters, Vol. 11 (1972), p. 41.

[8] KORENMAN I. M., *Photometric analysis* (in Polish), WNT, Warszawa 1976.

[9] LESZCZYŃSKA D., KOWAL A. L., *Destruction of the selected phenol compounds with ozone* (in print).

[10] MINCZEWSKI J., MARCZENKO Z., *Analytical chemistry* (in Polish), PWN, Warszawa 1965.

[11] PIOTROWSKA A., *Ultrasounds in chemistry* (in Polish), PWN, Warszawa 1968.

[12] *Standard Methods for Examination of Water and Wastewater*, American Public Health Association INC, 1960.

WPŁYW FALI ULTRADŹWIĘKOWEJ NA UTLENIANIE FENOLU OZONEM I NADTLENKIEM WODORU

Aby przyspieszyć utlenienie fenolu w roztworze modelowym z nadtlenkiem wodoru i ozonem zastosowano fale ultradźwiękowe. Rozkład fenolu badano w zależności od dawek czynnika utleniającego, metod dozowania, pH roztworu i mocy wejściowej generatora fali ultradźwiękowej. Fale ultradźwiękowe poprawiały wydajność utlenienia nadtlenkiem wodoru, ale najlepszym czynnikiem utleniającym był ozon.

EINFLUSS DER ULTRASCHALLWELLEN WÄHREND DES PHENOLABBAUS MIT OZON UND WASSERSTOFFPEROXYD

Um die Oxydation des Phenols mittels Ozon und Wasserstoffperoxyd in einer Modellösung zu beschleunigen, zur Anwendung kamen Ultraschallwellen. Der Phenolabbau wurde anhand der Dose des Oxydationsmittels, der Dosierungsmethoden, des pH-Wertes der Lösung und der Eingangskraft des Ultraschallgenerators verfolgt und bewertet. Die Ultraschallwellen begünstigen die Oxydation mit Wasserstoffperoxyd, aber beste Resultate sind der Wirkung des Ozons zuzuschreiben.

ВЛИЯНИЕ УЛЬТРАЗВУКОВОЙ ВОЛНЫ НА ОКИСЛЕНИЕ ФЕНОЛА ОЗОНОМ И ПЕРЕКИСЬЮ ВОДОРОДА

Чтобы ускорить окисление фенола в модельном растворе с перекисью водорода и озоном, были применены ультразвуковые волны. Распределение фенола исследовалось в зависимости от доз окислителя, методов дозирования, pH раствора и входной мощности генератора ультразвуковой волны. Ультразвуковые волны улучшили выход окисления перекисью водорода, однако наилучшим окислителем был озон.