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## DESTRUCTION OF THE SELECTED PHENOL COMPOUNDS WITH OZONE

Phenolic compounds with the increasing number of hydroxyl groups and different arrangement of the groups in benzene ring have been selected. The process of aromatic ring opening by means of ozone has been investigated at elevated, lowered and nonadjusted pH, characteristic of the water solutions of phenols.

It has been stated that pH directly influences the direction of ozone reaction with phenols, the formation of intermediate products, and the process efficiency. No direct relationship has been stated between the arrangement of hydroxyl groups in aromatic ring and the efficiency of the process conducted at the given pH of the medium.

The purpose of the paper was to establish the effects of the pH value and concentrations of the compounds investigated and ozone on the course of phenol destruction in water.

The following compounds: phenol (1-hydroxybenzene), pyrocatechol (1,2-dihydroxybenzene), resorcinol (1,3-dihydroxybenzene), hydroquinone (1,4-dihydroxybenzene), pyrogallol (1,2,3-trihydroxybenzene) have been selected and examined at the concentrations of 100, 200, 300, 400, and 500 mg/dm<sup>3</sup>. The experiments have been conducted at elevated initial pH increased to pH 10, lowered to pH 3, and without initial correction (pH 5-6), depending on the kind and concentration of the compound examined. Decomposition of compounds was investigated at temperature of  $292 \pm 2$  K and at identical intensity of ozone flow and way of its dosage. Ozone was introduced into two systems operating parallelly [7]. In system I the reactor was fed with an established (100 dm<sup>3</sup>/h) volume of air with ozone. The excess of unreacted oxygen was retained in a gas washer placed behind the reactor and containing 2% solution of potassium iodate. In the system II the initial amount of ozone introduced into reactor was measured. The difference gave the amount of ozone consumed in the given sample. The concentration of ozone was determined according to Standard Methods [9] using iodometric method.

Solutions of phenolic compounds were prepared immediately before the experiments. Their final concentrations were determined spectrophotometrically, using the reaction coupling phenolic compounds with diazo-p-nitroaniline in alkaline medium [6].

The colour of solution ozonized was also determined spectrophotometrically at the wavelength  $\lambda = 500$  nm.

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Total organic carbon (TOC) was determined using the Beckman model 915 of total organic carbon analyser.

The pH of solutions was measured potentiometrically on a pH-meter of the type N-512. The pH was corrected with solution of sulphuric acid 1:5 or 1M solution of sodium hydroxide.

## 2. RESULTS OF INVESTIGATIONS

The conducted investigations allowed to state a distinct influence of the medium pH on the mechanism and efficiency of the destruction of benzene ring and the products of its decomposition. The reaction efficiencies of the examined phenolic compounds with

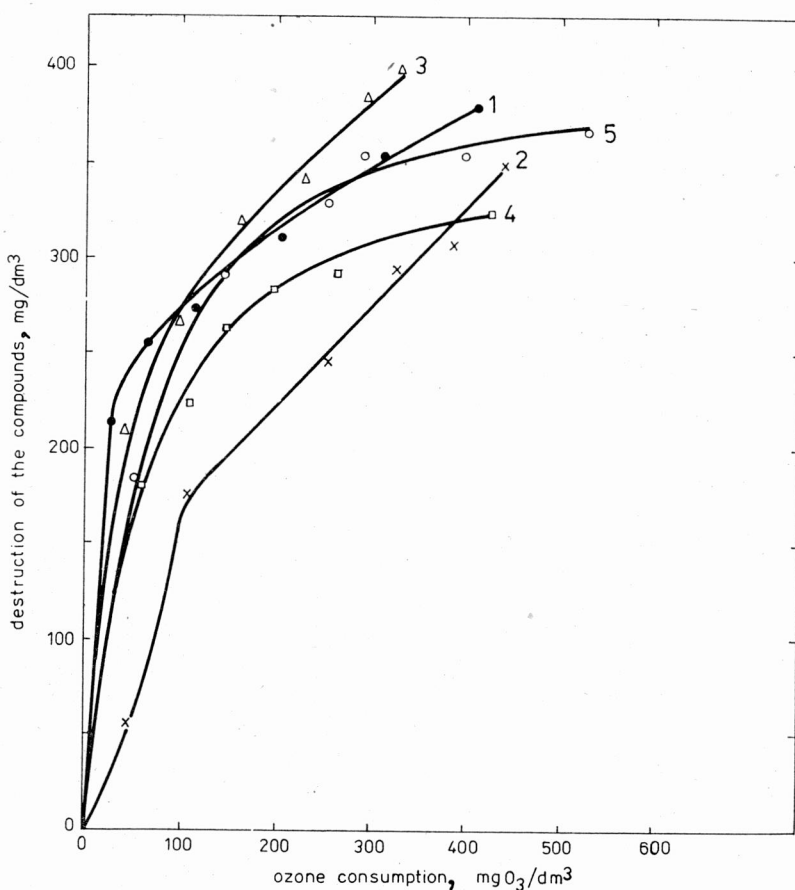


Fig. 1. Destruction of the phenolic compounds vs. ozone consumption at pH 9.8-10.1

$C_0 = 400 \text{ mg/dm}^3$ ; 1 - phenol, 2 - catechol, 3 - resorcinol, 4 - hydroquinone, 5 - pyrogallol

Rys. 1. Zależność przereagowania związków fenolowych od ilości zużytego ozonu przy pH 9,8-10,1

$C_0 = 400 \text{ mg/dm}^3$ ; 1 - fenol, 2 - katechina, 3 - rezorcyna, 4 - hydrochinon, 5 - pirogalol

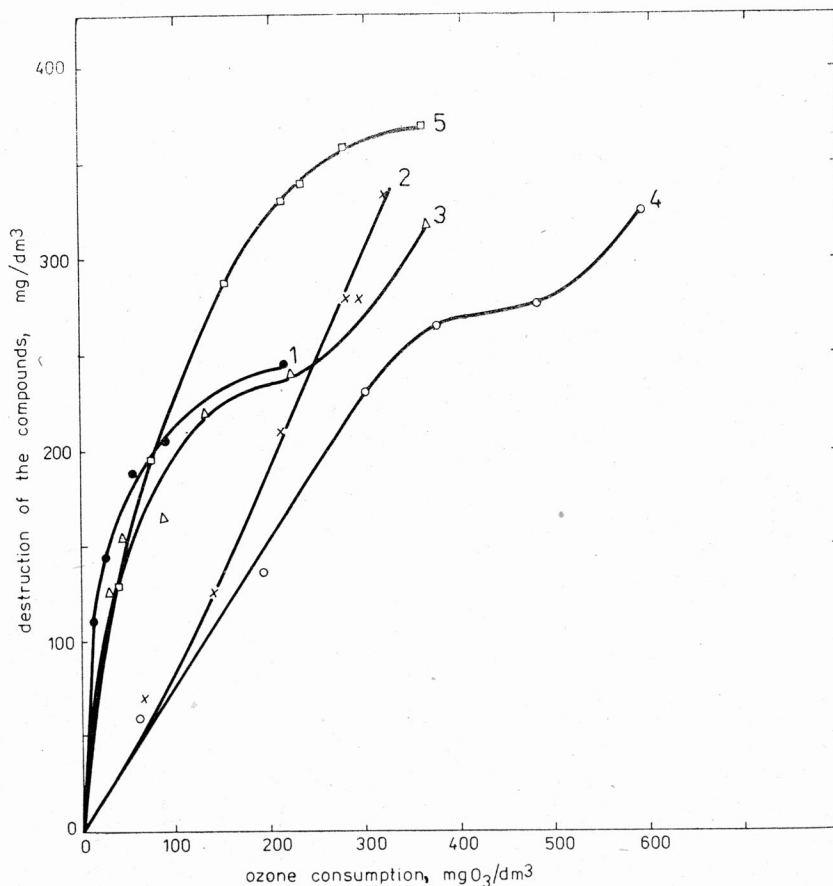


Fig. 2. Destruction of the phenolic compounds vs. ozone consumption at pH 3.0-3.3

For explanations-see fig. 1

Rys. 2. Zależność przereagowania związków fenolowych od ilości zużytego ozonu przy pH 3,0-3,3

Objaśnienia jak na rys. 1

ozone at the initial pH 9.8-10.1, 3.0-3.3, and 5.0-6.1 are presented in figs. 1, 2, 3, respectively. Ozone consumption required for the destruction of the same amount of the given phenolic compound depended on the pH of the medium (figs. 1, 2, 3). In reaction of ozone with the selected compound pH decreased with the formation of acidic compounds coming from destruction of the benzene ring (figs. 4, 5, 6). The amount of acids depended on the initial pH and the kind of compound. For the given phenolic compound reacting with ozone the increments of hydrogen ion concentration in acid (pH 3) and slightly acid solution (pH 5-6) were similar (figs. 5 and 6, respectively). A distinctly smaller increment of the hydrogen ion concentration was stated when ozonation was conducted at initial pH ele-

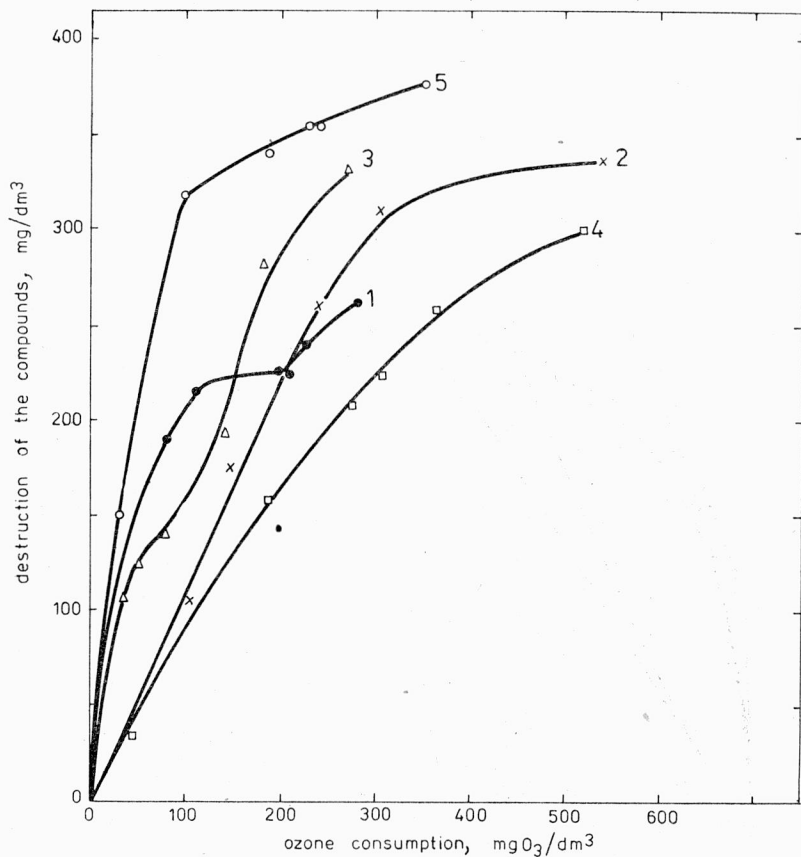


Fig. 3. Destruction of the phenolic compounds vs. ozone consumption at pH 5.0-6.1

For explanations see fig. 1

Rys. 3. Zależność przereagowania związków fenolowych od ilości zużytego ozonu przy pH 5,0-6,1

Objaśnienia jak na rys. 1

vated to pH 10 (fig. 4). Under the above condition the reaction run through the stage of colour products manifested by the colouring of the ozonized solution, its increasing intensity (fig. 7 A, B) and, finally, by its disappearance (fig. 7 A). The maximum colouring of the solutions, due to the formation of quinones, occurred at varying amounts of the compounds reacting (fig. 7 A), whereas the amount of oxygen required for the maximum colour was similar for all the phenols (fig. 7 B).

Theoretically, ozonation of phenolic compounds should lead to carbon dioxide and water [2]. Under the investigation conditions a total destruction was achieved only for a part of phenols, for the remaining compounds the decomposition stopped at intermediate products. The efficiency of TOC removal from the system during ozonation of phenolic com-

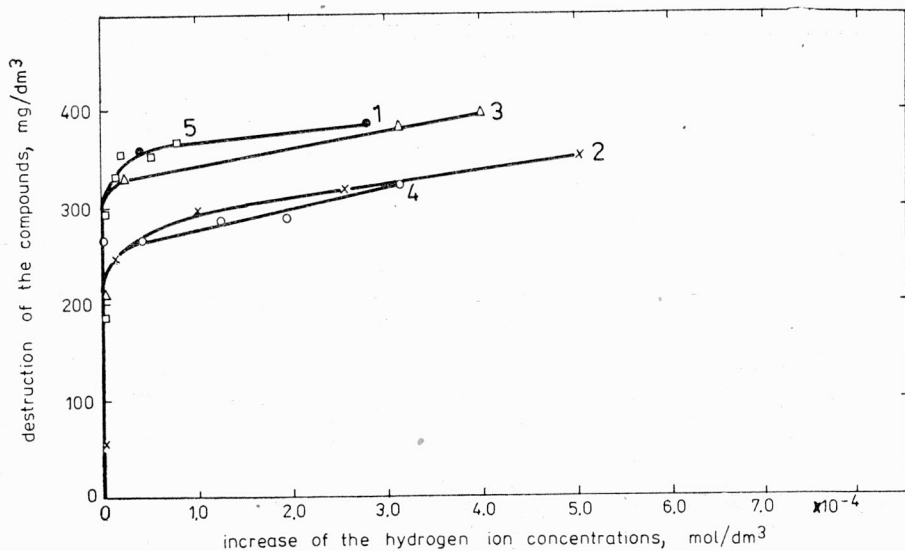


Fig. 4. A comparison of the increase of hydrogen ion concentrations for various phenolic compounds at pH 9.8-10.1

For explanations see fig. 1

Rys. 4. Porównanie przyrostu stężenia jonów wodorowych w reakcji ozonowania związków fenolowych przy pH 9,8-10,1

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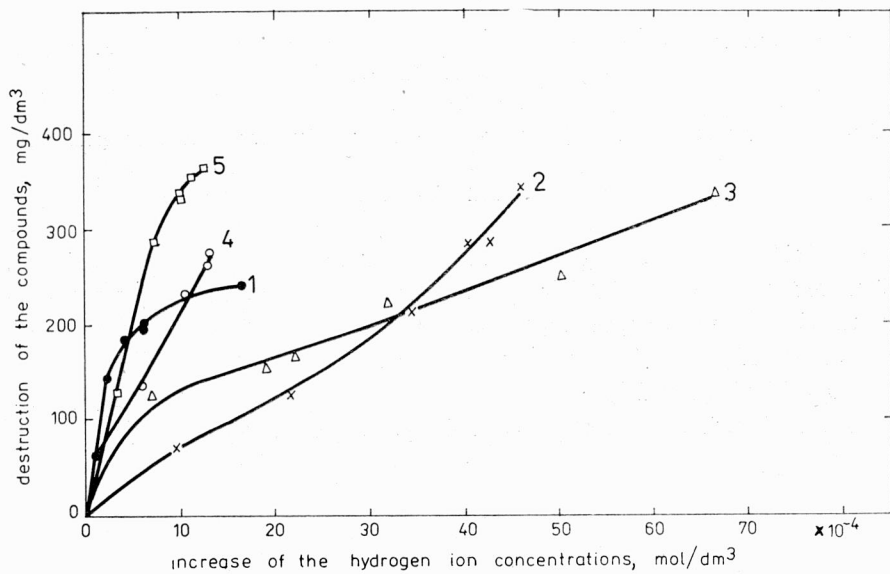


Fig. 5. A comparison of the increase of hydrogen ion concentrations for various phenolic compounds at pH 3.0-3.3

For explanations see fig. 1

Rys. 5. Porównanie przyrostu stężenia jonów wodorowych w reakcji ozonowania związków fenolowych przy pH 3,0-3,3

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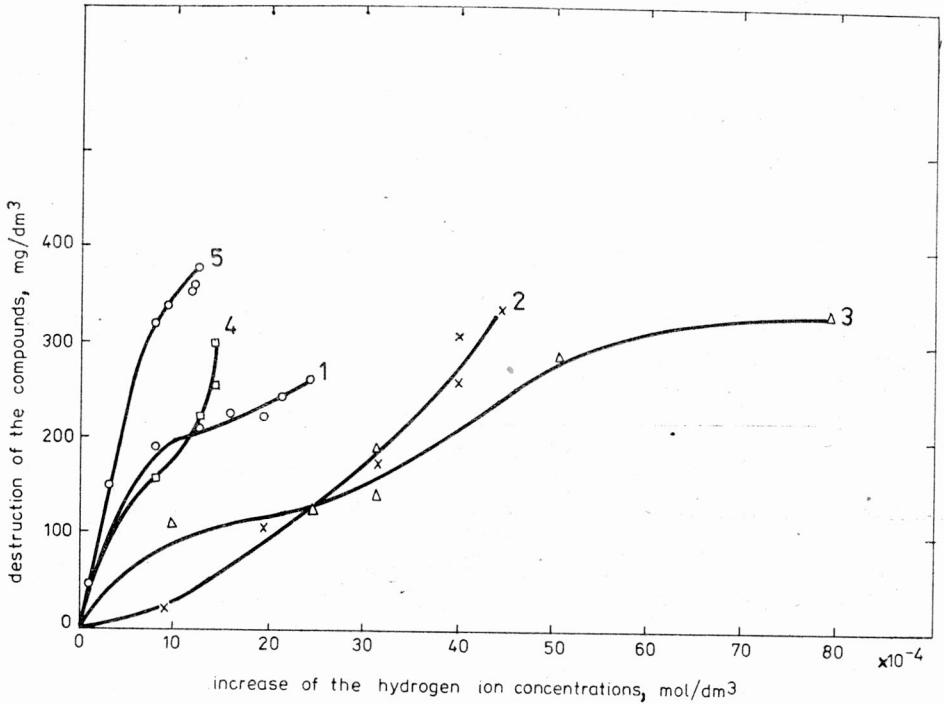


Fig. 6. A comparison of the increase of hydrogen ion concentrations for various phenolic compounds at pH 5.0-6.1

For explanations see fig. 1

Rys. 6. Porównanie przyrostu stężenia jonów wodorowych w reakcji ozonowania związków fenolowych przy pH 5,0-6,1

Objaśnienia jak na rys. 1

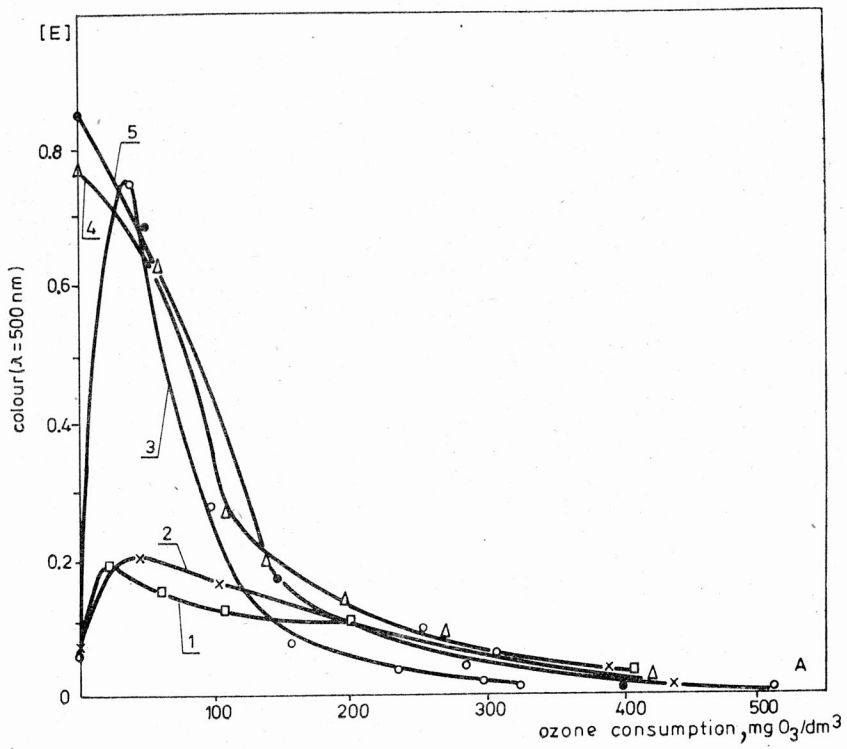
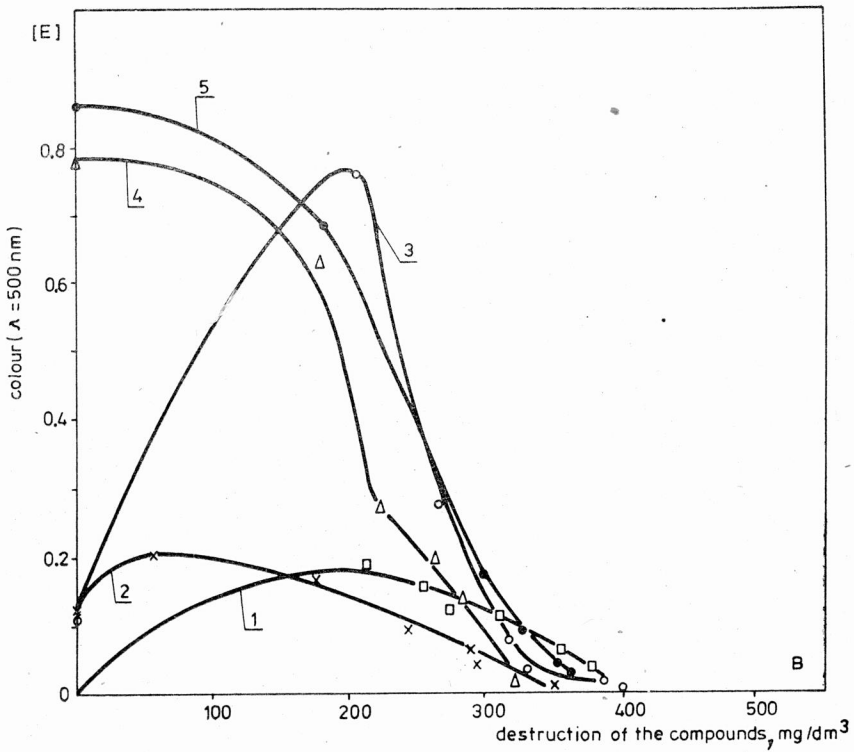
pounds in alkaline, acid, and slightly acid media was presented in figs. 8, 9 and 10, respectively. The reduction of the TOC in ozonation process, taken as a measure of the total destruction of phenolic structure, depended on pH, the ratio of ozone to the given phenol, and on its kind. In none of the systems examined the reduction of TOC concentration exceeded 40%. The highest degree of destruction has been stated when phenols were ozonized at the pH of medium characteristic of the given compound (fig. 10).

Fig. 7. Colour variation during ozonation of phenolic compounds at pH 9.8-10.1

For explanations see fig. 1

Rys. 7. Porównanie zmian natężenia barwy w reakcji ozonowania związków fenolowych przy pH 9,8-10,1

Objaśnienia jak na rys. 1



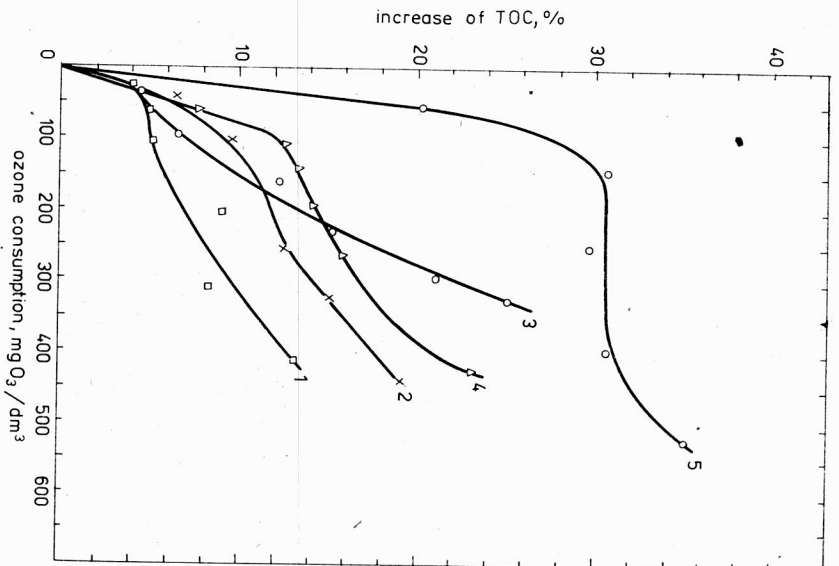


Fig. 8.

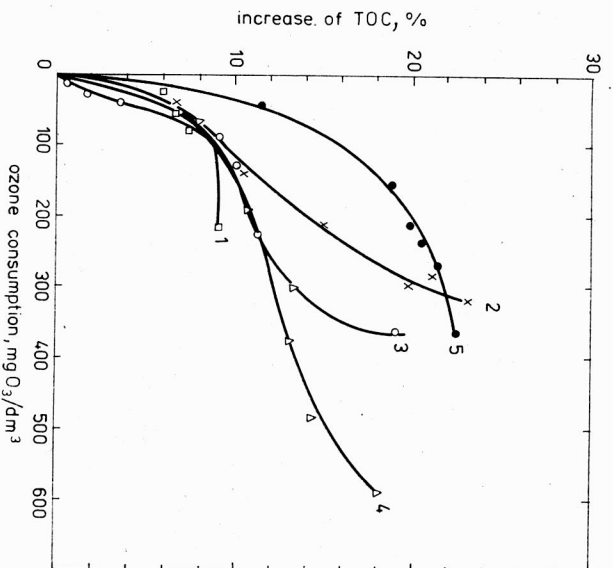


Fig. 9.



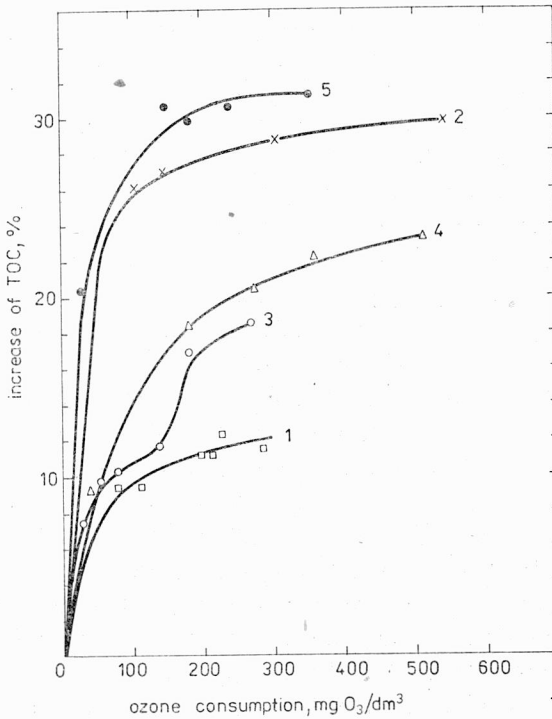


Fig. 10. A removal of the TOC vs. ozone consumption during the phenolic compounds ozonation at pH 5.0-6.1

For explanations see fig. 1

Rys. 10. Efektywność usuwania CWO podczas ozonowania związków fenolowych przy pH 5,0-6,1  
Objaśnienia jak na rys. 1

Fig. 8. A removal of the TOC vs. ozone consumption during the phenolic compounds ozonation at pH 9.8-10.1

For explanations see fig. 1

Rys. 8. Efektywność usuwania CWO podczas ozonowania związków fenolowych przy pH 9,8-10,1  
Objaśnienia jak na rys. 1

Fig. 9. A removal of the TOC vs. ozone consumption during the phenolic compounds ozonation at pH 3.0-3.3

For explanations see fig. 1

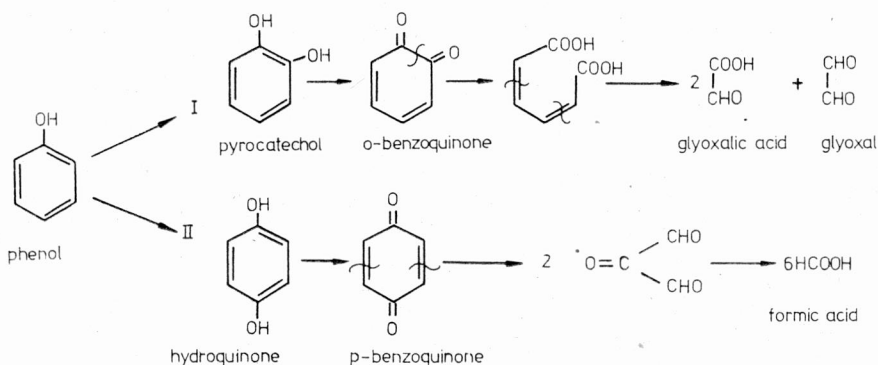
Rys. 9. Efektywność usuwania CWO podczas ozonowania związków fenolowych przy pH 3,0-3,3  
Objaśnienia jak na rys. 1

## 3. DISCUSSION OF RESULTS

Destruction of phenolic compounds with different number of hydroxyl groups and different arrangement of these groups in aromatic ring led, depending on the pH, through different intermediate products, hence different amounts of ozone were required. The pH decided also whether ozone introduced into reactor reacted directly or it was dissociated in water into more reactive ions and radicals [8]. In acid medium only small amount of ozone was dissociated, hence the reaction occurred directly between ozone molecules and substances dissolved in water [5]. In alkaline medium the active products of ozone dissociation were reacting, hence a number of oxidation reactions characterized by a low selectivity took place simultaneously [4, 5].

Investigations conducted on model solutions of phenolic compounds allowed to state that at the given pH the reaction with ozone takes a different course up to the moment of the ring opening. The products, being the fragments of the ring, were similar for each compound examined.

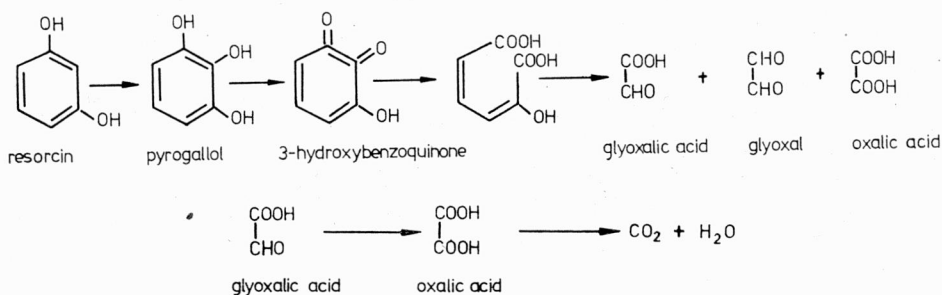
Investigations by EISENHauer [2], GOULD and WEBER [3], and DORE [1], conducted in phenol solutions at elevated pH and referring among others to the structure of intermediate products, have confirmed the presence of pyrocatechol and hydroquinone at the initial stage of ozonation. Further course of reaction led to the formation of o-benzoquinone and p-benzoquinone, respectively, and then to glyoxal, glyoxalic acid, oxalic acid and formic acid. The data given by mentioned above scientists as well as the author's own results allowed to present a probable course of the phenol structure destruction at the elevated initial pH:



According to GOULD and WEBER [3] the reaction leading through pyrocatechol and then o-benzoquinone prevailed, whereas DORE [1] suggests the p-benzoquinone pathway. The concept presented above has been confirmed by the results obtained from ozonation of pyrocatechol and hydroquinone, conducted by the authors under the above conditions. Transition of hydroquinone into p-benzoquinone (colour compound) can be obtained

very soon in the presence of atmospheric oxygen (fig. 7). Analogical transformation of pyrocatechol into o-benzoquinone required much more time or the presence of greater amounts of oxygen. With a given amount of oxygen consumed, the greatest (in %) reduction of TOC (fig. 8) has been obtained for hydroquinone, and then to pyrocatechol. The smallest effects have been obtained for phenol, which may be due to the consumption of oxygen for the increased amount of intermediate products and to inhibitory properties of some of these compounds.

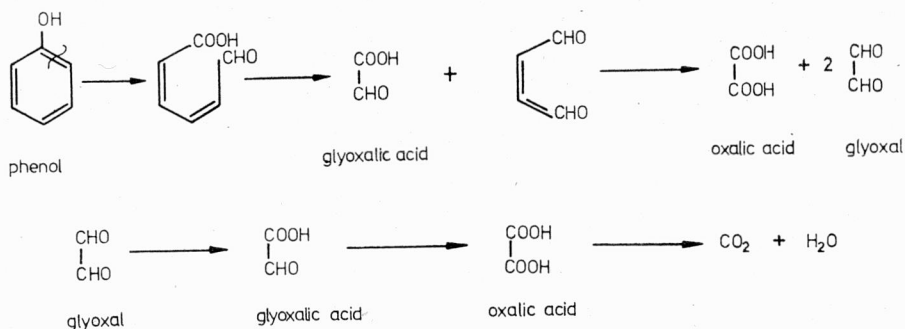
In the above conditions the ozonation of resorcin took initially a different course, namely:

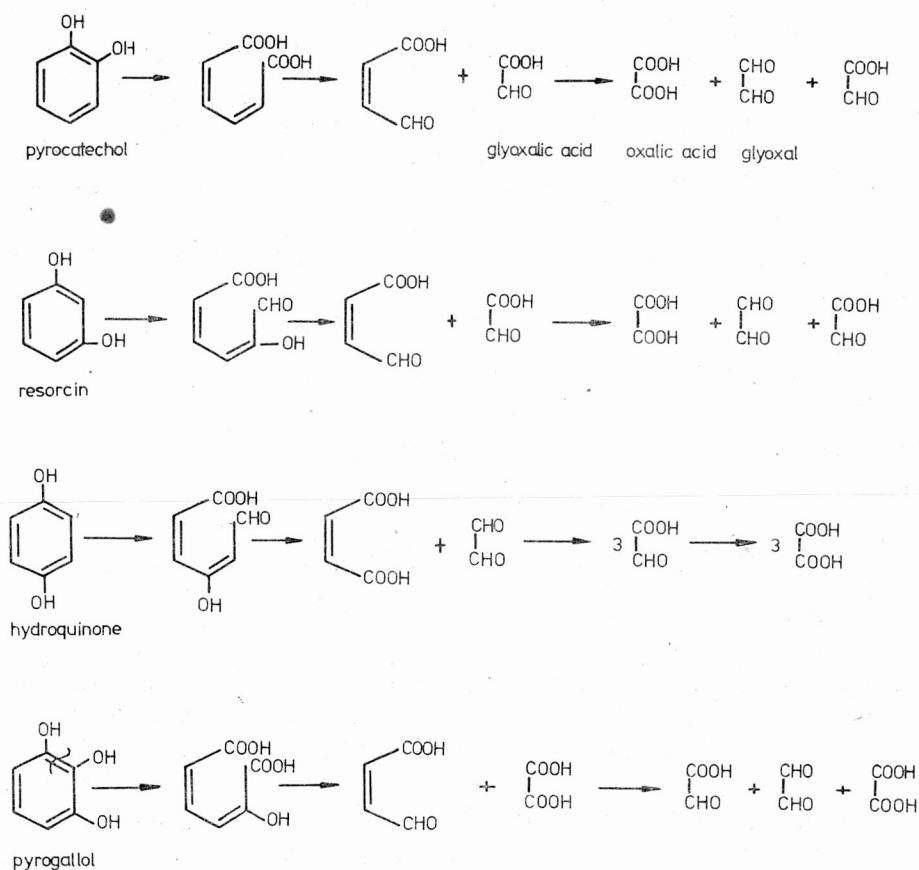


The first intermediate product — pyrogallol — was transformed into the respective quinone which coloured the solution. Under the influence of atmospheric oxygen pyrogallol is directly transformed into a quinone compound (fig. 7). A higher increment in concentration of hydrogen ions was obtained during ozonation of resorcin (fig. 4), whereas a greater reduction of TOC was observed during ozonation of pyrogallol (fig. 8), proving that the oxidation reaction run directly without intermediate products.

In ozonization of phenolic compounds at the reduced initial pH the stage of quinone compounds formation was omitted (absence of colour or a slight colouring of solutions) and the process led to a direct opening of aromatic ring.

Basing on the results obtained the following pathways have been proposed for the selected compounds:





During ozonation of phenolic compounds in slightly acid medium, characteristic of the given compound, the reaction run probably through quinones and simultaneously a direct opening of the ring (colouring of solution was less intense than during ozonation at higher pH). At pH 5-6 ozone was partly dissociated in water, thus the ozonation of double bonds in aromatic ring and oxidation with oxygen from ozone and products of its dissociation in water occurred simultaneously.

Reduction of the initial concentration of phenolic compounds with the lowest dosage of oxygen cannot be used as a basic criterion for determining the efficiency of ozonation process, as it has been assumed till now. The drop in the concentration is not tantamount to the course of reaction till its very end, i.e. to carbon dioxide and water.

Fig. 11 represents a comparison of the destruction of phenolic compounds versus ozone consumption for various pH values. It follows that the greatest decrease of the initial amount of the phenolic compound can be obtained in ozonation at the elevated pH 10. The oxidation occurred according to the following order:



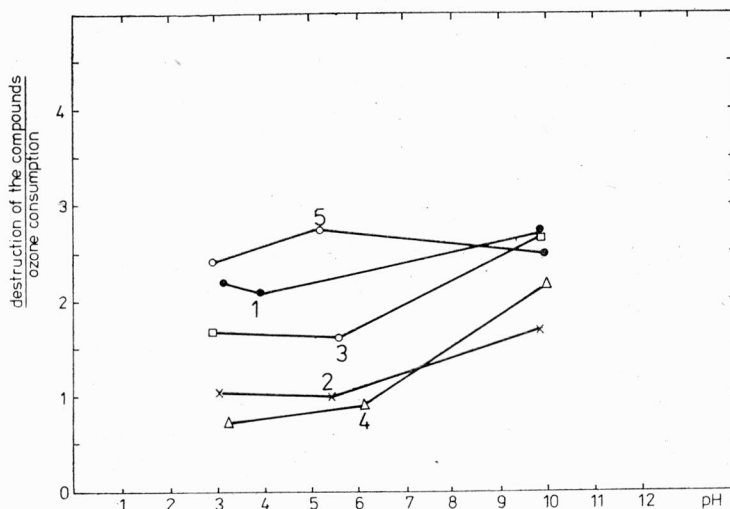


Fig. 11. A comparison of the destruction of phenolic compounds vs. ozone consumption for various pH values

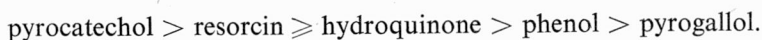
For explanations see fig. 1

Rys. 11. Porównanie zależności przereagowania związku fenolowego od ilości zużytego ozonu dla różnych wartości odczynu środowiska

Objaśnienia jak na rys. 1

Pyrallogol was the only exception to this rule, since its optimum pH in this system was 5.

The efficiency of a total destruction of phenols by ozonation can be established from the relationship shown in fig. 12. The best effects in reduction of TOC was obtained when the reaction occurred at noncorrected pH (pH 5-6). In this case the compounds being oxidized were arranged in a different order:



pH 10 being the optimum value for pyrogallol.

The comparison of ozonation effects of the given compound at different values of pH and using as basic criterion either the reduction of the concentration of this compound (being the first stage of the reaction) or the reduction of TOC (characterizing the last stage of this process) gave the quantitatively different results (table).

From the data presented in the table it follows that:

for phenol the greatest reduction of TOC was obtained at pH 5, although at this pH value the reduction of the initial concentration of this compound was the smallest;

for pyrocatechol the effect of TOC removal was optimal at pH 5, while at higher pH the destruction degree was higher;

for hydroquinone TOC removal was the same independently of the initial pH, and the effect was similar to that of phenol ozonation at pH 3 or that of resorcinol and pyrogallol

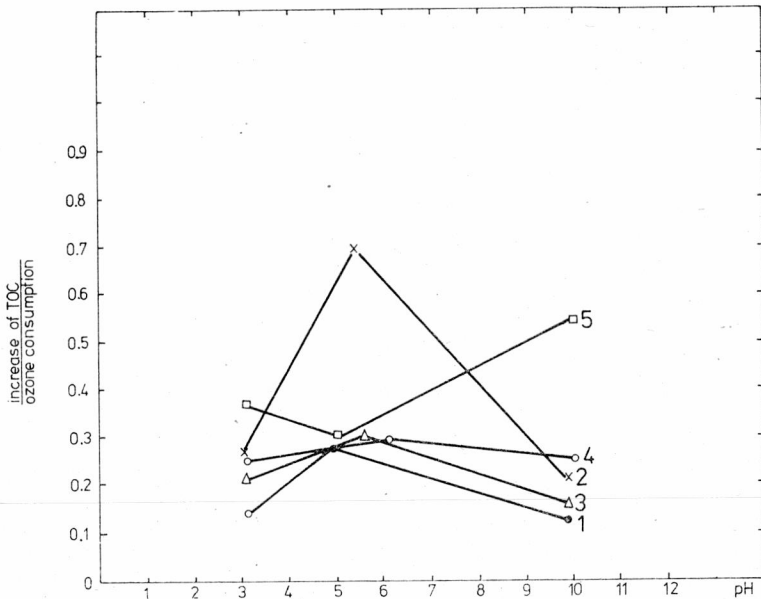


Fig. 12. A comparison of the decrease of TOC vs. ozone consumption for various pH values

For explanations see fig. 1

Rys. 12. Porównanie zależności obniżenia CWO od ilości zużytego ozonu dla różnych wartości odczynu środowiska

Objaśnienia jak na rys. 1

Table

Optimal pH in phenolic compound concentration and TOC reductions

Optymalne pH przy obniżaniu stężenia związku fenolowego i CWO

Compound	Compound reacted/O <sub>3</sub> consumed	Reduction of TOC/O <sub>3</sub> consumed
Phenol	pH 10 > pH 3 > pH 5	pH 5 > pH 3 > pH 10
Pyrocatechol	pH 10 > pH 3 > pH 5	pH 5 > pH 3 > pH 10
Resorcin	pH 10 > pH 3 > pH 5	pH 5 > pH 3 > pH 10
Hydroquinone	pH 10 > pH 5 > pH 3	pH 5 > pH 3 = pH 10
Pyrogallol	pH 5 > pH 10 > pH 3	pH 10 > pH 3 > pH 5

at pH 5, whereas a distinctly increased degree of destruction was observed at pH 10;

for pyrogallol the highest degree of destruction occurred at pH 5, and the greatest TOC removal at pH 10.

#### 4. CONCLUSIONS

1. Effectiveness of phenolic compounds ozonation depends on the pH of the medium.

2. At the given pH the reactions of ozone with phenolic compounds follow similar directions.

3. The highest reduction of the initial concentrations of the compounds examined occurred at elevated pH (except for pyrogallol).
4. The highest TOC removal was obtained at noncorrected initial pH (except for pyrogallol). Reduction of the TOC is equivalent to the total destruction of the product to carbon dioxide and water.

## REFERENCES

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## NISZCZENIE OZONEM WYBRANYCH ZWIĄZKÓW FENOLOWYCH

Wybrano związki fenolowe o wzrastającej liczbie grup hydroksylowych i różnym ich ułożeniu w pierścieniu benzenowym. Badano przebieg otwierania pierścienia aromatycznego za pomocą ozonu w podwyższonym, obniżonym oraz niekorygowanym, charakterystycznym dla roztworów fenoli w wodzie, odczynie środowiska. Stwierdzono bezpośredni wpływ pH na kierunek przebiegu reakcji ozonu z fenolami, na powstające produkty pośrednie oraz na efektywność procesu. Nie stwierdzono prostej zależności między ułożeniem grup hydroksylowych w pierścieniu aromatycznym a efektywnością procesu prowadzonego przy danym odczynie środowiska.

## VERNICHTUNG AUSGEWÄHLTER PHENOLVERBINDUNGEN MIT HILFE VON OZON

Untersucht wurden Phenolverbindungen mit wachsender Zahl der Hydroxylgruppen und verschiedener Placierung im Benzolring. Untersucht wurde der Zerfall des Aromatringes durch Ozon in einem erhöhten, abgesenkten sowie nicht korrigierten, für wässrige Phenollösungen charakteristischen pH-Wert.

Festgestellt wurde ein direkter Einfluß des pH-Wertes auf den Reaktionsverlauf des Ozons mit den Phenolen, auf die Derivatbildung sowie auf die Effektivität des Verfahrens. Leider konnte man nicht feststellen, ob zwischen der Placierung der Hydroxylgruppen im Aromatring und dem Resultat des Verfahrens bei festgelgtem pH eine direkte Beziehung besteht.

## РАЗРУШЕНИЕ ОЗОНОМ ИЗБРАННЫХ ФЕНОЛЬНЫХ СОЕДИНЕНИЙ

Были избраны фенольные соединения с возрастающим числом гидроксильных групп и с различным их расположением в бензольном кольце. Исследовался ход раскрытия ароматического ядра с помощью озона, в повышенной, пониженной и некорректированной, характерной для расщепления фенолов в воде, реакции среды. Выявлено непосредственное влияние рН на направление хода реакции озона с фенолами, на образующиеся промежуточные продукты, а также на эффективность процесса. Не выявлено прямой зависимости между расположением гидроксильных групп в ароматическом ядре и эффективностью процесса, проводимого при данной реакции среды.