Effect of pH to the Decomposition of Aqueous Phenols Mixture by Ozone

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Abstract. The degradation of the mixture of phenol and its chlorinated derivatives with ozone is studied. The studied compounds are phenol (Ph), 4 – chlorophenol (4-CPh) and 2,4 – dichlorophenol (2,4-DCPh). The kinetic performances of each phenolic compound in the model mixture are examined. The pH influence to the decomposition dynamics for different phenolic compounds in the range 2 – 12 is investigated. The increase of the decomposition rate under the pH increasing was observed. In the studied pH range, phenol and chlorophenols ozonation proceeds rapidly. The UV absorvency is used for the preliminary control of the phenols decomposition degree. The HPLC analysis was used to identify intermediates and final products formed during ozonation of the phenols mixture. It is shown that the basic intermediates are muconic and fumaric acids, malonic and maleic acids, catechol and hydroquinone. The final products are oxalic acid and formic acid. In the case of alkaline media, the principal final product is oxalic acid. Furthermore, intermediates and final decomposition products obtained at the different pH are compared. According to the obtained results, the possible mechanism of ozonation by the reaction of hydroxylation and dechloration in the early stage is proposed. The BOD₅/COD ratio is used as a biodegradability measure for the comparison of biodegradability of initial compounds and final products composition.
Key words: ozonation, water, phenols, decomposition, pH.

Resumen. Se estudió la degradación con ozono de la mezcla de fenol y sus derivados clorados. Los compuestos estudiados fueron fenol (Ph), 4-clorofenol (4-CPh) y 2,4-diclorofenol (2,4-DCPh). Se determinó el comportamiento cinético de cada compuesto fenólico en la mezcla modelo. Se investigó la influencia del pH en la dinámica de descomposición de los diferentes compuestos fenólicos en un intervalo de 2-12. Se observó el incremento en la velocidad de descomposición conforme aumentaba el pH. En el intervalo de pH's estudiado, la ozonación del fenol y clorofenoles se realizó eficientemente. La absorbancia en UV de cada compuesto fue utilizada como método de control preliminar del grado de descomposición de cada compuesto fenólico. Se realizó el análisis usando cromatografía de líquidos (HPLC) para identificar los productos intermediarios y finales formados durante la ozonación de la mezcla de fenoles. Dicho análisis mostró que los compuestos intermediarios principales son: los ácidos mucónico, fumárico, malónico y maléico; al igual que ácido oxálico y fórmico. En el caso del medio básico, el producto final principal es ácido oxálico. Además, se realizó una comparación de la descomposición de los productos intermediarios y finales a diferentes pH's. De acuerdo a los resultados obtenidos, se proponen las reacciones de hidroxilación y decloración como etapas iniciales del mecanismo de ozonación. La relación BOD₅/COD es utilizada como una medida de la biodegradabilidad del sistema para comparar la biodegradabilidad de la mezcla inicial y la mezcla final una vez ozonada.
Palabras Clave: ozonización, agua, descomposición, fenoles, pH.

Introduction

Phenol and chlorinated phenols (CPHs) are commonly found as micro pollutants in water. They can be formed indirectly during chlorination of municipal or industrial wastewater, bleaching in paper industry, or during bioconversion of low molecular weight compounds. They are also widely used in pesticides production. Phenolic compounds are common pollutants in wastewater of oil refinery, petrochemical, coke, and grease, due, steel and textile industries [1-2]. These contaminants are difficult to be decomposed in the wastewater [3, 4]. CPHs constitute the characters of toxicity, refractory and difficulty to be oxidized by the traditional biological treatment. The efficiency of conventional biological treatment is usually not satisfactory due to long time and limited initial concentration of pollutants [5-8]. Recently, the combination of the biodegradation with the preliminary ozonation for water treatment has drawn great attention [9-11].

In this study, the decomposition of phenols model mixtures in aqueous solution with ozone is examined. The studied

organic pollutants are phenol (Ph), 4 – chlorophenol (4-CPh), 2,4 – dichlorophenol (2,4 – DCPh). The pH influence to decomposition dynamics for different phenols in the range 2 – 12 is studied too. The objective of this study is to identify intermediates and final reaction products in the phenols mixtures ozonation and to compare the final compounds in reaction of individual phenols with ozone [12]. The UV absorbency is used for preliminary control of the phenols decomposition degree. The HPLC analysis is applied to identify intermediates and final products. The measure of BOD₅/COD ratio is proposed for the biodegradability comparison of the initial phenols mixture and the final products composition [13–18].

Experimental

Studied Compounds

The mixtures of phenols (Ph) (J.T. Baker), 4 –chlorophenol (4-CPh) (Sigma Chemical Co), and 2,4–dichlorophenol (2,4 –

DCPh) (Sigma Chemical Co) were studied. All chemicals were of analytical grade.

Ozonation Procedure

The ozonation of the phenols mixtures were conducted with synthetic solutions in distilled water with the variation of the initial organics concentration (see Table 1). The reactor was a semi-batch type (0.500 L). Initial ozone concentration was 27-30 mg L^{-1}. The ozone-oxygen mixture flow was 0.5-L min^{-1}. All experiments were carried out at 20°C with agitation by bubbling of an ozone-oxygen mixture and by a magnetic agitation (operated at 120 rpm). All ozonation experiments have been produced varying the pH from 2 to 12. The pH variation was performed with sulfuric acid and sodium hydroxide (0.05 N). For all experiments, aliquots of 3 mL reaction solution were withdrawn at desired time intervals from the reactor for sequent analyses. Figure 1 represents the schematic diagram of the ozonation apparatus.

Ozone Generation and Ozone Consumption Control

Ozone was generated from dry oxygen by the ozone generator (corona discharge type) HTU500G ("AZCO" Industries Limited - Canada). The Ozone Analyzer BMT 963 (BMT Messtechnik, Berlin) provides the ozone detection in the gas phase in the reactor outlet for the ozone monitoring to control the ozonation degree, the ozone consuming and the ozone decomposition [12].

Table 1. Variation of the initial composition of phenols in the model mixtures.

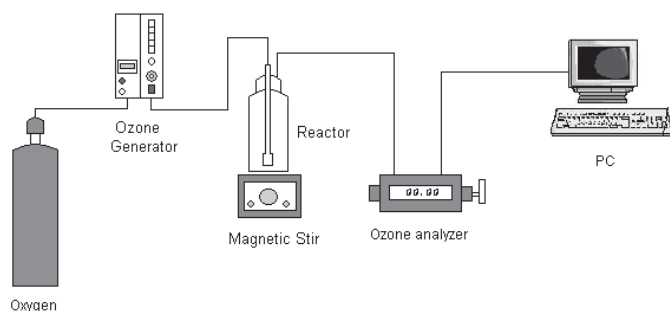| Model mixture number	Ph, mg/L	4-CPh, mg/L	2,4-DCPh, mg/L	Total concentration, mg/L
1	100	100	100	300
2	125	125	50	300
3	83.33	33.33	83.33	200
4	33.33	83.33	83.33	200

Fig. 1. Schematic diagram of the ozonation apparatus.

Determination of the BOD$_5$/COD ratio for the biodegradability measure

The effect of ozonation to the biodegradability of the studied phenols mixtures was investigated by the determination of the BOD$_5$/ COD ratio before and after ozonation. The BOD$_5$ and COD parameters were measured according to Mexican norms (NMX-AA-030-SCFI-2001 for COD and NMX-AA-028-SCFI-2001 for BOD$_5$) [20, 21].

Analytical methods

The control of the phenols mixtures decomposition as well as the intermediates and final products identification has been realized by the high performance liquid chromatography (HPLC), (Perkin Elmer) equipped with UV-VIS detector series 200 (190 – 460 nm). A reverse phase column was of C-18 (Nova Pack C-18, Waters), 300 mm in length and 3.9 mm in diameter. The used mobile phase was combined as water - acetonitrile-phosphoric acid 50: 50: 0.1 for phenols analysis and as 89.9: 10: 0.1 for the acids identification with the flow rate of 0.8 mL min^{-1}. The identification of sub-products and final reaction products was realized by the comparison of the retention time and the UV spectra of the patterns at $\lambda = 210$ nm. The retention times at $\lambda = 210$ nm, used in the HPLC analysis for the initial, intermediate and final products identification, are given in Table 2.

Results and Discussion

Effect of pH on the ozone decomposition

The observation of the ozone concentration variation in the gas phase permits the monitoring of this parameter during the ozonation. Then it is used to obtain the summary characteris-

Table 2. Retention times of compounds used in the HPLC analysis.

Compound	Retention time, min
Hydroquinone	3.18
Catechol	3.70
Ph	4.87
4-CPh	6.87
The mobile phase	**Water: ACN: H$_3$PO$_4$ 50: 50: 0.1**
Oxalic acid	2.68
Formic acid	3.40
Maleic acid (Malonic acid)	3.87
Fumaric acid	4.39
Hydroquinone	6.18
Muconic acid	8.06
Catechol	14.85
The mobile phase	**Water: ACN: H$_3$PO$_4$ 89.9: 10: 0.1**

tic curve of the ozone decomposition. The area limited by this curve is proportional to the amount of dissolved ozone. The difference between the initial ozone concentration and the ozone concentration after dissolution in water (see Figure 2) is the degree of the ozone auto-decomposition at the pH > 7 with the OH radical formation [22-24]. Since the ozone concentration in liquid and gas phases are in the equilibrium, the ozone decomposition degree in the liquid phase is proportional to this in the gas phase [25]. To investigate the pH effect to the ozone decomposition in water, the variation of the ozone concentration in the gas phase in the reactor outlet was measured. Figure 2 shows the ozone gas phase variation at different pH (2, 7 and 12) in the case of the ozone saturation without chemical reaction. In Figure 3 the effect of the pH on the ozone decomposition degree in water is depicted. It is interesting to note that ozone is degraded in alkaline water solution (pH 8-12) with the maximum degradation degree up to 34% of the initial concentration, but not completely.
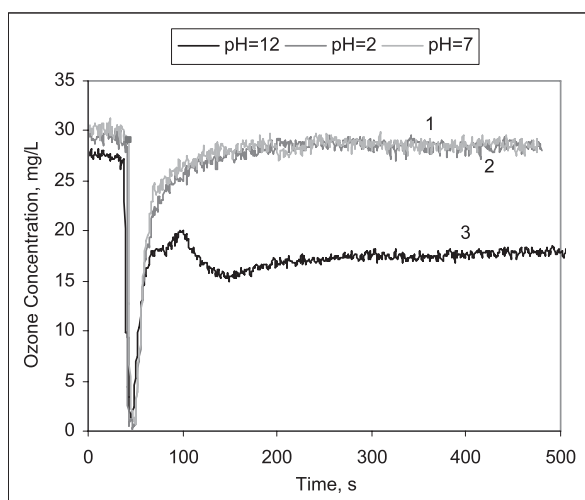
Effect of pH on the phenols decomposition dynamics

It is well know [26–28], that the pH effect to phenols decomposition with ozone is significant. To study the pH effect to the ozonation kinetics of the phenols mixtures, the pH variation from 2 to 12 has been performed. In Figure 4 (a, b and c)

Fig. 2. Variation of the ozone gas phase concentration at different pH without chemical reaction: pH 2 (1), pH 7 (2) and pH 12 (3).
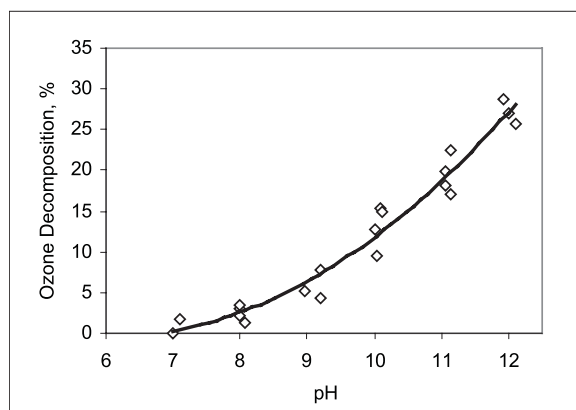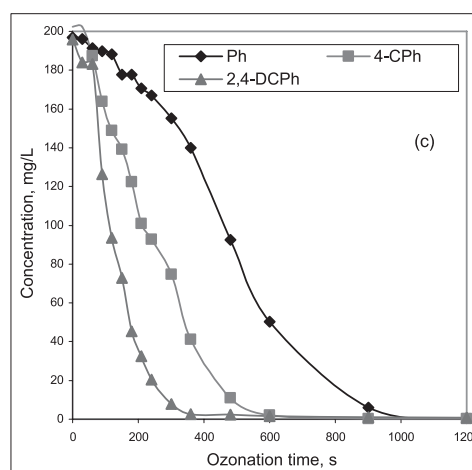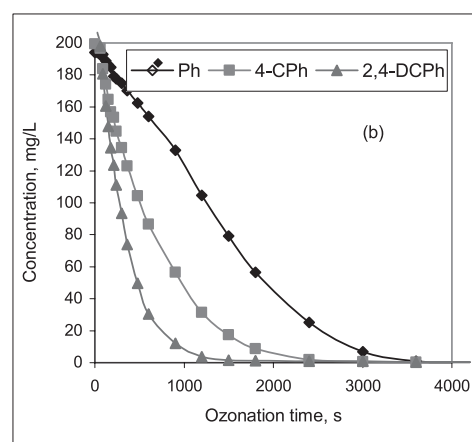

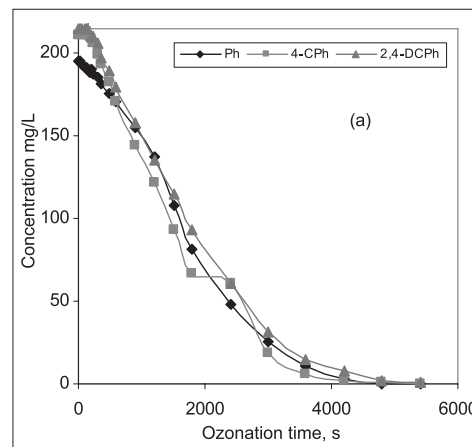**Fig. 3.** Effect of the pH to the ozone decomposition degree.

Fig. 4. Decomposition dynamics of the Ph, 4-CPh and 2,4-DCPh in the model mixture number 1 (the initial concentration of each phenol 100 mg/ L) at the different pH: 2.0 (a), 7.0 (b) and 12.0 (c).

the decomposition dynamics of Ph, 4-CPh and 2,4– DCPh in model mixture number 1 with ozone are depicted as a function of the ozonation time at different pH. It indicates that the phenols decomposition occurs without notable variations at the pH 2.0. The total decomposition time for three compounds is similar (about 75 minutes) (Fig. 4 (a)). The effect of the pH increase to the dynamics decomposition of the phenols with ozone turns out to be also very essential. So, at pH 7.0, Ph completely decomposes within 60 min against to 40 min for the 4-CPh and 25 min for 2,4 – DCPh (Fig. 4 (b)). We observe also a decrease of a total decomposition time of phenols at the pH 12.0. Indeed, Ph was decomposed completely in 17 min, 4-CPh in 10 min and 2,4 – DCPh in 6 min (Fig. 4 (c)).

Based on the obtained results, we may conclude that the pH has a significant influence to initial reaction rate for the phenols mixture. This effect has very similar tendency for three phenols within the studied pH region, but its influence to initial rate turns out to be different. This means that in the Ph ozonation in the pH region 2 - 7 we do not observe the decomposition time variation. For 4- CPh and 2,4 – DCPh, the pH increasing decreases the reaction time significantly. The same tendency for other three mixtures is observed.

Effect of pH on the phenols decomposition mechanism

According to references [29-33], a variety of intermediates were formed by several mechanism of the reaction of ozone with phenols. Only some studies have looked carefully at the examination of the reaction pathways and intermediates, and final products of phenols with ozone [8, 30–33]. Formation of chloride, hydroxylation products, such as 4-chlorocatechol, chlorohydroquinone, catechol and hydroquinone, unsaturated acids have been observed in the ozonation of monochlorophenols [8, 34-37]. After the electrophilic attack of ozone the aromatic ring was destroyed. Ozonation products with carbon-carbon double bonds, such as muconic acid, fumaric acid and maleic acid can react with ozone rapidly according to the Criege's mechanism. It was expected that the reaction products would be simple carboxylic acids and aldehydes. The nucleophilic reaction of ozone with a carboxyl group shows extremely low reaction constant, so the compounds with a carboxyl group will be accumulated during the ozonation.

It was found [12, 28, 31-34, 39] that ozonation induced the denitration, dechloration or desulfuration in the initial reaction step and the cleavage of the aromatic ring with the intermediates and final product formation. In Table 3 the intermediates and final products determined in this work by HPLC in the ozonation of the phenols mixture number 1 at the different pH are presented. As one can see from these data, the intermediate and final products of the phenols destruction by ozone are similar to ones cited before. They are as follows: catechol, hydroquinone, muconic acid, fumaric acid, maleic acid, oxalic acid, formic acid. According to the appearing time of by- products and their distribution during ozonation time, it

can be proven that muconic acid is the initial product; catechol, hydroquinone, fumaric acid, maleic acid are intermediate products. Oxalic and formic acids prolong accumulation with the ozonation time and they are final products. As it follows from the table 3, the pH effect to the by-products and the final composition in water solution during ozonation is very significant. So, the presence of catechol (or derivatives of catechol) and hydroquinone in aqueous solution at the pH 2 and 7 confirms the hydroxylation before the cleavage of aromatic ring. The principal final products at pH 2 and 7 are oxalic and formic acids. On the other hand, at pH 12 catechol, hydroquinone, phenol and 4-CPh have not been found in water solution. The final product is only oxalic acid.

The presence of unsaturated acids at the different pH confirms the cleavage of aromatic ring, but by different mechanism. According to [12, 33, 37, 38], the mechanisms of the phenols ozonation under basic and acidic conditions appear to be different. Based on the obtained results, we may conclude that ozonation at low pH (2 or 7) proceeds mainly through the reaction with molecular ozone. In ozonation at high pH (> 7) the radical mechanism takes place (since at the pH alkaline we observe the ozone decomposition (35%)) together with the direct reaction of molecular ozone. It is important to notice that the increasing the phenol concentration in the first stage of 4-chlorophenol ozonation as well as the increasing of the 4-chlorophenol concentration in the first stage of the 2,4-dichlorophenol ozonation are detected in the ozonation at pH 2, 7, 9 and 12. The formation of these compounds in the phenols mixtures ozonation confirms the dechloration of 4-CPh and 2,4-DCPh at the initial reaction stage. The principal final products at pH's 2 and 7 are oxalic and formic acids. On the other hand, at the pH 12 catechol, hydroquinone, phenol and 4-CPh have not been found in water solution. At this pH the final product is only oxalic acid. These results are consistent with the same obtained in [39]. In the studied case, the ozonation could be interrupted just when the oxalic acid has produced. The further oxidation up to mineralization does not seem to be economically reasonable, if the biodegradation of this mixture in the next stage is applied.

Table 3. Intermediates and final species in the ozonation of the phenols mixtures.

	Model Mixture 1		
Compound	pH 2	pH 7	pH 12
Catechol, mg/L	8.3	14.5	NO
Hydroquinone, mg/L	33.3	48	Traces
Muconic acid, mg/L	Traces	Traces	NO
Fumaric acid, mg/L	Traces	9.7	Traces
Maleic acid, mg/L	25	42.1	Traces
Oxalic acid, mg/L	139.6	174	436.7
Formic acid, mg/L	235.2	270.9	NO

Effect of the pH on the phenolates formation

Phenols can exist in aqueous solution as phenols molecules and as phenolates (phenoxide anions [38]) with the degree of the dissociation increasing with the pH increase. In a dilute solution at a fixed pH, the total absorbance measured by an UV spectrometer is the sum of absorbance's exhibited by molecular and ionic phenols [41]. The phenols solution absorbance increases with pH since of increase in the degree of dissociation, and in turn; the fraction of phenolates, and approaches an asymptotic value in strongly alkaline solutions at pH 12. Thus, the solution absorbance exhibited by phenols at pH 2 and 12 can be taken as the absorbance's of molecular phenols and phenolates, respectively. So, the measured absorbances at various pHs may be used to determine the dissociation degree of phenols. Fig. 5 represents the variation of the UV spectra of phenol with the pH increasing. As it can be seen from these data, the phenolates are formed at pH 10 and their maximal concentration is at pH 12. The same tendency is observed for the three considered phenols.

**Effect of pH on the phenols ozonation kinetics
in their mixtures**

It was shown [12, 35, 46] that the ozonation kinetics of the individual compounds and the same organics in their mixture is different. So, the difference of the ozonation constants value for individual phenols and for their mixture at the different pH was demonstrated in [12]. The bimolecular ozonation constant of phenol increases in 3.7 times in the mixture with mono- and di-chlorophenol comparative with it aqueous solution. In other study, the naphthalene sulfonic acid decomposes in water solution more slowly compared with the ozonation in the mixture of phenol and phenol sulfonic acid [35].

In the present study the effect of pH variation and the initial concentration of the phenols in the mixture to the ozonation kinetics were studied. There isn't an adequate model of the ozonation which is driven at high pH, since in this case t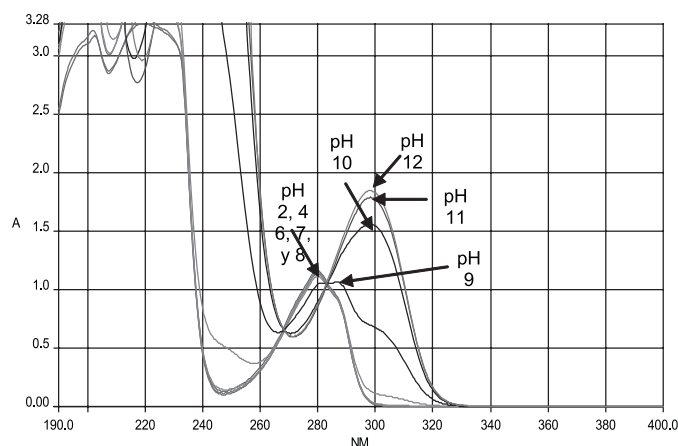wo different mechanisms are possible: a direct attack by molecular ozone to the organic compound and an indirect reaction with OH radicals. In this complex case, a new technique based on the dynamic neural network observer (DNNO) [45, 46] is applied to estimate kinetic parameters of the phenols mixture ozonation. In the preliminary stage, the ozonation mathematical model proposed before [12, 41-44] for the training of the applied DNNO is used.

In the case of complexity composition in water, the reaction rate constant is an important parameter for the reaction mechanism interpretation. Observe that $\hat{c}_t$, $\hat{Q}_t$ as well as $\frac{d}{d\tau}\hat{c}_\tau^i$ are available once all experimental data has been treated by DNNO technique [47]. Under these conditions at the different pH of water it is possible to define the LS (Least Square) estimates of the corresponding ozonation rate constant $k_i(t)$ as the solution to the following optimization problem:

$$k_{i,t}^* = \arg\min_{k_i} \int_0^t \left(\frac{d}{d\tau}\hat{c}_\tau^i + k_i \frac{\hat{c}_\tau^i \hat{Q}_\tau}{v^{liq}} \right)^2 d\tau \tag{1}$$

where $k_{i,t}^*$ is the "best" estimated rate constant value obtained by this optimization method. The solution is as follows

$$k_{i,t}^* = v^{liq} \frac{\int_o^t \hat{c}_\tau^i \hat{Q}_\tau \frac{d\hat{c}_\tau^i}{d\tau} d\tau}{\int_o^t (\hat{c}_\tau^i \hat{Q}_\tau)^2 d\tau + \vartheta} \quad \vartheta > 0 \tag{2}$$

Here ϑ is a small regularizing parameter (0.01).

It's important to emphasize that the constant calculation for individual compounds can be performed by another simple method, but for an organic mixture does not exist another approach for the estimation of kinetic parameters even at basic pH.

The reaction constants, estimated for three phenols in the mixture 1, as well as for the other mixtures, have an excellent correspondence with the experimental dynamics (see Figures 6 (a-c)). Here the decomposition dynamics exactly corresponds to the value of the obtained ozonation constants, which are given in Table 4.

As it can be seen from these data, the ozonation constants of phenols, considered for the mixture 1, have insignificant tendency of increasing (2.6 -5.7%) with the increase of pH up 9 to 12 (excluding 2,4-DCPh), where the initial phenols concentrations are equal to 100 ppm. As for three others mixtures (2, 3 and 4), the pH effect is more significant. So, the constant increases up 3.9% to 7.2 % for the mixture 2 (excluding 2,4-DCPh that decreases to 23 %), up 2.2% to 30 % for the mixture 3 and up 15% to 29% for the mixture 4. So, the reaction constants as a function of the initial concentration of phenols in the mixtures are also changed. In this particular case, it is difficult to explain the observed tendency, since in the corresponding experiments two main parameters (pH and the initial mixture composition) are changed. In this case, the pH effect is more significant if the initial composition of phenols is varied.
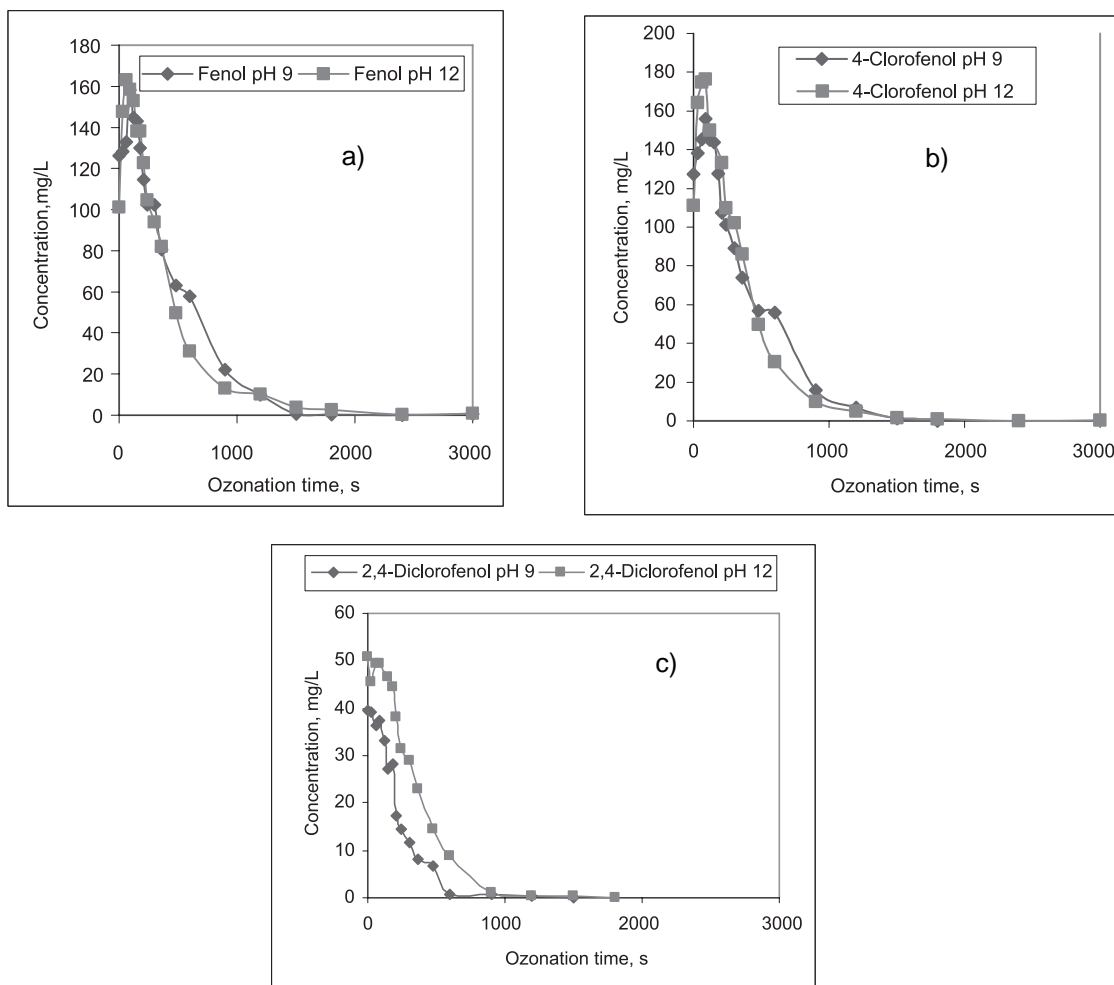

Fig. 5. Variation of the UV spectra of phenol with the pH increasing.

Fig. 6. Phenols decomposition in the model mixture 1 at the pH 9 and 12: phenol (a), 4-CPH (b) and 2,4-DCPH (c).

Table 4. The comparative results of pH effect on the ozonation kinetics (k, L/ mole s) in the different phenols mixtures.

	Mixture 1		Mixture 2		Mixture 3		Mixture 4	
	pH 9	pH 12	pH 9	pH 12	pH 9	pH 12	pH 9	pH 12
Ph	5.38×10^3	5.52×10^3	2.57×10^3	2.77×10^3	2.29×10^3	3.28×10^3	1.61×10^3	1.90×10^3
4-CPh	5.20×10^3	5.43×10^3	2.71×10^3	2.82×10^3	3.13×10^3	3.74×10^3	1.73×10^3	2.45×10^3
2, 2,4-DCPh	6.4610^3	6.09×10^3	6.82×10^3	5.23×10^3	7.24×10^3	7.40×10^3	3.19×10^3	4.17×10^3

Comparison of the effect of the ozone decomposition and the phenolates formation on the phenols ozonation kinetics

Based on the obtained results (Table 4) we may conclude that with pH increasing in the region 9 – 12, where the effect of the phenolates formation is more significant, the increasing of the constant values (30%) for the mixtures 3 and 4, probably, demonstrates this effect.

In the case of the pH increasing in the region 2 – 12, the effect of the ozone decomposition on the phenols ozonation

kinetics is also observed. We use the value of the reaction constants, obtained in the previous study [46], for the phenols mixture 1 at pH 2, 7 and 12 (see Figure 7). As it can be seen from these data, for three studied phenols with the pH-increasing the value of the ozonation rate constant also increases (71-120%), and, in this case, pH effect is more significant.

We claim that it is very difficult to separate the effects of ozone decomposition and the phenolates formation on the phenol ozonation kinetics.
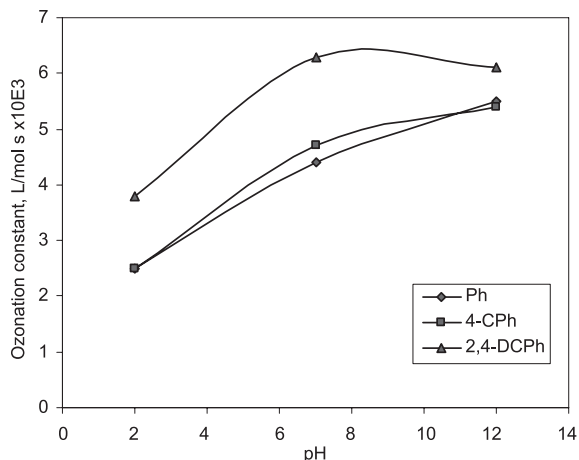
Fig. 7. Effect of the pH to the value of the ozonation constant for phenols (the initial concentration of each phenol is 100 mg/ L).
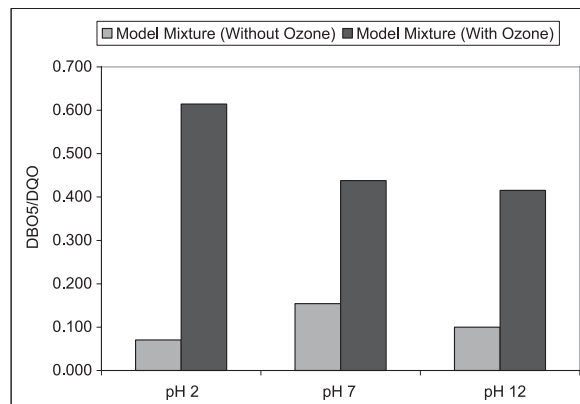

Fig. 8. The variation of the BOD$_5$/COD-ratio for the model mixture 1without and with preliminary ozonation at different pH.

Effect of ozonation on the biodegradability of the phenols decomposition products

As proposed in the literature, the BOD$_5$/ COD ratio is commonly used as a biodegradability measure [13-18]. The effect of ozonation to the biodegradability of the phenols decomposition products by the determination of the BOD$_5$/ COD ratio before and after ozonation was investigated. An increase of the BOD$_5$/ COD ratio after ozonation would indicate an increase in the proportion of COD amenable to biodegradation. Table 5 presents the BOD$_5$ and the COD variation before and after preliminary ozonation. Based on the results obtained, we observe that the COD decreasing after ozonation of phenols mixture is insignificant; the COD decreasing is very small (1-14%). This result is reasonable, because in this particular case, in the ozonation are formed simple acids and it is not observed their mineralization. The biodegradability of the studied pollutants without and with the pre-ozonation has been compared. As one can see from Figure 8, the effect of the preliminary ozonation to the biodegradability of the phenols mixture is very significant. So, the BOD$_5$/COD-ratio increases from 0.071 to 0.614 at the pH 2, from 0.154 to 0.438 at the pH 7 and from 0.1 to 0.416 at the pH 12, but it decreases from 0.614 to 0.416 with the pH increase.

Conclusions

In view of the results obtained, we may conclude the following:

1. The ozone is decomposed in water solution at pH >7 with the maximal decomposition degree of 34% of the initial concentration.
2. In the initial stage of the ozonation, the dechloration of the 4-CPh and 2,4 – DCPh occurs and then the destruction mechanism of these compounds is similar to the decomposition of the individual phenols. The formation of Ph and 4-CPh in the ozonation of 4-CPh and 2,4 – DCPh, respectively, at the pH 2 and 7 confirms the dechloration in the initial reaction stage.
3. The pH effect to the phenols decomposition by ozone is very significant. With the pH increasing the phenols decomposition time decreases from 75 min at pH 2 up to 17 min at pH 12.
4. At pH 2 and 7, the final products of the phenols mixtures ozonation are oxalic and formic acids. At pH 12, the final product is oxalic acid only.
5. The increase of the initial pH of the phenols solutions provokes the phenolates formation at pH 10 with the maximal phenolates concentration at pH 12.

Table 5. Variation of BOD$_5$, COD and the relation of BOD$_5$/COD without (initial) and with preliminary ozonation (final).

	Mixture 1			BOD$_5$/COD		
				pH 2	pH 7	pH 12
BOD$_5$ initial	35.0	75.0	45.0			
COD initial	496.0 ± 59.5	486.5 ± 1.2	450.5 ± 50.0	0.071	0.154	0.100
BOD$_5$ final	260. 0	210.0	175. 0			
COD final	423.2 ± 33.1	479.3 ± 39.8	421.1 ± 51.3	0.614	0.438	0.416

6. For all phenols mixtures the ozonation constants of phenols have the insignificant tendency to the increasing with the increase of pH up 9 to 12 (excluding 2,4-DCPh en the mixtures 1 and 2); and their values are changed also in the dependence of the initial concentration of phenols in the mixtures.

7. The effect of the preliminary ozonation on the biodegradability of the phenols mixture is significant.

Acknowledgements

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