

# Photochemical treatment of phenol aqueous solutions using ultraviolet radiation and hydrogen peroxide

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## Abstract

The potential of purifying phenol aqueous solutions (0.0006–0.0064 M) using ultraviolet (UV) radiation and hydrogen peroxide ( $\text{H}_2\text{O}_2$ ; 0.005–0.073 M) was investigated. Although the direct photolysis of phenol and its oxidation by hydrogen peroxide (without ultraviolet light) were insignificant, the combination of UV and  $\text{H}_2\text{O}_2$  was extremely effective on phenol degradation. However, the chemical oxygen demand was on no occasion entirely eliminated, indicating the resistance of the intermediate products formed to the photo-oxidation. Increasing the initial concentration of phenol had as a result lower phenol conversions achieved, whereas the increase in hydrogen peroxide initial concentration enhanced significantly the degradation of phenol. In contrast, COD removal was less sensitive to these changes.  
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## 1. Introduction

One of the greatest problems nowadays is the lack of drinking water. Despite the fact that the greatest part of earth is covered by water, only a small percentage of this water is appropriate for drinking. According to WHO estimations [1], one quarter of the world's population lack hygienic drinking water. That problem combined with health and hygienic problems may pose a threat to mankind in the near future. It is apparent that the chemical treatment of contaminated drinking water sources and of toxic wastewaters before their discharge into the environment is of great importance.

Among the various ways of water purification, Advanced Oxidation Processes (AOPs) can be proved to be very effective on the elimination of hazardous compounds. The term "AOPs" is used to describe the oxidation mechanism that depends on the production of very active species like hydroxyl radicals ( $\bullet\text{OH}$ ). Hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) is a very common source of these radicals by its decomposition after being irradiated with ultraviolet (UV) light. Due to the high cost of hydrogen peroxide,

this method is usually used as a pre-treatment stage before the biological process.

Phenol is one of the most abundant pollutants in industrial wastewaters and its toxicity makes that compound dangerous for the aquatic life. Phenol is also a concern in the biological stage of wastewaters treatment, due to its bio-resistance and toxicity to microbial population.

In the present study, the photochemical oxidation of phenol using UV and hydrogen peroxide in a batch recycle photochemical reactor was investigated as a pre-treatment to biological stage of phenol wastewaters. The effect of the combined use of UV and  $\text{H}_2\text{O}_2$ , phenol initial concentration and hydrogen peroxide initial concentration on phenol conversion, COD removal, hydrogen peroxide decomposition and pH evolution were examined. Finally, a kinetic model that is taking into account series-parallel reactions was applied to the experimental data obtained.

## 2. Experimental details

### 2.1. Chemicals and reagents

All reagents (purchased from Fluka) were used as received without further purification. Fresh phenol solutions were used. The initial concentration of each phenol solution was 0.0032 M

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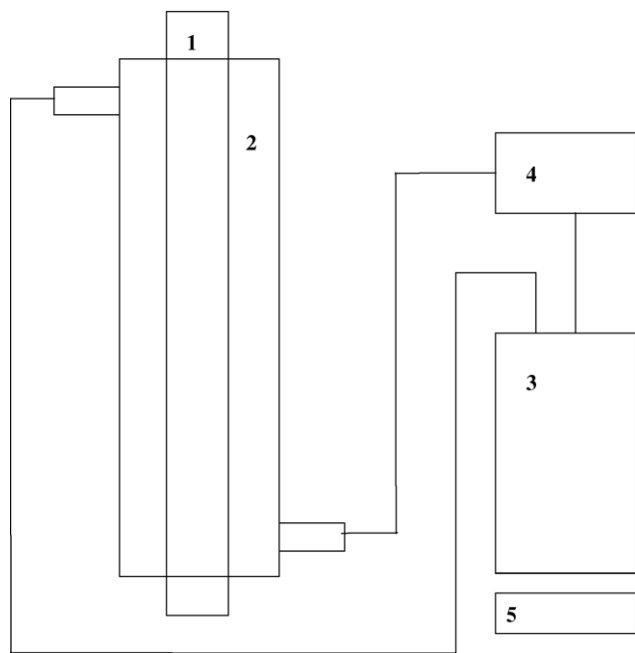


Fig. 1. Experimental apparatus: (1) UV lamp, (2) photochemical reactor, (3) feed, (4) pump and (5) magnetic stirrer.

unless otherwise stated.  $\text{H}_2\text{O}_2$  solution 28% (w/w) was used as source of hydroxyl radicals. Only deionised water was used.

## 2.2. Experimental procedure and analysis

The photochemical oxidation of phenol was investigated with the apparatus shown in Fig. 1. This essentially consisted of a low-pressure mercury vapor lamp of 18 W, which produced monochromatic ultraviolet light of 253.7 nm. The reactor operated in batch recycle mode and was a cylindrical vessel of 20 mL effective volume. The total volume of the solution was 200 mL. The non-irradiated part of the solution was continuously agitated by a magnetic stirrer. A peristaltic pump was used to re-circulate the solution with a rate of  $112 \text{ mL min}^{-1}$ . A WTW-pH90 pH-meter was used for pH measurements. A sample was withdrawn from the reaction vessel at specific time periods and was analysed. A gas chromatograph (Perkin-Elmer Sigma 3B) equipped with a flame ionisation detector was used to determine the phenol concentration. The column used (10% SP-1000 +  $\text{H}_3\text{PO}_4$ ) was operated at  $170^\circ\text{C}$ . Chemical oxygen demand measurements were carried out using the standard dichromate reflux method. The concentration of hydrogen peroxide was measured using the standard titanate (IV) method. Each experiment lasted 120 min.

## 3. Results and discussion

### 3.1. UV photolysis versus $\text{H}_2\text{O}_2$ oxidation versus UV/ $\text{H}_2\text{O}_2$ photo-oxidation

Firstly, the degradation of phenol by UV photolysis,  $\text{H}_2\text{O}_2$  only and with UV/ $\text{H}_2\text{O}_2$  was studied. Although there are a lot of studies related to the comparison between these methods, their effect on phenol degradation had to be studied because they show

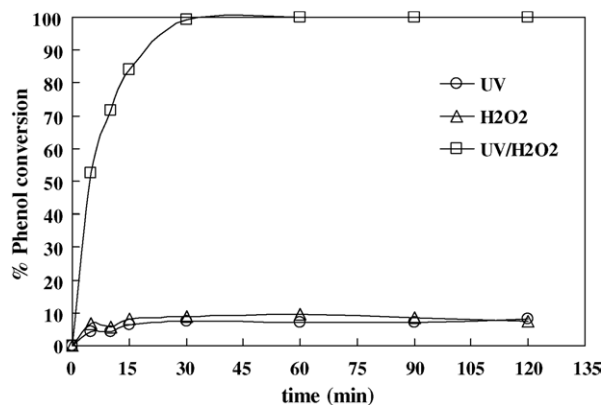


Fig. 2. Photochemical oxidation of phenol using UV and hydrogen peroxide.

considerable dependence on the existing photo-oxidation system to be used (apparatus and conditions). The conversion of phenol in aqueous solution ( $0.0032 \text{ mol L}^{-1}$ ) versus time is presented in Fig. 2. The conversion of phenol by direct photolysis or by hydrogen peroxide ( $0.024 \text{ M}$ , without UV) did not exceed 10% after 2 h. In contrast, less than 10 min were required for 50% conversion of phenol and 30 min for total destruction of phenol by hydrogen peroxide ( $0.024 \text{ M}$ ) mediated photo-degradation.

The intensity of the irradiation and the initial concentration of the compound are key factors to the effectiveness of the direct photolysis. Benitez et al. [2] and Lipczynska-Kochany and Bolton [3] achieved high rates of chlorophenols conversions by photolysis, whereas the results obtained by De et al. [4] are in accordance with those obtained in this study. On the other hand, De et al. observed higher conversions in the presence of hydrogen peroxide only. It is reported that hydrogen peroxide dissociates in aqueous solutions, forming  $\text{HO}_2^-$  anion [5] and  $\text{O}_2$  in a chain reaction, which convert substrates to other oxygenated intermediate compounds. It seems that higher concentrations of hydrogen peroxide have to be used in order to achieve higher conversions of phenol in the absence of UV light.

The combination of UV light and a small amount of  $\text{H}_2\text{O}_2$  enhanced strongly the efficiency of phenol destruction. In the first step, hydrogen peroxide absorbs UV light and decomposes to highly reactive hydroxyl radicals ( $\bullet\text{OH}$ ). Then, hydroxyl radicals, which are non-selective powerful oxidants, react with most organic compounds with very high rate constants ( $K \sim 10^6\text{--}10^{10} \text{ M}^{-1} \text{ s}^{-1}$ ) [6–8]. They can abstract an H-atom from many sites of an organic molecule or add to any C=C bond or accept an electron, producing therefore a wide spectrum of products [9]. Only by using UV light was  $\text{H}_2\text{O}_2$  decomposed noticeably, as confirmed from its concentration measurements.

### 3.2. The effect of phenol initial concentration

Phenol degradation was studied for various initial concentrations of phenol (0.0006, 0.0032 and  $0.0064 \text{ M}$ ) at a constant initial concentration of  $\text{H}_2\text{O}_2$  ( $0.024 \text{ M}$ ,  $\varphi = 40.0, 7.7, 3.8$ ,  $\text{H}_2\text{O}_2/\text{phenol}$  molar ratio). As it is apparent in Fig. 3, lower conversions were observed with increasing the initial concentration of phenol. Less than 16 min were required for 100%

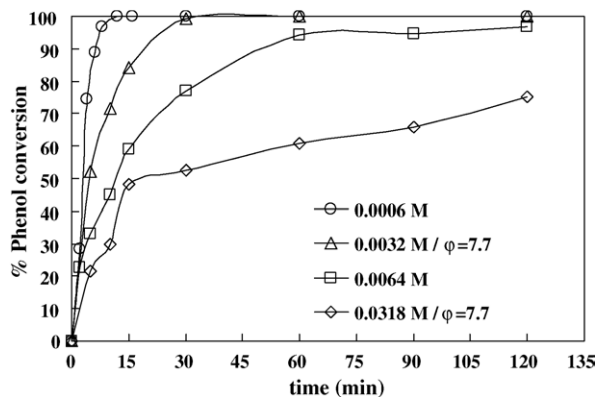


Fig. 3. The effect of phenol initial concentration on its conversion.

phenol destruction when its initial concentration was 0.0006 M, whereas the corresponding time for initial phenol concentration 0.0032 M was 30 min. When phenol initial concentration was increased to 0.0064 M, phenol was still detected in the solution after 120 min. This negative impact of phenol initial concentration on the phenol decomposition can be associated with different reaction pathways due to different  $\text{H}_2\text{O}_2$ /phenol molar ratios. Lipczynska-Kochany and Bolton [3] found that the distribution of products changed markedly with varying the  $\text{H}_2\text{O}_2$ /phenol molar ratio.

Consequently, the effect of phenol initial concentration was also studied keeping the same  $\text{H}_2\text{O}_2$ /phenol molar ratio  $\phi$  (Fig. 3, curves 0.0032 M/ $\phi=7.7$  and 0.0318 M/ $\phi=7.7$ ). The adverse effect of phenol initial concentration on phenol observed again was due to the fact that the fraction of light absorbed by hydrogen peroxide decreased with increasing the phenol concentration. These experimental results confirm previous ones obtained from De et al. [4] and Alnaizy and Akgerman [10].

On the contrary, COD removal seemed to be insensitive to phenol initial concentration (Fig. 4), with the exception of 0.0006 M, demonstrating the difficulty of the oxidation of the intermediate products [11,12], which contained organic acids as indicated from the drop of pH values with time (Fig. 5). The conversion of hydrogen peroxide decreased by increasing the initial concentration of phenol due to less fraction of light available to hydrogen peroxide photolysis (Fig. 6).

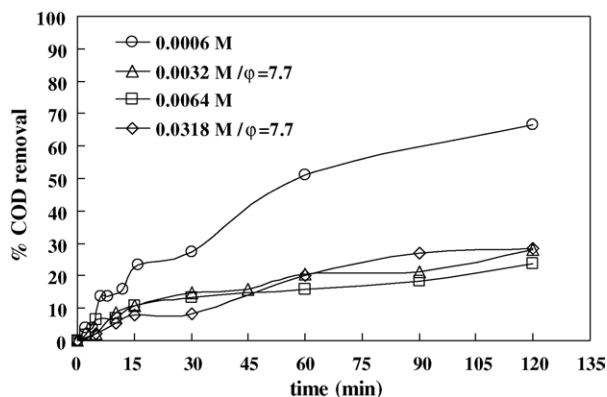


Fig. 4. The effect of phenol initial concentration on COD removal.

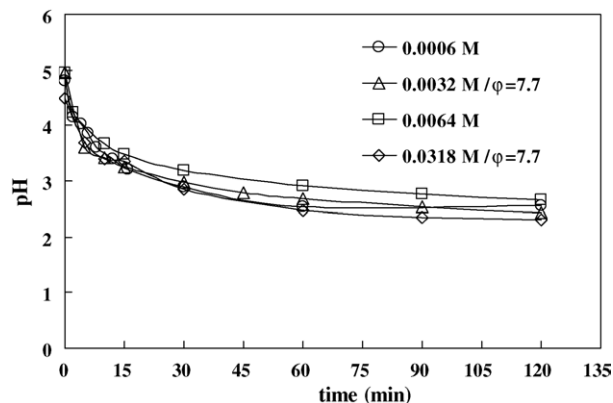


Fig. 5. The effect of phenol initial concentration on pH evolution.

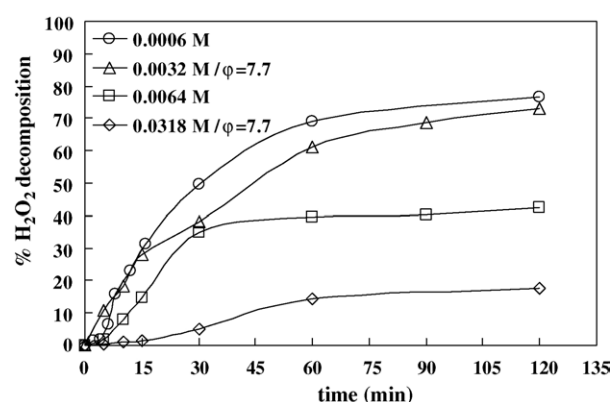


Fig. 6. The effect of phenol initial concentration on hydrogen peroxide decomposition.

### 3.3. The effect of hydrogen peroxide initial concentration

The degradation of phenol (0.0032 M) was investigated varying the initial concentration of hydrogen peroxide (0.005, 0.024, 0.049 and 0.073 M). As it is clear in Fig. 7, the phenol conversion increased with increasing the initial concentration of hydrogen peroxide. This is due to the fact that the solution was enriched with hydroxyl radicals when the concentration of hydrogen peroxide was increased. The hydroxyl radical scavenging effect

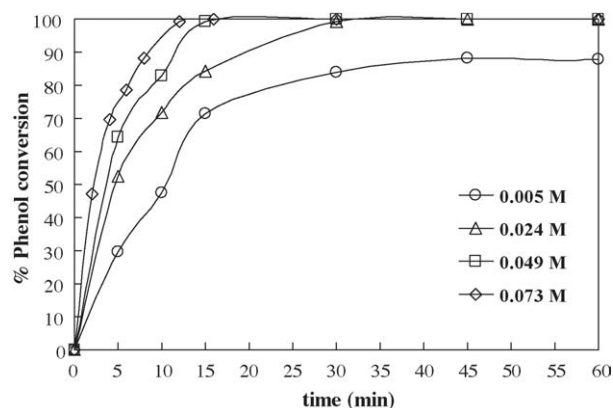


Fig. 7. The effect of hydrogen peroxide initial concentration on phenol conversion.

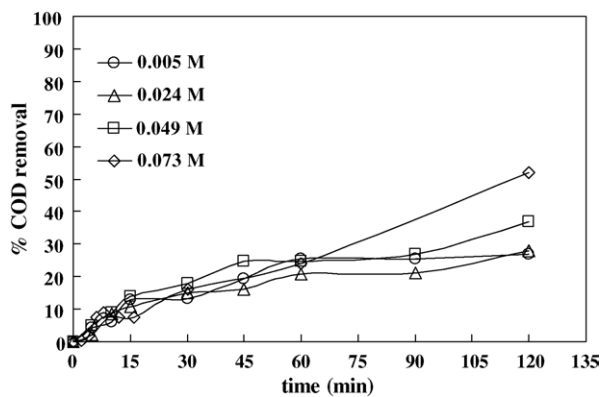
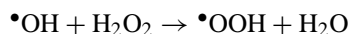


Fig. 8. The effect of hydrogen peroxide initial concentration on COD removal.

of hydrogen peroxide [4,10,13] was not observed in this study. Higher concentrations of hydrogen peroxide are required for this phenomenon to be appeared. In such a case, the hydroxyl radical concentration would decrease via the following reaction despite the higher free-radical production rate.



According to Alnaizy and Akgerman [10],  $\text{H}_2\text{O}_2$ /phenol molar ratios higher than 300 are required for this effect, a value higher than the used ones in the present study. On the other hand, the differences in COD removal curves due to different amounts of hydrogen peroxide were not so distinct in the first 90 min (Fig. 8) and the reason for that was not the lack of hydrogen peroxide. The conversion of hydrogen peroxide was adversely affected by the increase in its initial concentration. Moreover, the acidic pH measured in all cases reveals the formation of organic acids as a result of phenol oxidation. These observations support the view that the intermediate products of phenol photo-oxidation are extremely resistant to hydroxyl radicals' attack. Alnaizy and Akgerman [10] detected maleic, oxalic, fumaric, mucanic and formic acid as intermediates or final products of phenol photo-oxidation in the presence of hydrogen peroxide under all conditions. They also measured very low rates of acids decomposition from carbon dioxide concentration calculations.

### 3.4. Kinetic model

Various models have been proposed for describing the photo-oxidation of various compounds using ultraviolet radiation and hydrogen peroxide. A simple pseudo-first-order model is often employed to represent the data obtained in the photo-oxidation [13–16], whereas other more complex kinetic schemes have also been proposed [4,9,10,17].

In this study, a model that has commonly been used to represent the experimental data of the wet oxidation process [18] was employed to interpret the data obtained in terms of COD. According to this model, the initial organic compound is partly directly oxidized to carbon dioxide and water, whereas another part of the initial compound and the unstable intermediate products are converted to a resistant intermediate product (usually an organic acid), which in turn is converted to carbon dioxide.

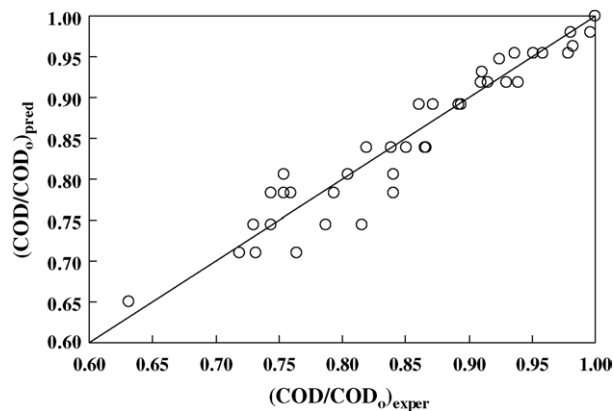
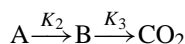
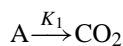


Fig. 9. The predicted COD/COD<sub>0</sub> values vs. the experimental ones.

The so-called generalized kinetic model is represented by the following scheme:



where A is initial and unstable intermediate organic compounds and B is resistant intermediate product.

The slow change of COD and the presence of organic acids in the solution during the photo-oxidation process make the adoption of this model sound. Assuming first order kinetics for each reaction path, the generalized kinetic model is given by [19]:

$$\frac{[\text{A} + \text{B}]_t}{[\text{A} + \text{B}]_0} = \frac{K_2}{[K_1 + K_2 - K_3]} \exp(-K_3 t) + \frac{[K_1 - K_3]}{[K_1 + K_2 - K_3]} \exp(-[K_1 + K_2] t)$$

where  $K_i$  are the rate coefficients,  $t$  time and  $[\text{A} + \text{B}]$  is the concentration of the total organic load expressed in terms of COD. Assuming initial values of  $K_1$ ,  $K_2$  and  $K_3$ , the values of  $(\text{COD}/\text{COD}_0)$  were estimated via the above equation. Marquardt–Levenberg method was used for the minimization of the objective function for the residual sum of squares (RSS) =  $\sum ((\text{COD}/\text{COD}_0)_{\text{pred}} - (\text{COD}/\text{COD}_0)_{\text{exper}})^2$ .

The predicted values of  $\text{COD}/\text{COD}_0$  are plotted versus the experimental values in Fig. 9. The estimated value of  $K_2$  ( $0.0526 \text{ min}^{-1}$ ) is five times the value of  $K_1$  ( $0.0105 \text{ min}^{-1}$ ), which indicates that the prevalent reaction pathway is the oxidation to intermediate products and not the direct oxidation to carbon dioxide. The value of  $K_3$  ( $0.0016 \text{ min}^{-1}$ ) is significantly lower than those of  $K_1$  and  $K_2$ , which confirms the resistance of the organic acids formed to photo-oxidation.

## 4. Conclusions

In the present work, the photochemical treatment of phenol aqueous solutions using ultraviolet radiation and hydrogen peroxide was studied. It was shown that although phenol was efficiently eliminated with this process, slow rates of total mineralization were observed, indicating the resistance of

intermediate organic acids formed to the attack of hydroxyl radicals. However, organic acids are readily oxidized in the biological process. The main results of this study are:

- (a) The combination of UV light and hydrogen peroxide enhanced considerably the efficiency of phenol destruction compared to direct photolysis and oxidation by hydrogen peroxide.
- (b) Increasing the initial concentration of phenol resulted in a decrease in the obtained phenol conversions. The COD removal showed less sensitivity to changing the initial phenol concentration.
- (c) In contrast to phenol initial concentration, an increase in hydrogen peroxide initial concentration lead to increased phenol conversions.

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