



Photo-assisted oxidation of an oily wastewater using hydrogen peroxide

C.J. Philippopoulos*, S.G. Pouloupoulos

*Chemical Process Engineering Laboratory, Department of Chemical Engineering, National Technical
University of Athens, Heroon Politechneiou 9, Zographou Campus, 157 80 Athens, Greece*

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Abstract

The primary objective was to study the purification of an oily wastewater from a lubricant production unit using ultraviolet irradiation and hydrogen peroxide. The influence of hydrogen peroxide concentration, initial pH of the solution and of the addition of ferric ions on the chemical oxygen demand (COD) was examined. In each case, the concentration of the compounds contained in the oily wastewater was determined. It was shown that a 20–45% COD removal was achieved with 830–1660 mg l⁻¹ H₂O₂. Gas chromatography–mass spectrometry analysis showed that the organic compounds of the wastewater decomposed to organic acids that were very resistant to photo-oxidation. Among these compounds, ethylene glycol remained almost unchanged by the attack from hydroxyl radicals. Acidic pH and Fe(III) addition enhanced significantly the photo-oxidation of the wastewater.

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1. Introduction

Much attention has been given to “*advanced oxidation processes*” for industrial wastewater treatment. This term is used to describe an oxidation mechanism, which depends on the production of active free radicals such as hydroxyl radicals ($\bullet\text{OH}$) that play the role of the oxidative agents. Hydrogen peroxide (H₂O₂) is a common source of these radicals. Ultraviolet irradiation is used (near 250 nm) to decompose hydrogen peroxide into hydroxyl radicals. This oxidation process can be used as a pretreatment stage before a biological process.

* Corresponding author. Tel.: +301-772-3224; fax: +301-772-3155.
E-mail address: kphilip@chemeng.ntua.gr (C.J. Philippopoulos).

Numerous studies have been conducted on the photo-degradation of phenol and chlorophenols in the presence of hydrogen peroxide [1–12]. Fewer studies have involved other pollutants [13–15] and only a limited number of studies related to the treatment of real wastewaters [16].

In the present work, UV-light and hydrogen peroxide were used for the purification of an oily wastewater from the lubricant production unit of a petroleum company. This industrial wastewater had high concentrations of organic matter (COD \approx 9000) and therefore biological treatment, without dilution, was ineffective. Consequently, another process had to be employed as a pretreatment stage before the biological process. Oxidation using UV/H₂O₂ was chosen for that process. The effect of hydrogen peroxide concentration, reaction mixture pH and the presence of ferric ions on the oxidation of the wastewater is presented in this paper. Much emphasis was given to the profile of the compounds contained in the wastewater after each treatment.

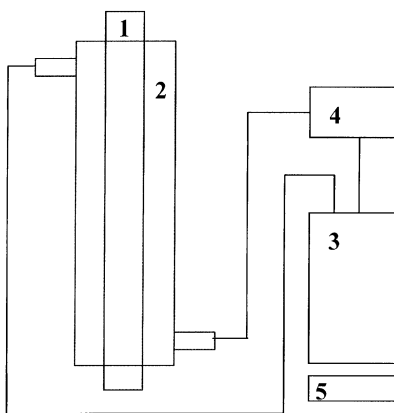
2. Experimental details

2.1. Chemicals and reagents

All reagents were used as received without further purification. H₂O₂ solution 28 wt.% was used as a source of hydroxyl radicals. HCl solution (30 wt.% or KCl solution (1N) were used for pH correction. FeCl₃ was used as source of Fe(III). Only deionised water was used.

2.2. Experimental procedure

The photochemical oxidation of the wastewater was investigated with the apparatus shown in Fig. 1. UV-light of 253.7 nm was provided by a low pressure 18 W Hg lamp. The



1. UV lamp, 2. Photochemical reactor, 3. Feed, 4. Pump, 5. Magnetic stirrer.

Fig. 1. Experimental apparatus used for the photo-oxidation of an oily wastewater.

Table 1
GC–MS analysis details

Apparatus	Hewlett-Packard GC 6890–MSD 5973
Column	HP1–MS
Length	30 m
Internal diameter	250×10^{-6} m
Carrier gas	Helium
Total flow	9.7 ml min^{-1}
Mode	Pulsed split (1:10)
Injector temperature	250 °C
Detector temperature	MS quad: 150 °C MS source: 230 °C
Oven temperature	Initial: 50 °C for 5 min 50 °C \rightarrow 200 °C, $10 \text{ }^\circ\text{C min}^{-1}$ 200 °C \rightarrow 280 °C, $20 \text{ }^\circ\text{C min}^{-1}$ Final: 280 °C for 2 min

reactor was cylindrical and was operated in batch recycle mode. The effective volume of the cylindrical vessel was 20 ml and the total volume of the solution was 200 ml (reactor and the non-irradiated liquid volume). The non-irradiated part of the wastewater was continuously agitated by a magnetic stirrer. A peristaltic pump was used to recirculate the solution at a rate of 110 ml min^{-1} . Continuous pH measurements were recorded by a WTW-pH90 pH-meter. A sample was withdrawn from the reaction vessel at specific time periods and analysed with gas chromatography–mass spectrometry. COD measurements for each sample were also made. Each experiment lasted 150 min.

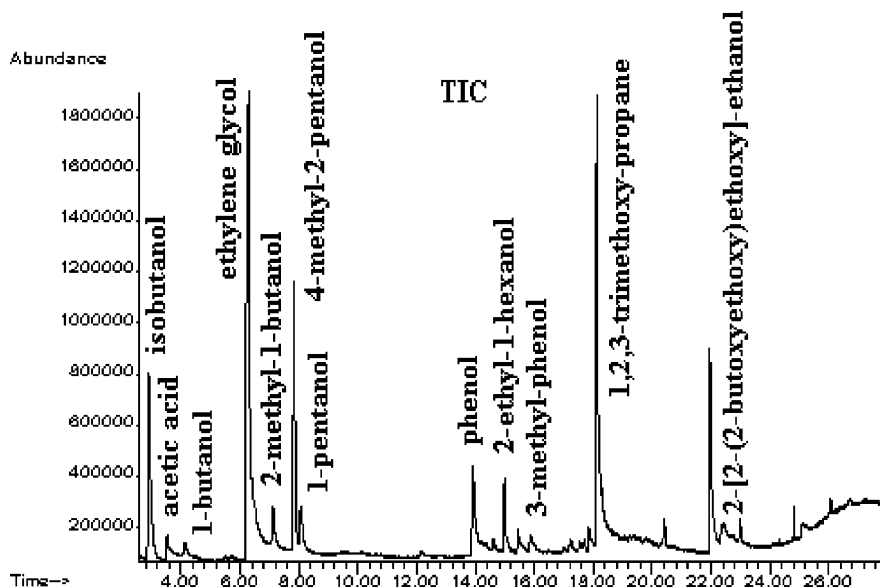


Fig. 2. A GC–MS chromatogram of the oily wastewater.

Table 2
The composition of the wastewater

Compound	Percentage
Isobutanol	11.2
Acetic acid	1.0
Ethylene glycol	30.8
2-Methyl-1-butanol	2.7
4-Methyl-2-pentanol	8.5
1-Pentanol	4.4
Phenol	3.1
2-Ethyl-1-hexanol	2.3
<i>o</i> -Cresol	1.3
<i>p</i> -Cresol	1.2
2,5-Dimethyl-phenol	0.5
3,5-Dimethyl-phenol	0.5
3,4-Dimethyl-phenol	0.7
1,2,3-Trimethoxy-propane	15.2
2-[2-(2-Methoxy ethoxy)ethoxy]-ethanol	11.0

2.3. Analysis

Chemical oxygen demand measurements were performed using the standard dichromate reflux method. The concentration of hydrogen peroxide was measured using the standard titanate(IV) method [17].

The profile of the compounds contained in the wastewater was determined with a Hewlett-Packard gas chromatograph HP 6890 equipped with a mass spectrometry detector HP 5973 (GC–MS). The column used was an HP1–MS (HP 19091S-733). Details about the analysis with GC–MS are given in Table 1.

A typical chromatogram of the oily wastewater is presented in Fig. 2. The wastewater from the production unit of a lubricant petroleum company (LPC Hellas) contained mainly various alcohols and phenolic compounds. The exact composition of the wastewater is found in Table 2. Its initial COD was $9000 \pm 500 \text{ mg l}^{-1}$ and its pH was 7.82.

3. Results and discussion

3.1. The effect of H_2O_2 concentration

Firstly, the effect of hydrogen peroxide concentration ($1665\text{--}6660 \text{ mg l}^{-1}$) on the COD removal was examined. An increase in H_2O_2 concentration from 1665 to 3330 mg l^{-1} had an adverse effect on COD removal, as shown in Fig. 3. This phenomenon can be explained by considering the scavenging effect of hydrogen peroxide on hydroxyl radicals. H_2O_2 may react with $\bullet\text{OH}$ to form oxygen and perhydroxyl radicals and thus decreasing the concentration of free hydroxyl radicals [4,5,8]. Another possible explanation could be the different reaction pathways depending on H_2O_2 concentration that lead to more resistant intermediate products to oxidation [2]. A further increase of hydrogen peroxide

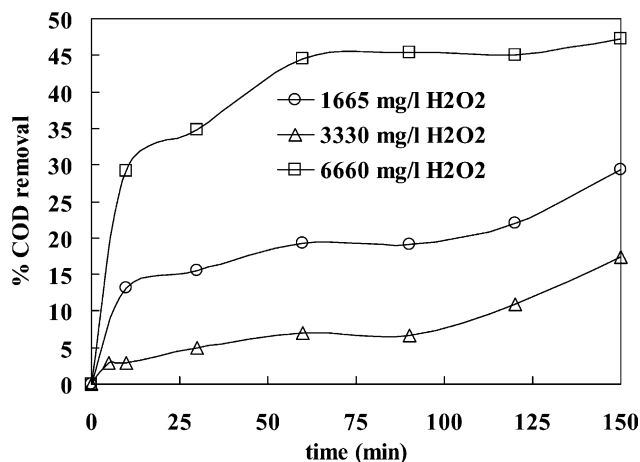


Fig. 3. Effect of H₂O₂ concentration on COD removal in photo-oxidation of an oily wastewater.

to 6660 mg l⁻¹ enriched the solution with photo-produced hydroxyl radicals and resulted in a great decrease in COD from the first minutes of the photo-oxidation. A plateau of about 40% COD removal was reached after the first hour. It has to be noted that COD does not include hydrogen peroxide COD and refers only to hydrocarbons COD. As shown in Fig. 4, the conversion of hydrogen peroxide did not exceed 55% in all experiments. Lower conversion of hydrogen peroxide was observed with increasing its initial concentration above 3330 mg l⁻¹.

A matter of great interest is the evolution of the concentration of selected compounds, as it is shown from GC–MS chromatograms. The ultimate conversions of isobutanol, ethylene

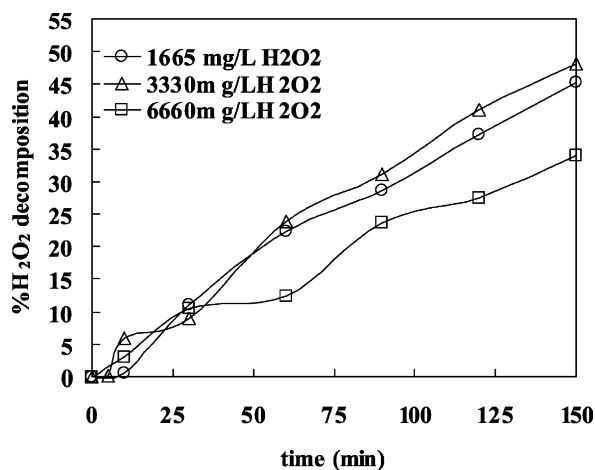


Fig. 4. Effect of H₂O₂ concentration on its decomposition in photo-oxidation of an oily wastewater.

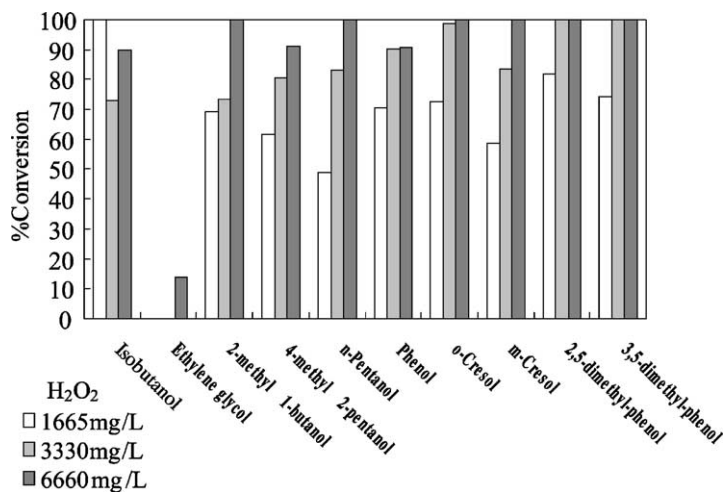


Fig. 5. Effect of H₂O₂ concentration on the conversion of selected compounds in photo-oxidation of an oily wastewater.

glycol, 2-methyl-1-butanol, 4-methyl-2-pentanol, *n*-pentanol, phenol, *o*-cresol, *m*-cresol, 2,5-dimethyl-phenol and 3,5-dimethyl-phenol are shown in Fig. 5. It is evident that when hydrogen peroxide concentration was increased to 6660 mg l⁻¹, these compounds were almost totally decomposed within 150 min, with the exception of ethylene glycol. This compound was reported to have been efficiently decomposed by hydroxyl radicals in a UV/H₂O₂ system [18]. Although hydroxyl radicals are generally non-selective oxidants, it seems that in such a complex wastewater its oxidation was competed by the oxidation of the other compounds present. Acetic and formic acid were produced and their concentration increased with time because of the decomposition of the various compounds in the mixture. Organic acids are very resistant to photo-oxidation with H₂O₂, which explains the slow change of COD above 40%, whereas most of the initial compounds in the wastewater are totally decomposed.

From the above experiments, it was illustrated that there was enough hydrogen peroxide not decomposed in the mixture, since its maximum conversion was 50%. Consequently, the target of the next experiments should be its further decomposition that would lead to a greater oxidation of the organic compounds. Key factors to achieve this target are the pH of the solution and the presence of iron ions.

3.2. The effect of the pH

Aiming at a swifter decomposition of 3330 mg l⁻¹ hydrogen peroxide, the initial pH of the wastewater was adjusted to 12.0 and 3.5. At pH = 12, a significant decrease in COD was observed in the first 100 min, but the same level of COD removal was achieved after 2.5 h, compared to pH = 7.8. On the contrary, a considerable decrease in COD was achieved when the solution pH was adjusted to 3.5 (Fig. 6).

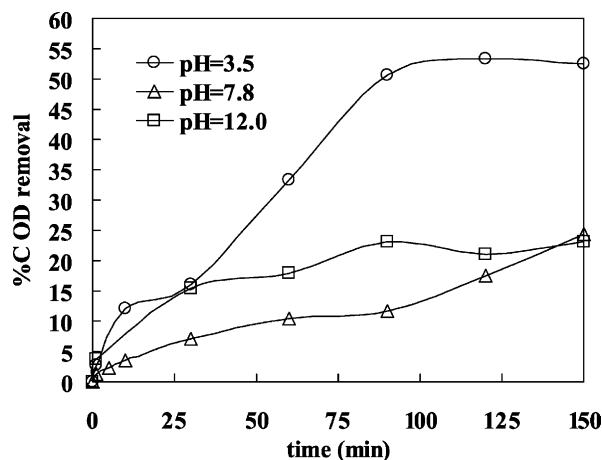


Fig. 6. Effect of pH on COD removal in photo-oxidation of an oily wastewater.

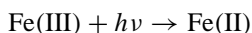
These observations are in accordance with those reported from Kawaguchi [19]. He studied the oxidation efficiency of hydroxyl radical in the photo-oxidation of 2-chlorophenol using UV/H₂O₂. The oxidation efficiency at pH = 3 was almost unity, whereas at pH = 13 was below 0.05. Hydrogen peroxide exists in the form of anions at pH > 12 since its pK_a is 11.7. As a result, the rate constant for the reaction of hydroxyl radical with hydro-peroxide anion (HO₂⁻) becomes comparable with the rate constant of the reaction of hydroxyl radical with 2-chlorophenol, whereas it was 300 times lower at acidic pH.

Moreover, the value of pH affects the structure of the compounds in aqueous solutions and thus also affects their light absorbency [4]. At acidic pH, the phenolic compounds are present in the solution as molecules and they therefore absorb a very small part of the irradiation. Consequently, almost the entire radiation contributes to the decomposition of hydrogen peroxide.

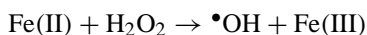
The effect of the solution pH on the decomposition of specific compounds is shown in Fig. 7. The decomposition of the phenolic compounds was pronounced at basic pH, whereas the alcohols were more readily oxidised at approximately neutral pH (the initial pH of the wastewater). It is noteworthy that the acetic acid produced at pH = 3.5 was significantly less (almost half) than that at pH = 7.8, whereas formic acid was not detected at all.

3.3. The effect of Fe(III) addition

The effect of Fe(III) addition (0.03 g l⁻¹) on the wastewater oxidation in the presence of 3330 mg l⁻¹ H₂O₂ was also studied. Fe(III) absorbs ultraviolet irradiation and transforms into Fe(II) at pH values of 3–8, according to the reaction:



Then, it reacts with hydrogen peroxide granting hydroxyl radicals to the solution:



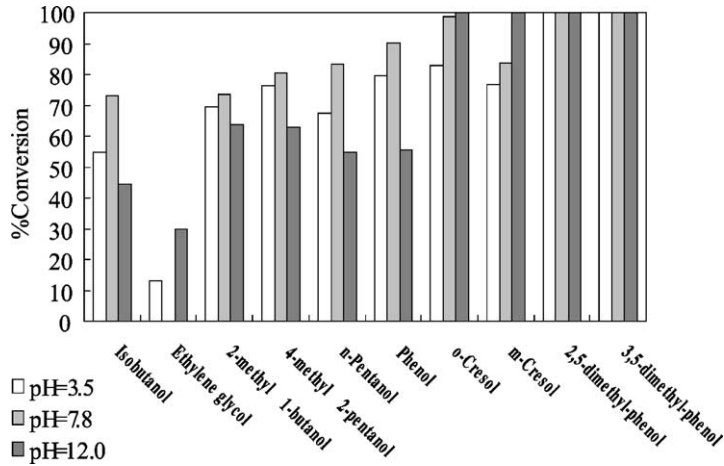
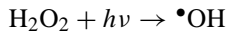


Fig. 7. Effect of pH on the conversion of selected compounds in photo-oxidation of an oily wastewater.

at rates significantly higher than these of the reaction:



The experimental results confirmed the above conclusions. As obvious in Fig. 8, a decrease of 30% in COD was achieved within the first 10 min in the presence of iron ions. No further COD removal was observed because of the formation of organic acids, as it was shown from GC–MS chromatograms. As a result, that explicit difference in the oxidation with and without iron at the first minutes decreased considerably after 2.5 h, as also confirmed from individual compounds (Fig. 9). These results are in total accordance with those obtained in previous studies [3,7,8].

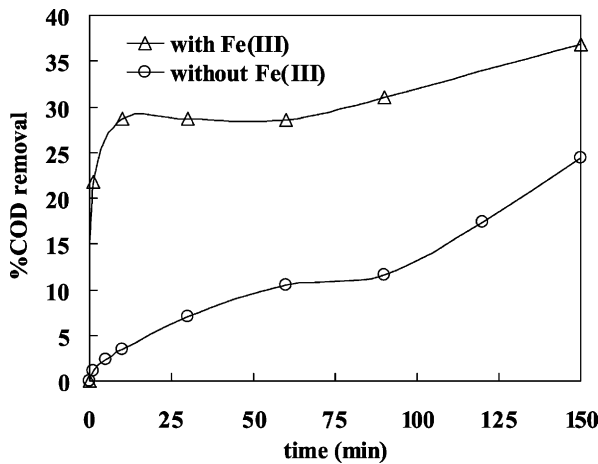


Fig. 8. Effect of Fe(III) addition on COD removal in photo-oxidation of an oily wastewater.

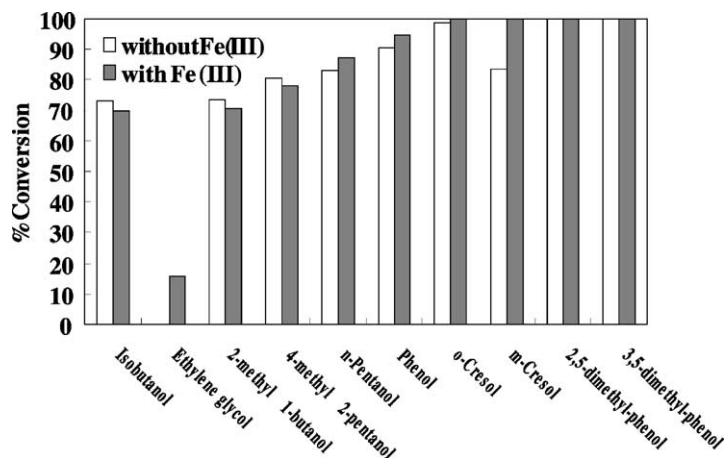


Fig. 9. Effect of Fe(III) addition on the conversion of selected compounds in photo-oxidation of an oily wastewater.

4. Conclusions

In this work, we studied the effect of hydrogen peroxide concentration, initial pH and Fe(III) on the oxidation of a complex wastewater and reached the following conclusions:

- Organic compounds contained in the wastewater were oxidised to organic acids with UV/H₂O₂. Ethylene glycol was almost entirely unaffected by photo-oxidation.
- Oxidation of the wastewater was enhanced at acidic pH.
- Rate of the oxidation increased significantly in the presence of Fe(III), especially at the first minutes of the process.

Acknowledgements

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