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<td><strong>Author(s)</strong></td>
<td>Tony, Maha A.; Purcell, Patrick J.; Zhao, Y.Q.; Tayeb, Aghareed M.; El-Sherbiny, M.F.</td>
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<tr>
<td><strong>Publication date</strong></td>
<td>2009-01</td>
</tr>
<tr>
<td><strong>Publisher</strong></td>
<td>Taylor &amp; Francis</td>
</tr>
<tr>
<td><strong>Link to online version</strong></td>
<td><a href="http://dx.doi.org/10.1080/10934520802539830">http://dx.doi.org/10.1080/10934520802539830</a></td>
</tr>
<tr>
<td><strong>Item record/more information</strong></td>
<td><a href="http://hdl.handle.net/10197/3136">http://hdl.handle.net/10197/3136</a></td>
</tr>
<tr>
<td><strong>Publisher's statement</strong></td>
<td>This is an electronic version of an article published in Journal of Environmental Science and Health, Part A: Toxic/Hazardous Substances &amp; Environmental Engineering, 44 (2): 179-187, available online at: <a href="http://www.tandfonline.com/doi/abs/10.1080/10934520802539830">http://www.tandfonline.com/doi/abs/10.1080/10934520802539830</a></td>
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Photo-Catalytic Degradation of an Oil-Water Emulsion Using the Photo-Fenton Treatment Process: Effects and Statistical Optimization

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ABSTRACT

The application of advanced oxidation processes (AOPs) to the treatment of an effluent contaminated with hydrocarbon oils was investigated. The AOPs conducted were Fe2+/H2O2 (Fenton’s reagent), Fe2+/H2O2/UV (Photo-Fenton’s reagent) and UV-photolysis. These technologies utilize the very strong oxidizing power of hydroxyl radicals to oxidize organic compounds to harmless end products such as CO2 and H2O. A synthetic wastewater generated by emulsifying diesel oil and water was used. This wastewater might simulate, for example, a waste resulting from a hydrocarbon oil spill, onto which detergent was sprayed. The experiments utilising the Photo-Fenton treatment method with an artificial UV source, coupled with Fenton’s reagent, suggest that the hydrocarbon oil is readily degradable, but that the emulsifying agent is much more resistant to degradation. The results showed that the COD (chemical oxygen demand) removal rate was affected by the Photo-Fenton parameters (Fe2+, H2O2 concentrations and the initial pH) of the aqueous solution. In addition, the applicability of the treatment method to a ‘real’ wastewater contaminated with hydrocarbon oil is demonstrated. The ‘real’ wastewater was sourced at a nearby

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car-wash facility located at a petroleum filling station and the experimental results demonstrate the effectiveness of the treatment method in this case. A statistical analysis of the experimental data using the Statistical Analysis System (SAS) and the response surface methodology (RSM) based on the experimental design was applied to optimize the Photo-Fenton parameters (concentrations of Fe$^{2+}$, H$_2$O$_2$ and initial pH) and to maximize the COD removal rate (more than 70%).

Key Words: Fenton, Photo-Fenton, diesel oil, wastewater, photo-catalysis, response surface methodology

INTRODUCTION

As a result of human activities, there are many accidental discharges of hydrocarbon oil to the natural environment during its processing, transportation and storage. For example, it is estimated that, in US alone, at least 2 million litres of petroleum are spilled annually.\textsuperscript{[1]} Oil-spills cause many problems in the environment depending on the volume of the oil spilled.\textsuperscript{[2]} For instance, water resources as well as habitats where fish, birds, and other wildlife live can be damaged.\textsuperscript{[3]} To address this problem, oil wastewater treatment methods traditionally have included phase-separation and skimming, evaporation, filtration and dissolved air flotation. However, these methods transform the pollutants from one phase to another without mineralizing them. In other words, these methods are non-destructive and generate lower volumes of more concentrated waste. Furthermore, these methods are also less effective in removing the smaller oil droplets and emulsion.\textsuperscript{[4, 5]}

Advanced oxidation processes (AOPs) have emerged as alternative wastewater treatment methods which are environmentally friendly producing harmless end-products such as CO$_2$ and H$_2$O$_2$. AOPs are in-situ treatment processes characterized by the generation of highly reactive intermediates (OH radicals) which can oxidise the target organic pollutants.\textsuperscript{[6]} Photo-Fenton’s reagent is one of the
AOPs that require iron ions in the presence of hydrogen peroxide and UV radiation to produce the hydroxyl radicals. The Photo-Fenton reaction occurs in two steps:

1. Fe$^{2+}$ ions are oxidized by H$_2$O$_2$ producing OH radicals and Fe$^{3+}$;
2. Fe$^{3+}$ is then reduced again to Fe$^{2+}$ by the effect of UV light to produce more °OH.\[7\]

Photo-Fenton’s reagent is one of the more widely applied AOPs since it is effective in treating different kinds of wastewater. For instance, Rivas et al.\[8\] investigated the treatment of the olive oil mills wastewater by Fenton’s reagent and the result was a positive influence on TOC (total organic carbon). In addition, the treatment of the complex oily wastewater obtained from a lubricant production using Fenton’s reagent in the presence of the ultraviolet light was investigated by Philippopoulos and Poulopoulos.\[9\] Moraes et al.\[10\] applied the Photo-Fenton process in the treatment of the wastewater contaminated with hydrocarbons using model raw gasoline oil. The impact of hydrogen peroxide, iron and sodium chloride concentrations on process performance was evaluated using the TOC technique; their results demonstrated that the Photo-Fenton process is a feasible treatment process for this wastewater. Coelho et al.,\[11\] concluded that a satisfactory treatment by the Photo-Fenton treatment process was obtained in the case of a petroleum refinery wastewater, achieving over 80% reduction in DOC (dissolved organic carbon). The treatment of the contaminated wastewater with gasoline by the Photo-Fenton method was carried out by Galvao et al.\[12\], resulting in the TOC removal of 99% compared with 71% when the UV/H$_2$O$_2$ process was used.

The concentrations of the ferrous ions (Fe$^{2+}$), hydrogen peroxide (H$_2$O$_2$) and the pH of the wastewater are the most important factors in determining the efficiency of the Photo-Fenton treatment process. Optimization of these parameters is an obvious research goal. A statistical technique known as the response surface methodology (RSM) was used to optimize these variables.
RSM has previously been applied to optimize the Photo-Fenton treatment process in the treatment of contaminated soil and wastewater.\cite{14, 15, 16} The study presented below describes the application of the Photo-Fenton reagent to the mineralization of a synthetic diesel-oil wastewater emulsion and a ‘real’ car-wash wastewater contaminated with diesel oil. The effect of the reaction operating conditions was investigated and the RSM methodology was used to maximize COD removal rates.

**MATERIALS AND METHODS**

**Materials**

Commercial diesel oil was used as the model pollutant using sodium dodecyl sulphate ($C_{12}H_{25}Na_4S$) emulsifier to prepare the oil-water emulsion. Car-wash wastewater collected at a petroleum filling station was the source of the ‘real’ wastewater effluent. Ferrous chloride tetrahydrate ($FeCl_2\cdot4H_2O$) and hydrogen peroxide ($H_2O_2$; 30 wt %) from Sigma-Aldrich were used as the source of the Fenton’s reagent. Sulphuric acid was used to adjust pH. For the radiated experiments a UV lamp (high intensity 254nm UV, model R-52Grid Lamp) was used as a source of the UV light.

**Preparation of the Oil-water Emulsion**

Oxidation experiments were performed on the synthetic oil-water emulsion obtained by adding 2.5 mL of 0.1 g/L emulsifier solution to 1L of distilled water to which a 100 mL of diesel oil was added gradually while stirring. The resulting emulsion was then stirred using a magnetic stirrer for 24 hours and left to stand for 1 hour to ensure separation of the non-dispersed oil in the water. The subnatant was then filtered using a quantitative filter paper (Whatman 22 µm), generating an emulsion with a COD (chemical oxygen demand) concentration of 1500 mg/L. This emulsion was then diluted with distilled water to produce emulsion concentrations in the range of 200 to 800 mg-COD/L.
**Car-wash Wastewater**

‘Real’ wastewater samples were collected from a car washing wastewater tank at a petroleum filling station in the south of Dublin City, Ireland. The principal properties of this wastewater are: 82 mg-COD/L, pH 8.2 and a suspended solids of 55 mg/L. To ensure saturation of the wastewater with diesel oil, some samples, after the collection, were subjected to 24 hours of stirring following the addition of the commercial diesel oil (100 mL/L). Thereafter, the wastewater, augmented with diesel oil, was filtered through a quantitative filter paper (Whatman 22 µm) to produce an emulsion with a COD of 404 mg-COD/L.

**Experimental Procedure**

The experiments were carried out in a batch mode at laboratory-scale using a 250 mL beaker. Firstly, to produce the hydroxyl radicals, ferrous ions were added to a 200 mL sample of the wastewater. The Fenton reaction was then enhanced by adding hydrogen peroxide. In the case of the experiments where the effect of the pH was examined, the pH of the emulsion was adjusted by adding sulphuric acid before Fenton’s reagent was added. Thereafter, the mixture was subjected to magnetic stirring and UV radiation (254nm wavelength), as illustrated in Fig. 1. Samples were taken at a regular time intervals to determine the degree of COD removal from the wastewater. In order to investigate different AOPs, experiments were conducted using UV-photolysis alone Fenton’s reagent without UV radiation and compared with the Fenton’s reagent with the UV radiation (Photo-Fenton). In addition, the effect of the initial concentration of oil-water emulsion, the pH and the initial concentration of H$_2$O$_2$ and Fe$^{2+}$ were studied.

**Analytical Methods**

Measurements of COD were performed using the HACH instrument (model HACH DR-2400) in order to measure the effect of AOPs on the mineralization of the emulsion and for each
measurement, three samples were taken and the average value is reported. The pH of the emulsion was measured using a digital pH-meter (model PHM62 supplied by Mason).

RESULTS AND DISCUSSION

Comparison of Different Degradation Systems

Fig. 2 shows the investigation of the different AOPs and the comparison of their performance with the Photo-Fenton’s reagent. The doses for the Fenton’s reagent were: \([\text{Fe}^{2+}] = 40 \text{ mg/L}; \ [\text{H}_2\text{O}_2] =100 \text{ mg/L}\) and the starting pH of the emulsion was 8 without any adjustment. Examination of the results shows that the UV-photolysis without the Fenton’s reagent addition only achieved a 5% reduction after 6 hours in the COD concentration. However, Fenton’s reagent alone achieved a COD reduction of 42%. Clearly, the reaction between the ferrous ions and hydrogen peroxide produced the \(\cdot\text{OH}\) radicals which played an important role in the oil degradation. As reported in the literature, diesel oil consists of aromatic compounds and Fenton’s reagent is efficient in the destruction of these aromatic compounds. The \(\cdot\text{OH}\) radicals attack these aromatic compounds opening the rings and producing reaction intermediates which are ultimately converted to harmless end products such as \(\text{CO}_2\) and \(\text{H}_2\text{O}\). Furthermore, when the UV was used in conjunction with the Fenton’s reagent in the Photo-Fenton process a more pronounced degradation was obtained (COD reduction=50%). The UV photolysis in addition the chemical reagent enhanced the generation of more reaction hydroxyl intermediates which resulted in enhanced degradation of the pollutants. These observations are in accordance with that obtained by Moraes et al.\textsuperscript{[17]} and Galvao et al.\textsuperscript{[12]}

Effect of the Initial Emulsion Concentration

The effect of the initial concentration of the oil-water emulsion on its photo-catalytic degradation is shown in Fig. 3. It is clear from Fig. 3 that the reaction rate is increased by decreasing the initial emulsion concentration and the percentage COD removals are 60, 71, 72, 75, 82 for the initial emulsion concentrations of 1500, 800, 600, 400 and 200 mg-COD/L, respectively. The increasing
percentage COD removal with decreasing initial COD concentration can be attributed to the
decrease in turbidity of the emulsion. The emulsion turbidity for an initial COD of 1500 mg/L was
49 NTU, whereas when the initial COD was 200 mg/L the emulsion turbidity was only 5 NTU.
Decreasing turbidity clearly enhances the penetration of the UV light, resulting in enhanced COD
removal. This observation of increasing the photo-catalytic reaction rate with decreasing the initial
pollutant concentration was also reported by Najjar et al., \cite{19} in the photo-catalytic degradation of
the nitrophenol.

**Effect of Iron Concentration**

Photo-Fenton treatment of the emulsion was undertaken at different Fe$^{2+}$ concentrations (10-100
mg/L) to examine the role of Fe$^{2+}$ concentration in the Photo-Fenton degradation process. The
results in Fig. 4 show that the mineralization rate increased with Fe$^{2+}$ concentration, the optimal
value being 40mg/L which results in a 60% removal of COD after 150 minutes of reaction time.
Iron concentrations above this optimal value result in reduced process performance because more
species of iron ions are produced rather than the more useful ·OH radicals. This finding is in
agreement with the previous observation of Kositzi et al. \cite{20}

**Effect of H$_2$O$_2$ Concentration**

To investigate the effect of hydrogen peroxide on the Photo-Fenton treatment process the
concentration of the former was varied and all the other parameters were kept constant. The results,
illustrated in Fig. 5, show a significant enhancement of the degradation process when the H$_2$O$_2$
concentration was increased from 50 mg/L to 400 mg/L. Increasing H$_2$O$_2$ concentration results in
the generation of additional reaction intermediates (·OH) radicals which enhances the degradation
process. However, at higher peroxide concentrations, the excess hydrogen peroxide can act as an
·OH scavenger, forming HO’2, which is also a free radical produced in-situ from the H$_2$O$_2$ but is a
less reactive oxidizing agent and therefore has a longer life time than the `OH and the result is a reduction in the overall reaction rate.\textsuperscript{[21-23]}

**Effect of the Initial pH**

As the effect of the pH plays an important role in the Photo-Fenton treatment process, its dependence was studied by varying the initial pH of the emulsion.\textsuperscript{[12, 20, 24, 25]} The natural pH of the oil-water emulsion was 8.5. In this study, pH in the range 2 to 8.5 was examined. The natural pH of the wastewater was altered by adding sulphuric acid. It is clear from the results in Fig. 6 that the performance of the Photo-Fenton process is highly dependent on the initial pH of the aqueous emulsion. The optimal performance was found to be at the pH of the emulsion without any adjustment. These results imply that the initial pH plays an important role in the initiation of the reaction intermediates. In other words, pH is the controlling parameter in the hydrogen peroxide decomposition; at very low pH, the peroxide decomposes slowly and the reaction rate becomes very slow.\textsuperscript{[24]}

The optimal pH value found in this case accords with the findings of Philippopoulos and Poulopoulos\textsuperscript{[9]} who found that an alkaline pH was most effective in the Fenton treatment process of wastewater polluted with phenol solution. However, Paterlini and Nogueira\textsuperscript{[7]} found that an acidic pH (2.5) was best for the treatment of an herbicide solution. Moreover, Kang and Hwang also found the pH in the range 2.5-4 to be the most efficient pH for the treatment by Fenton’s reagent of the landfill leachate.\textsuperscript{[25]} Thus, it is reasonable to conclude that the optimum pH for Photo-Fenton wastewater treatment is very dependent on the wastewater composition.

**Application of Photo-Fenton’s Reagent to ‘Real’ Wastewater**

The applicability of this technology to the treatment of ‘real’ wastewater is demonstrated in the case of car-wash wastewater sourced at a petroleum filling station. The optimum concentrations of Fenton’s reagent determined in the experiments using the synthetic oil-water emulsion were applied
to the ‘real’ car-wash wastewater: \( [\text{Fe}^{2+}] = 40 \text{ mg/L}; [\text{H}_2\text{O}_2] = 400 \text{ mg/L} \). The pH of the wastewater was 8.2 and no adjustment was made. The wastewater was continuously stirred in the presence of the UV light for a total reaction time of 4 hours. The results of this experiment are graphically illustrated in Fig. 7 and demonstrate the ability of the Photo-Fenton method to degrade this wastewater. A second experiment was undertaken with this ‘real’ wastewater augmented with diesel oil. Examination of Fig. 7 shows that, although the initial COD concentrations of ‘real’ wastewater (82 mg/L) and the ‘real’ wastewater augmented with diesel oil (404 mg/L) significantly differ, the rates of degradation are similar in both cases. It should also be noted that the ‘model’ and ‘real’ wastewater rates of degradation are also comparable.

**STATISTICAL ANALYSIS OF PHOTO-FENTON PROCESS**

Optimization of the Photo-Fenton treatment process (by determining the optimum of the independent variables; \( \text{Fe}^{2+}, \text{H}_2\text{O}_2 \) and pH) to degrade the oil-water emulsion was conducted using the response surface methodology (RSM) design. \(^{[13]}\) As indicated in Table 1, fifteen sets of experimental data were used in the numerical analysis. A Box-Behnken factorial design and analysis of the experimental data was undertaken. \(^{[13]}\) In the numerical analysis (see Table 1) the \( \text{Fe}^{2+} \) concentration, \( \text{H}_2\text{O}_2 \) concentration and initial pH are denoted as \( X_i, X_2 \) and \( X_3 \), respectively, corresponding to their experimental values \( x_1, x_2 \) and \( x_3 \). The experimental data collected was analysed by performing the analysis of variance (ANOVA) using the Statistical Analysis System (SAS) \(^{[26]}\) and fitted with a second-order polynomial model. The following response function (1) was used to correlate the dependent and independent variables in the response surface:

\[
S = \beta_0 + \sum \beta_i X_i + \sum \beta_i^2 X_i^2 + \sum \sum \beta_{ij} X_i X_j
\]  

(1)

where \( S \) is the predicted response (COD removal, %); the model regression coefficients are: \( \beta_0 \) the constant coefficient, \( \beta_i \) the linear coefficients, \( \beta_{ij} \) the quadratic coefficients and \( \beta_{ij} \) are the model regression coefficients; \( X_i \) and \( X_j \) are the independent variables. Mathematica software version 5.2.
was used to obtain the optimum conditions for the operating variables and for the COD percentage removal. The response surfaces of two-dimensional contour plots and three-dimensional curves were developed using MATLAB 7 software. The experiments were planned and conducted according to the three-level factorial Box-Behnken design as presented in Table 2. Analysis of the data by SAS yielded the following second order polynomial equation:

\[
S(\%) = 63.797 - 2.94X_1 - 0.324X_2 + 5.60X_3 - 9.56X_1^2 + 2.08X_1X_2 - 4.12X_1X_3 - 16.66X_2^2 + 0.58X_2X_3 - 0.55X_3^2
\]

Table 2 presents a statistical analysis of the data by SAS. The analysis was done by means of the coefficient of correlation \((R^2)\) of the experimental data and by means of Fisher’s \((F)\) test. The correlation coefficient is a measure of the goodness of fit between the model and experimental data. The \(F\) test is used to determine the significance of the regression coefficients of the parameters. The analysis of variance table is composed of the following columns: Source (the source of the variation); DF (the degree of freedom); SS (the sums of squares); MS (the mean squares); Fisher \(F\) values; Probability \(P\) values. The sum of the squares (SS) is the summation of the squares of the dependent variables. The mean squares (MS) column lists the mean squares which are the sums of squares divided by the degree of freedom. The \(F\) value is defined as follows:

\[
F \text{ value} = \frac{\text{Between groups variance}}{\text{Pooled variance}}
\]

In general, the larger the magnitude of the \(F\) and the smaller the value of \(P\) (the probability of exceedance of \(F\)) the more significant is the corresponding coefficient term. The model is significant when the \(P\)-value is less than 0.05. Examination of the table shows that the model is highly significant as the Fisher \(F\)-test is 8.476 with a low probability \(P\) of exceedance value of 0.0149. The high correlation coefficient \((R^2)\) of 0.94 demonstrates how well the model fits
the experimental data (as shown in Fig. 8), the model being rejected if the $R^2$ value is less than 0.8.

By fixing one parameter at its zero level, it was possible to graphically represent the relationship between the percentage COD removal and the other two independent variables using MATLAB 7.0 (Figs. 9-11). The optimum values of the selected variables in the Photo-Fenton process were obtained using Mathematica software (V 5.2): $[\text{Fe}^{2+}] = 33 \text{ mg/L}; [\text{H}_2\text{O}_2] = 397 \text{ mg/L}; \ \text{pH} = 8.5; \ \text{COD percentage removal} = 70.$

Table 3 provides the comparison of the results obtained in the literature with those from the presented study. With the exception of $^{[29]}$, removal efficiencies reported in the literature for gasoline/diesel wastewaters varied from 66% to 96%, the present study being 70%. The range of the removal efficiencies is attributable to the variety of hydrocarbon compounds and their concentrations in the wastewaters.

**CONCLUSIONS**

The present study demonstrates the suitability of advanced oxidation processes for the treatment of oil-water emulsion and car-wash wastewater. The Photo-Fenton process using the artificial UV light is more efficient than the Fenton and UV-radiation treatment processes on their own. After 150 min of the Photo-Fenton reaction, the COD removal rate ranged from 60-82 %, depending on the initial concentration of the emulsion (for the concentration range 1500-200 mg-COD/L, respectively). However, after 240 minutes reaction time, the final COD percentage removals achieved were 74% for the car-wash wastewater and 65% for the car-wash wastewater augmented with the diesel oil. Moreover, the removal efficiencies were improved by increasing the hydrogen peroxide and ferrous ion concentrations, but once $[\text{Fe}^{2+}]_o$ and $[\text{H}_2\text{O}_2]_o$ concentrations exceeded 40 and 400 mg/L respectively little improvement resulted. Finally, an increase in the efficiency of the COD removal from this wastewater could be achieved by optimizing the Photo-Fenton parameters using RSM. The maximum response (COD percentage removal) exceeded 70 % for the initial emulsion
concentration of 800 mg-COD/L using the optimum values of 33 and 397 mg/L for Fe$^{2+}$ and H$_2$O$_2$.

respectively at a pH of 8.5.

ACKNOWLEDGMENTS

Maha Tony gratefully thanks the Ministry of Higher Education, Missions Department, Egypt for the financial support granted through the Channel Scheme Mission. The authors would like to thank Mr. P. Kearney for his technical assistance during this study.

REFERENCES


### Table 1. Statistical Analysis System (SAS) input and output data

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<td>H$_2$O$_2$ (mg/L)</td>
<td>pH</td>
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<td>6</td>
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* $X_i = \frac{(x_i \text{ upper level} + x_i \text{ lower level})}{2} - \frac{(x_i \text{ upper level} - x_i \text{ upper level})}{2}$

### Table 2. Analysis of Variance (ANOVA) for response surface

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<th>Source</th>
<th>Degree of freedom (df)</th>
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$R^2 = 93.85\%$; adj $R^2 = 82.78\%$
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<tr>
<th>Type of wastewater</th>
<th>Initial organic concentration</th>
<th>Experimental conditions</th>
<th>UV source</th>
<th>% organic removal Ref.</th>
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<td>Synthetic emulsion of diesel wastewater</td>
<td>800 mg-COD/L</td>
<td>33 mg/L (FeCl$_2$ .4H$_2$O) 397 (30%, m/v)</td>
<td>254nm high intensity UV lamp</td>
<td>70% (COD removal) This study</td>
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<td>80-90 mg-TOC/L</td>
<td>3400 (FeSO$_4$ .7H$_2$O) 1 mM</td>
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<td>Sourwater from petroleum refinery</td>
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<td>83% (DOC removal) [11]</td>
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<td>3400 (FeSO$_4$ .7H$_2$O) 1 mM</td>
<td>450W Hg UV lamp</td>
<td>66-91% (TOC removal) [18]</td>
</tr>
<tr>
<td>Olive mill wastewater</td>
<td>34000 mg-COD/L</td>
<td>5000 (FeSO$_4$ 5 mM)</td>
<td>Solar UV source</td>
<td>50% (COD removal) [28]</td>
</tr>
<tr>
<td>Synthetic gasoline wastewater</td>
<td>-</td>
<td>500 (FeSO$_4$ .7H$_2$O) 10 mg/L</td>
<td>125 W medium pressure Hg UV lamp</td>
<td>20% (Evaluated by fluorescence spectroscopy) [29]</td>
</tr>
</tbody>
</table>
FIGURE CAPTIONS:

**Figure 1.** Schematic diagram of the experimental set-up

**Figure 2.** Effect of different degradation systems on the oil-water emulsion (Fenton and Photo-Fenton reagents: [Fe$^{2+}$] = 40 mg/L; [H$_2$O$_2$] = 100 mg/L, pH = 8)

**Figure 3.** Effect of the initial emulsion concentration (operating parameters: [Fe$^{2+}$] = 40 mg/L; [H$_2$O$_2$] = 400 mg/L; pH = 8)

**Figure 4.** Effect of the iron concentration on the Photo-Fenton treatment process (operating parameters: [H$_2$O$_2$] = 400 mg/L; pH = 8)

**Figure 5.** Effect of the H$_2$O$_2$ concentration on the Photo-Fenton treatment process (operating parameters: [Fe$^{2+}$] = 40 mg/L; pH = 8)

**Figure 6.** Effect of pH on the Photo-Fenton treatment process (operating parameters: [Fe$^{2+}$] = 40 mg/L; [H$_2$O$_2$] = 400 mg/L)

**Figure 7.** Effect of the Photo-Fenton’s reagent on the car-wash wastewater ([Fe$^{2+}$] = 40 mg/L; [H$_2$O$_2$] = 400 mg/L; pH = 8.2)

**Figure 8.** Plot of the measured COD removal (%) against the predicted values from the second order response surface model, ($R^2$ = 0.94)

**Figure 9.** 3-D surface and contour plot of the predicted % COD removal (S, %) showing the effect of the $X_1$ (Fe$^{2+}$ dose) and $X_2$ (H$_2$O$_2$ dose)

**Figure 10.** 3-D surface and contour plot of the predicted % COD removal (S, %) showing the effect of the $X_1$ (Fe$^{2+}$ dose) and $X_3$ (pH)

**Figure 11.** 3-D surface and contour plot of the predicted % COD removal (S, %) showing the effect of the $X_2$ (H$_2$O$_2$ dose) and $X_3$ (pH)
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