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Oil refinery wastewater treatment using physico-chemical, Fenton and Photo-Fenton

oxidation processes

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ABSTRACT

The objective of this study was to investigate the application of advanced oxidation processes (AOPs) to the treatment of wastewaters contaminated with hydrocarbon oil. Three different oil-contaminated wastewaters were examined and compared: 1) a 'real' hydrocarbon wastewater collected from an oil refinery (Conoco-Phillips Whitegate refinery, County Cork, Ireland); 2) a 'real' hydrocarbon

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wastewater collected from a car-wash facility located at a petroleum filling station; and 3) a 'synthetic' hydrocarbon wastewater generated by emulsifying diesel oil and water. The AOPs investigated were Fe^{2+}/H_2O_2 (Fenton's reagent), $Fe^{2+}/H_2O_2/UV$ (Photo-Fenton's reagent) which may be used as an alternative to, or in conjunction with, conventional treatment techniques. Laboratory-scale batch and continuous-flow experiments were undertaken. The photo-Fenton parametric concentrations to maximize COD removal were optimized: pH = 3, H_2O_2 = 400 mg/L, and Fe^{2+} = 40 mg/L. In the case of the oil-refinery wastewater, photo-Fenton treatment achieved approximately 50% COD removal and, when preceded by physico-chemical treatment, the percentage removal increased to approximately 75%.

Keywords: oil refinery wastewater; hydrocarbons degradation; photocatalysis; Fenton's reagent; Chemical oxygen demand (COD)

INTRODUCTION

Crude oil is transformed into petroleum and other useful by-products through refining processes. During those processes large quantities of water are consumed and there is therefore a corresponding quantity of wastewater produced which consists of cooling water, process water, storm water, and sewage. This wastewater may, however, contain some oil because of the origin of the wastewater.[1] The fraction of oil entrained in the wastewater depends on the oil processing undertaken. Coelho et al.[2] reported that the quantity of water used in the oil refinery processing industry ranges from 0.4 to 1.6 times the volume of processed oil and this wastewater may, if

untreated, cause serious damage to the environment. The development of treatment processes appropriate to wastewaters contaminated with oil is clearly very important. Typically, wastewaters generated in refinery processes are treated on-site and then discharged to publicly owned treatment works or discharged to an adjacent receiving water. [3]

Conventional chemical and physical treatment methods can be applied for treating these kinds of wastewaters. Petroleum refineries typically utilize primary and secondary wastewater treatment. Primary wastewater treatment consists of oil-water separation using physical methods which include the use of sedimentation or dissolved air flotation. Chemicals, such as ferric hydroxide or aluminum hydroxide, can be used to coagulate impurities into sludge which can be more easily removed. [1, 3] However, these processes result in concentrated sludges which require further processing and disposal. In addition, conventional treatment processes have difficulty in fully removing emulsified oil or small oil droplets. [1, 4-7]

Advanced oxidation processes (AOPs) have been investigated for the oil-contaminated wastewater treatment as an alternative to conventional treatment techniques. AOPs are characterized by the use of highly reactive intermediates, hydroxyl radicals ($\cdot OH$), that attack the organic pollutants in the wastewater and mineralize them. [8-12] Such processes include UV [2]; O_3/H_2O_2 [1]; O_3/UV [1, 2]; TiO_2 photo-catalysis [13-15] and Fenton and photo-Fenton processes [16].

In the present investigation, UV-light and Fenton's reagent were used to treat an oil process wastewater at an oil refinery. The photo-Fenton kinetics were investigated and the process was compared with conventional treatment methods. In addition, the treatment performance of two different types of oil-contaminated wastewaters with Fenton's reagent was compared with that of oil refinery wastewater.

MATERIALS AND METHODS

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Experimental Materials

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83   Samples of the raw wastewater were collected from a petroleum refinery at Whitegate, County

84 Cork, Ireland. For the purpose of comparison with the refinery wastewater, two other kinds of

85 wastewaters were compared: a synthetic oil-water emulsion and car-wash wastewater sourced from

86 a petroleum filling station. The synthetic model oil-water emulsion was prepared using commercial

87 automotive diesel oil and chemical emulsifier mixed in distilled water and the resulting mixture was

88 stirred as described in our previous work. [6] The principal parameters for these wastewaters are

89 listed in Table 1.

90   A solution of Fe^{2+} (prepared from ferrous chloride tetrahydrate ($FeCl_2.4H_2O$)) and hydrogen

91 peroxide (30%, by weight) was used in the experiments as the Fenton's reagent for hydroxyl radical

92 generation. Sulfuric acid and sodium hydroxide were used to adjust the pH to the desired values.

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95 **Experimental Procedures**

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98   A schematic of the experimental setup is illustrated in Figure 1. A 200 mL aliquot of the

99 wastewater sample was subjected to magnetic stirring, following the addition of Fenton's reagent.

100 The UV light was provided by a high intensity 254 nm UV grid lamp, manufactured by UVP Inc.

101 (model R-52). The physico-chemical treatment of the oil refinery wastewater undertaken in this

102 laboratory study includes conventional physical separation processes in conjunction with the Fenton

103 and photo-Fenton processes. Following the addition of Fenton's reagent, the wastewater was

104   subjected to 10 minutes of rapid mixing followed by 30 minutes of slow mixing to promote reaction

105   coagulation and flocculation respectively.

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108   **Analytical Determinations**

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111   The wastewater substrate concentration was measured by its Chemical Oxygen Demand

112   (COD) using a HACH analyser (model HACH DR-2400) following the standard procedure of

113   sample digestion.[17] In addition, the suspended solids (SS) and the colour were determined for the

114   raw wastewater using the HACH analyser. The turbidity of the wastewater was also measured using

115   a HACH 2100N IS Turbidimeter (USA). The pH of the wastewater was measured using a digital

116   pH-meter (model PHM62 Radiometer, Copenhagen).

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119   **RESULTS AND DISCUSSION**

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122   **Effect of Reaction Time**

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125   In order to find the reaction time required to reach a steady state, experiments were performed

126   over a 160 minute period for two different treatments: (a) Fenton's reagent and (b) photo-Fenton

127   reagent at the following operating parameters pH = 7.6; $[H_2O_2]_o$ = 400 mg/L; $[Fe^{2+}]_o$ = 40 mg/L.

128   The COD of the wastewater was monitored continuously during the course of the reaction. COD

129   removal efficiency increased with increasing reaction time, as illustrated in Figure 2, but after about

80 minutes, the rate of COD removal significantly diminished. Kim et al., [18]; Moraes, et al. [19]; Galavo et al. [16] and Tony et al. [6] recorded a similar result. These findings may be explained by the production of highly reactive intermediates (hydroxyl radicals) which primarily influence the reaction kinetics during the first phase of the reaction. Thereafter, the reaction rate diminished as the hydrogen peroxide, which is the primary source for the generation of the hydroxyl radicals, was consumed.

Examination of Figure 2 shows that UV light in conjunction with Fenton's reagent (photo-Fenton) is clearly more effective in the COD degradation than Fenton's reagent on its own. This observation implies that the UV photolysis generated more reaction hydroxyl intermediates, which resulted in enhanced degradation of the pollutants. Based on these results, further experiments were performed to examine the effects of the Fenton's reagent operating parameters, as will be described hereunder.

Effect of H_2O_2

In order to determine the optimum H_2O_2 concentration to treat the oil refinery wastewater using Fenton process, the H_2O_2 dose was varied from 100 to 800 mg/L. As illustrated in Figure 3, the COD removal increased as the H_2O_2 concentration increased from 100 to 400 mg/L and decreased thereafter. Clearly, the H_2O_2 concentration is a key factor that significantly influences the reaction kinetics since the number of OH radicals generated in the photo-Fenton reaction is directly related to the H_2O_2 concentration. However, when the concentration of H_2O_2 exceeds the optimum value, the reaction rates decreased as a result of the so-called scavenging effect of excess of H_2O_2 reacting with .OH, thereby decreasing the .OH available to degrade the wastewater organics. [20-22]

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Effect of Fe^{2+}

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To determine the optimum Fe^{2+} concentration for the mineralization of the refinery wastewater, the wastewater was dosed with Fe^{2+} concentration in the range of 10 to 80 mg/L, the H$_2$O$_2$ concentration kept at the optimum value of 400 mg/L. As illustrated in Figure 4, the optimum Fe^{2+} concentration was found to be 40 mg/L which resulted in 15% removal after approximately 2 hours reaction time. Increasing the Fe^{2+} concentration above the optimal value adversely impacted on the reaction kinetics and resulted in additional iron precipitation, one of the disadvantages of the Fenton process. Similar observations were made in earlier studies by Kositzi et al. [14] and Tony et al. [6].

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Effect of pH

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The pH significantly affects the Fenton process since the process has a preferred pH range for optimal performance. The pH affects the activity of both the speciation of iron, and hydrogen peroxide decomposition. Figure 5 shows the effect of pH on the COD removal efficiencies. Examination of the figure shows that the removal efficiency increases with decreasing pH, the optimal pH being 3.0. These observations are in accordance with those reported by Paterlini and Nogueira [23] and Kang and Hwang [24] who found that an acidic pH (2.5 - 4) was optimum for the photo-Fenton process. Hence, the optimal pH for the treatment of the oil refinery wastewater is 3.0

181 at which OH radical production is maximized, resulting in a reduction in the wastewater COD by

182 approximately 50%.

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185 **Effect of Continuous-flow**

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188   To access the COD removal efficiencies under continuous flow operating conditions, the

189 wastewater was pumped through the bench-scale reactor shown in Figure 1. The COD removal

190 efficiencies, from start-up until steady state was reached for various hydraulic residence times

191 (HRT) are shown in Figure 6. Examination of Figure 6 shows that, as expected, COD removal

192 efficiency improved with increasing HRT. The percentage COD removal was in the range of 35–

193 45% at steady state, as shown in Figure 6. COD removals greater than 45% were attained (steady-

194 state values) when HRT exceeded 1000 minutes. The results presented above are in accordance

195 with the published findings of Coelho et al. [2], who investigated the photo-Fenton treatment of sour

196 wastewater. A reactor design with better flow-though characteristics, coupled with a more efficient

197 UV radiation system, are likely to improve the process performance, and, thus, higher hydrocarbon

198 removal rates.

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201 **Effect of Fenton's Reagent on Different Wastewater Effluents**

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204   In this part of the study, experiments were undertaken to compare the performance of the photo-

205 Fenton's reagent in respect of three types of wastewater polluted with hydrocarbons:

206 (a) car-wash wastewater;

207   (b) car-wash wastewater augmented with 100 mL/L diesel oil;

208   (c) synthetic oil-water emulsion wastewater.

209   The experimental conditions are based on earlier work by the authors, in which the effect of the

210   main process variables was examined. [6, 7] The results of these earlier studies were used as a guide

211   for the choice of the H_2O_2 and Fe^{2+} concentration to be adopted in the present study for the

212   treatment of a car-wash wastewater and a synthetic oil wastewater emulsion. The photo-Fenton

213   experiments were performed simultaneously on each of the wastewaters. During the experiments,

214   the COD removal increased with reaction time, as illustrated in Figure 7. Removal rates of about

215   66% for the car-wash wastewater, 50% for the car-wash wastewater augmented with diesel oil and

216   43% for the synthetic oil-water emulsion were recorded in the experiments undertaken. The

217   synthetic oil-water was the most difficult wastewater to degrade and this finding is most likely

218   attributable to the difficulty in degrading the emulsion contained in the wastewater. Clearly, the

219   concentration and the type of organic compounds contained in the wastewater have a significant

220   effect on the reaction kinetics. These results are in accordance with previous observations

221   concerning the degradation rate of organic contaminants by photo-Fenton processes. [25, 26]

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224   **Effect of Combined Physico-chemical Treatment**

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227   The investigation of pre-treating the wastewaters prior to the application of the photo-Fenton

228   reagent is described below. The two-stage process consists of physico-chemical pre-treatment of oil

229   refinery wastewater followed by photo-Fenton treatment for hydroxyl radical production. The

230   purpose of combined physical and chemical treatment is to maximize process performance at

231   minimum cost. A schematic of the laboratory-scale treatment sequence is presented in Figure 8. As

232   illustrated in the figure, the process sequence consists of coagulation, flocculation, sedimentation,

233 filtration and photo-Fenton treatment. Following pre-treatment, the wastewater was subjected to

234 photo-Fenton treatment.

235 Physical treatment processes merely transfer pollutants from one phase to another without

236 mineralizing them. Physico-chemical processes can eliminate both suspended and dissolved solids.

237 Therefore, better removal rates can be obtained with physical separation followed by the Fenton

238 treatment than treatment with Fenton's reagent alone.

239 Figure 9 illustrates the COD removal efficiencies for the oil-refinery wastewater for two different

240 pre-treatments:

241 (a) coagulation, flocculation, sedimentation;

242 (b) coagulation, flocculation, sedimentation and filtration.

243 In the former case, a 61% COD removal efficiency was achieved while in the latter case a 69%

244 COD removal efficiency was achieved after 160 minutes. In the oxidation process, the contaminants

245 are treated with a combination of hydrogen peroxide and ferrous chloride (Fenton's reagent) and

246 artificially irradiated with ultraviolet light. Optimal conditions for Fenton's reagent were established

247 and the pH was adjusted to 3. The highest percentage COD removal achieved was 75%, which

248 occurred with pre-treatment including filtration followed by Fenton treatment. When the waste was

249 treated with Fenton's reagent alone, only 50% COD removal was achieved and when preceded by

250 physico-chemical treatment without filtration 64% COD was removed.

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253 **CONCLUSIONS**

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256 Two industrial wastewaters containing hydrocarbons (an oil-refinery wastewater and a car-wash

257 wastewater) were subjected to laboratory studies to investigate photo-Fenton treatment of the

258 wastewaters. Since the degradation rate by Fenton's reagent depends on the concentration of Fe^{2+},

259 H₂O₂ and pH, the optimal conditions were applied to maximize COD removal. The laboratory-scale

260 experimental results show that photo-Fenton oxidation is an effective treatment process for

261 industrial wastewater containing hydrocarbons. The results show that approximately 50% of the

262 COD of the wastewater was degraded in a reaction time of 1.5 hours. When the photo-Fenton

263 treatment was combined with physico-chemical pre-treatment, the percentage COD removal was

264 increased to approximately 75%.

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FIGURE CAPTIONS:

FIGURE 1:   Schematic diagram of the experimental setup

FIGURE 2: Effect of reaction time for Fenton and photo-Fenton treatment (operating parameter: pH = 7.6; $[H_2O_2]_o$= 400 mg/L; $[Fe^{2+}]_o$= 40 mg/L)

FIGURE 3: Effect of hydrogen peroxide (operating parameter: pH = 7.6; $[Fe^{2+}]_o$= 40 mg/L)

FIGURE 4: Effect of Fe^{2+} (operating parameter: pH = 7.6; $[H_2O_2]_o$= 400 mg/L)

FIGURE 5: Effect of pH (operating parameters: $[H_2O_2]_o$= 400 mg/L; $[Fe^{2+}]_o$= 40 mg/L)

FIGURE 6:   COD removal against time for continuous flow operation at different hydraulic residence times (HRT): Experimental conditions pH = 3; $[H_2O_2]_o$= 400 mg/L; $[Fe^{2+}]_o$= 40 mg/L

FIGURE 7:   Effect of photo-Fenton's reagent on different types of wastewater effluent: Experimental conditions (operating parameters: pH = 3; $[H_2O_2]_o$= 400 mg/L; $[Fe^{2+}]_o$= 40 mg/L)

FIGURE 8: Schematic laboratory physico-chemical treatment sequence for oil refinery wastewater

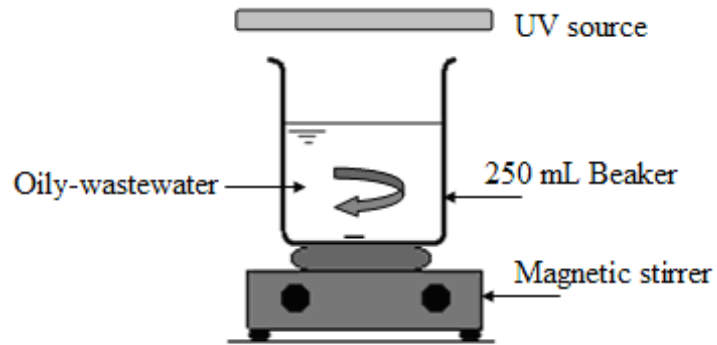**FIGURE 9:** Effect of physiochemical treatment processes followed by Fenton oxidation

364   **FIGURES:**
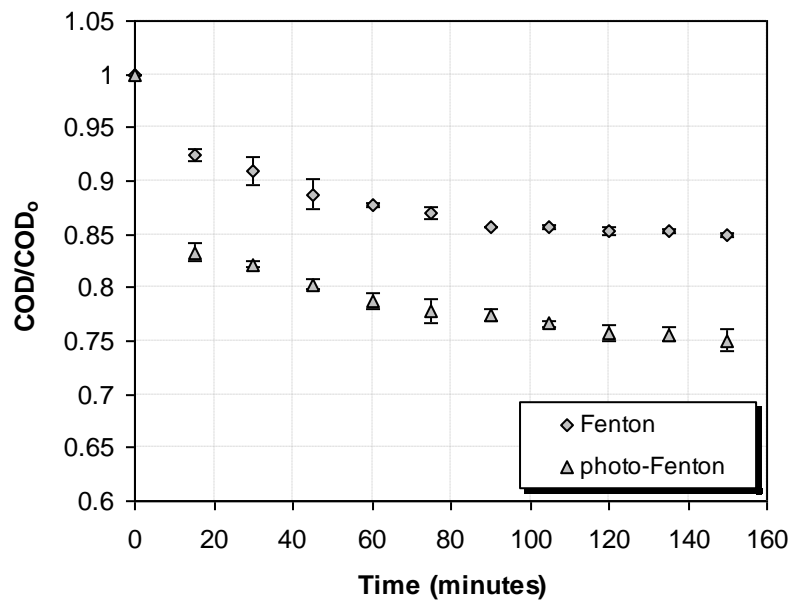
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372   **Fig. 1**
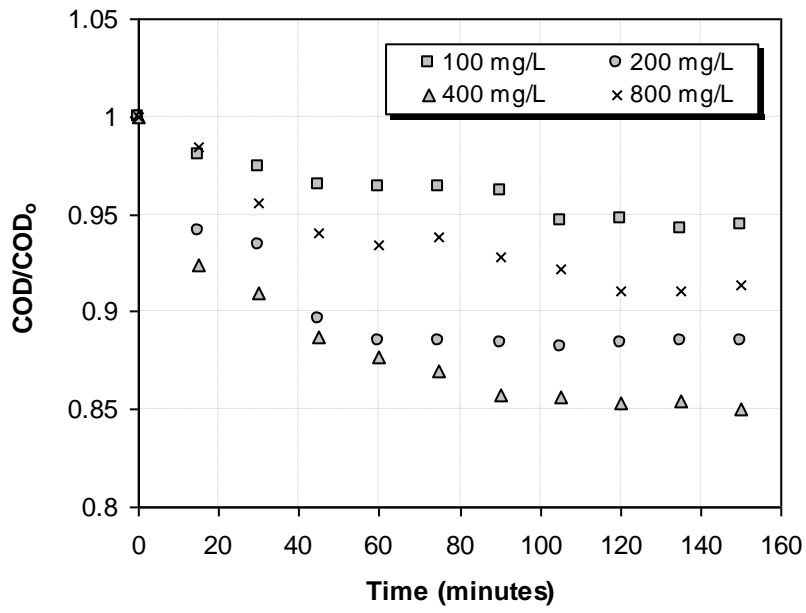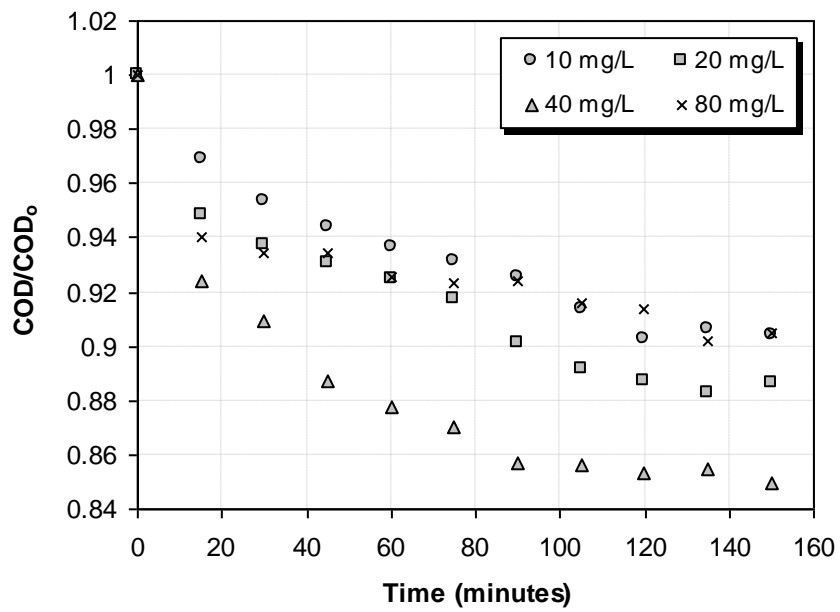
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375   **Fig. 2**

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Fig. 3

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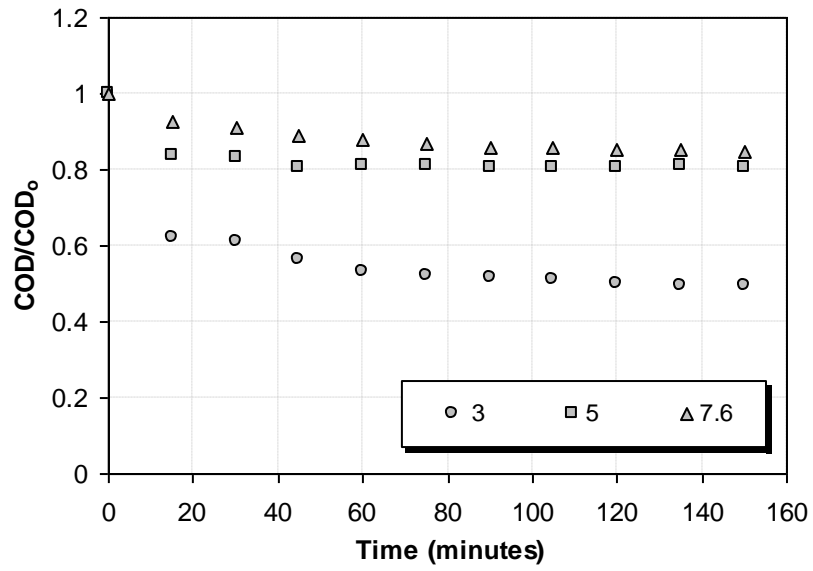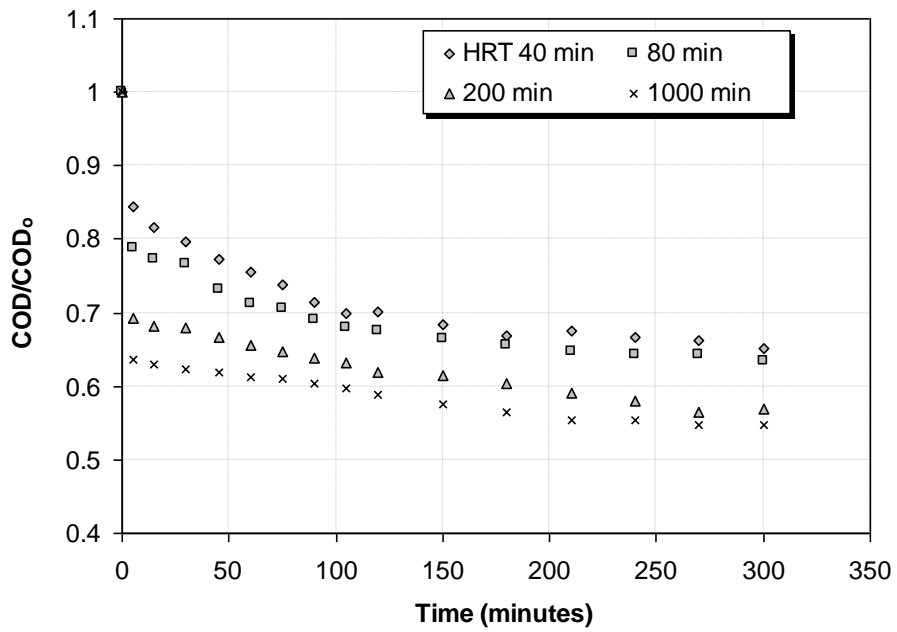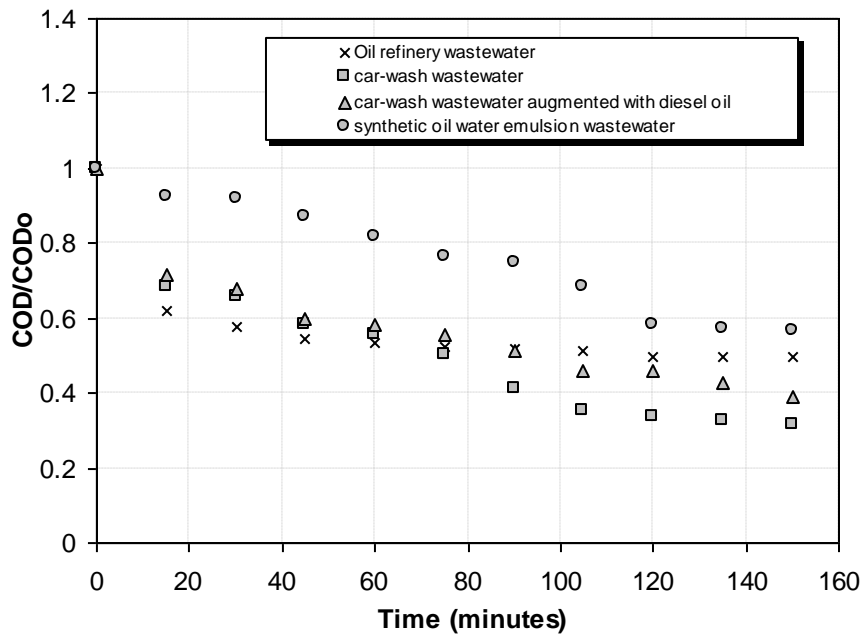379

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Fig. 4

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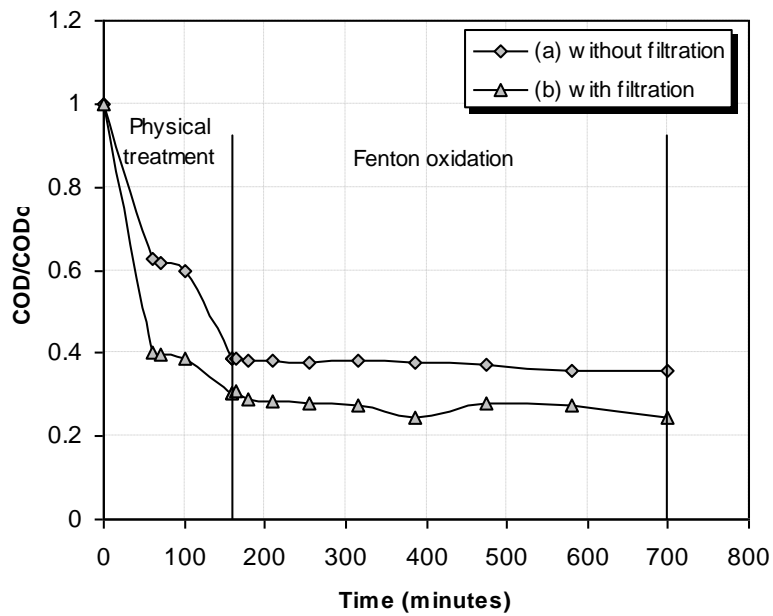397 **Fig. 8**

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408 **Fig. 9**

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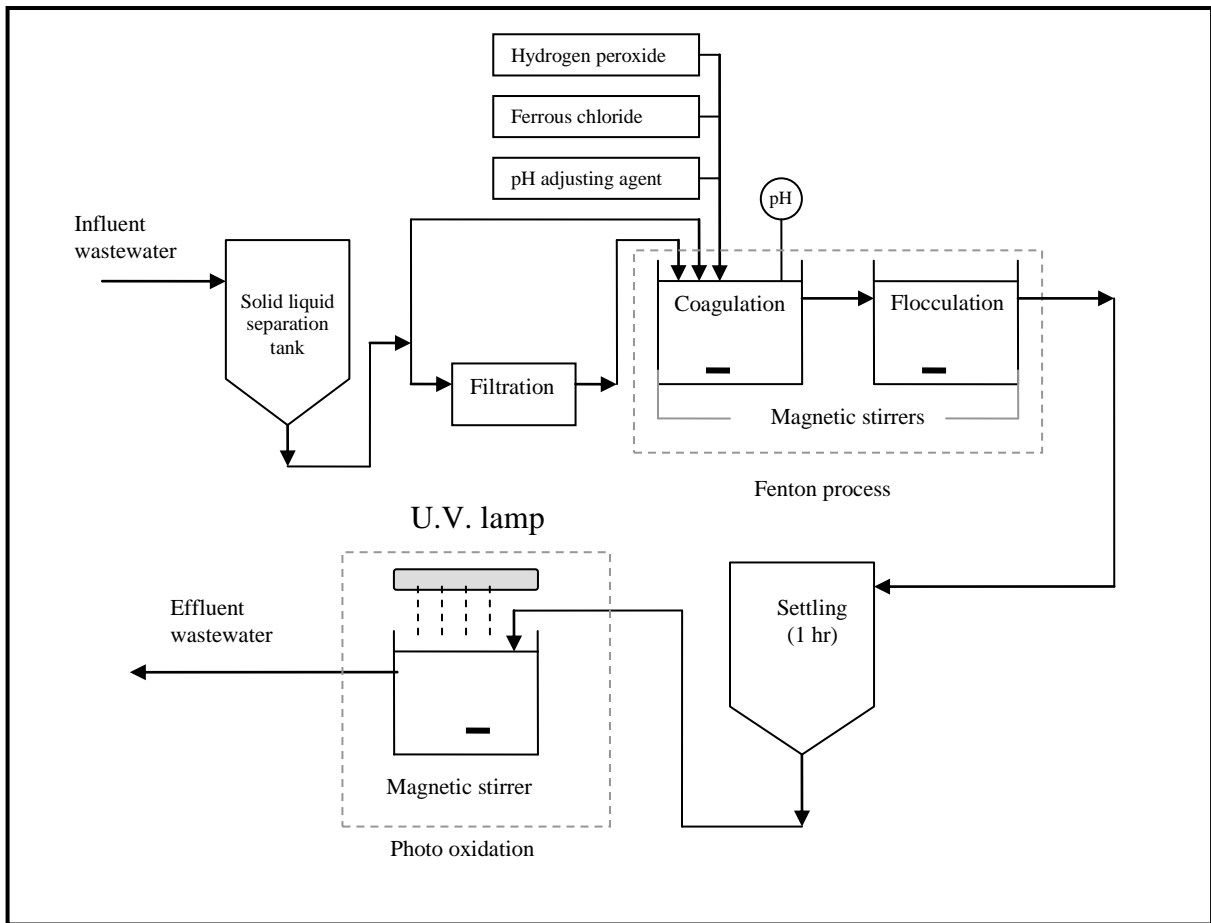
TABLES:

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Table 1 Properties of wastewaters used in this study

Parameter	COD[*] (mg-COD/L)	SS[**] (mg/L)	pH	Turbidity (NTU)	Colour (Pt Co)
Oil-refinery wastewater	364	105	7.6	42	946
Oil-water emulsion	1500	-	8.0	49	987
Car-wash wastewater	82	55	8.2	12	271

[*] Chemical Oxygen Demand, [**] Suspended Solids

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