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1 **Evaluating the Photo-catalytic Application of Fenton's Reagent Augmented with**
2 **TiO₂ and ZnO for the Mineralization of an Oil-water Emulsion**

3
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5

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10
11 **ABSTRACT**
12

13 In the present work, homogenous (photo-Fenton) and heterogeneous photo-assisted systems
14 (Fenton/TiO₂/UV, Fenton/ZnO/UV and Fenton/TiO₂/UV/Air) were investigated for the treatment of a
15 diesel-oil wastewater emulsion. The augmentation of the photo-Fenton process by heterogeneous TiO₂
16 increased the reaction rate, in terms of COD reduction efficiency from 61% to 71%. Furthermore, the
17 COD removal efficiency was increased to 84% when air was bubbled through the reactants. However,
18 if the Fenton/TiO₂/UV/Air process is to be utilized as a treatment for this wastewater, the separation of
19 the TiO₂ from the treated effluent would need further consideration.
20

21 **Keywords:** photo-catalytic mineralization; diesel oil; ultraviolet radiation; photo-Fenton; TiO₂; ZnO
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30 INTRODUCTION

31 Oil-contaminated wastewater can cause serious environmental problems due to its hazardous nature.
32 The volume of diesel-oil contaminated wastewater from petroleum filling stations has increased in line
33 with the number of such stations required to cater for the growing number of vehicles. ^[1] According to
34 data provided by International Energy Agency (IEA), the world consumption of diesel oil increased
35 during the period 1990 to 2003 from 454,747 to 684,022 millions liters, and the largest consumer
36 countries are US, China, France, Japan and Germany. As a result of this phenomenon, there has been
37 an increase in research activity focused on treating petroleum wastewaters. ^[2] Several conventional
38 techniques such as evaporation, phase separation, filtration, dissolved air flotation, de-emulsification,
39 coagulation and flocculation have been employed. ^[3,4] However, these processes can only transform the
40 pollutants from one phase to another without destroying them.

41 Advanced Oxidation Processes (AOPs) have the advantage of rapid oxidation of pollutants to
42 harmless end products. Such processes include heterogeneous photo-catalysis using semiconductors
43 such as TiO₂ and ZnO and homogenous processes such as Fenton's reagent, H₂O₂ and ozone. Amongst
44 these processes, Fenton's reagent and TiO₂ have received much attention especially when induced by
45 the ultraviolet radiation. ^[5-9]

46 Galvao et al., ^[1] studied the treatment of a synthetic emulsion of wastewater contaminated with
47 diesel using photo-Fenton's reagent. A TOC (Total Organic Carbon) reduction of 67% was reported.
48 Previous work by the authors demonstrate the application of Fenton's and the photo-Fenton's reagent
49 in the case of a diesel-oil emulsion and a real car-wash wastewater treatment and the optimization of
50 the process parameters. ^[10]

51 The application of UV/Fenton/TiO₂ has been reported extensively in the literature, though there is a
52 scarcity of literature published in the case of oily wastewater treatment. For example, Duran and
53 Monteagudo ^[11] studied the application of the UV/Fenton/TiO₂ for the mineralization of the reactive
54 blue 4 dye using solar light as the source of the UV radiation. They found that the pH and TiO₂
55 concentration were the main factors that affected the de-coloration process and an acidic pH was
56 recommended. Nogueira et al. ^[12] reported the effect of the combination between the photo-Fenton's
57 reagent and TiO₂ in the photodegradation of 4-chlorophenol and dichloroacetic acid in aqueous
58 medium and they concluded that the iron and H₂O₂ played a more important role than the presence of
59 TiO₂.

60 The aim of this study was to explore the effectiveness of photo-Fenton with TiO₂ or ZnO for
61 treating oil-water emulsion. Comparison of the three processes of Fenton/UV, Fenton/TiO₂/UV and
62 Fenton/ZnO/UV is presented in detail. The role of the process parameters (initial concentrations of
63 Fe²⁺, H₂O₂ and TiO₂ or ZnO as well as pH) for the mineralization of diesel oil wastewater emulsion
64 was studied. In addition, the iron residual following the treatment of the wastewater was evaluated.

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66

67 **EXPERIMENTAL METHODOLOGY**

68

69 **Materials**

70 Ferrous chloride tetrahydrate (FeCl₂.4H₂O) and hydrogen peroxide (H₂O₂; 30 wt %) from Sigma-
71 Aldrich were used as the source of the Fenton's reagent. TiO₂-P25 (supplied by Degussa) and ZnO
72 (supplied by Alfa Aesar) were used as semiconductors. TiO₂-P25 has a surface area of 50±15 m²/g
73 while the surface area of ZnO is 10-25 m²/g. Diesel oil was provided by a petrol station in Dublin city
74 and chemical emulsifier was used to prepare the synthetic model oil-water emulsion pollutant.

75 Sulphuric acid was used for pH adjustment. A high intensity 254nm UV, model R-52Grid Lamp was
76 used as the source of the UV light for the photo-chemical mineralization experiments.

77

78 **Artificial oily wastewater**

79 Oil-water emulsion was prepared as a model oily wastewater for performing the oxidation
80 experiments by contacting 1L distilled water with 100 mL of diesel oil (after 2.5 mL of 0.1 g/L
81 emulsifier solution was added), and stirred with a magnetic stirring at room temperature for 24 hours.
82 Thereafter, the resultant solution left to stand for 1h before filtration with a quantitative filter paper
83 (Whatman, 22 μ m) to remove the excess oil producing an emulsion with COD (Chemical Oxygen
84 Demand) of 1500 mg/L.

85

86

87 **Experimental method**

88 The experiments were performed in a batch mode test by pouring 200 mL of the emulsion solution
89 into a 250 mL beaker. The Fenton reagent was then introduced to the solution by adding the ferrous
90 solution (40 mg/L) and hydrogen peroxide (400 mg/L), these dosages having been determined in
91 previous work.^[10] For the experiments in which TiO₂ or ZnO were used, these reagents were added to
92 the oil-water emulsion prior to the addition of Fenton's reagent. In the case of the experiments where
93 the effect of the pH was examined, the pH of the emulsion was adjusted before all the reagents were
94 added. After the addition of the reagents, the solution was then subjected to stirring with a magnetic
95 stirrer for 120 minutes in the presence of UV radiation (placed 9 cm above the solution surface) for
96 photo-chemical reaction (see Fig. 1). An air diffuser was used to bubble air inside the beaker. The
97 treated model wastewater was then sampled at regular time intervals to determine the COD removal
98 efficiency.

99

100

101 **Analysis**

102 A DR/2400 HACH spectrophotometer was used for COD measurement following the standard
103 procedure of sample digestion. This instrument was also used to determine the total iron (FerroVer
104 method) in the final solution at the end of the treatment. The pH of the emulsion was measured using a
105 digital pH-meter (model PHM62 Radiometer, Copenhagen). For the TiO₂ and ZnO experiments, the
106 samples were subjected to the centrifugation before COD measurement.

107

108 **RESULTS AND DISCUSSION**

109

110 **Effect of TiO₂ concentration**

111

112 Fig. 2 shows the effect of TiO₂ initial concentration at given conditions (H₂O₂= 400 mg/L, Fe²⁺= 40
113 mg/L and pH 8). The results illustrate that increasing the catalyst concentration from 0.1 to 0.5 g/L has
114 a positive influence on the degradation rate. This may be explained by the increase in the number of
115 diesel-oil molecules that were adsorbed by the TiO₂, as been reported by Lee et al. ^[13] Moreover, when
116 TiO₂ is exposed to UV light, the light induction generates a hole in the valence band and an electron in
117 the conduction band. The oxidation of adsorbed water or hydroxyl ions by holes in the valence band at
118 the excited surface produces the hydroxyl radicals. ^[14] The resultant radicals degrade the diesel oil
119 molecules which increases the mineralization rate of wastewater. However, increasing the TiO₂ dosage
120 beyond an optimal value has a negative effect on the mineralization process. This is due to the fact that
121 excess TiO₂ particles increases the opacity of the suspension thereby decreasing the light penetration
122 into the solution, resulting in a reduction in the number of ·OH radicals.

123

124 **Effect of Fenton-reagent concentration**

125

126 Fig. 3 (a, b) illustrates the effects of the increase in both H_2O_2 and Fe^{2+} concentrations on the
127 reaction rate in the presence of TiO_2 . Examination of the figure shows there is an initial period of rapid
128 removal of COD followed by a period during which little further COD is removed and this correlates
129 with previous study by the authors. ^[10] Fig. 3 (a) shows that there is little benefit to be gained in terms
130 of COD removal once the H_2O_2 concentration has reached 400 mg/L. In the case of Fe^{2+} , the optimum
131 dose was about 40 mg/L and increasing the iron concentration above this concentration results in a
132 deterioration in the COD removal efficiency. This observation is most likely due to the fact that the
133 excess iron reacts with $\cdot\text{OH}$ radicals producing compounds which inhibit the reaction rates. ^[11, 12]

134

135 **Effect of pH**

136

137 According to the literature, both TiO_2 and Fenton's reagent catalysts are pH dependent. ^[1, 5, 15, 16]
138 The effect of the pH on the Fenton/ TiO_2 /UV system is shown in Fig. 4. Examination of the figure
139 shows that the pH of the emulsion has only a marginal effect on performance. The optimum pH for
140 COD removal was found to be 8.0, which corresponds with the findings of Lee et al. ^[13] who found that
141 the optimum pH for adsorption on the TiO_2 surface is approximately 7.0. In the previous work ^[10], it
142 has been demonstrated that the natural pH of the oil-water emulsion gave the optimum conditions for
143 photo-catalytic degradation.

144

145 **Effect of ZnO**

146

147 Several researchers have reported that ZnO is more active than TiO_2 since it absorbs more UV light
148 because the band gap energy of the ZnO is greater than that of TiO_2 . ^[17, 18] Accordingly, further
149 experiments were conducted to investigate the benefits of augmenting the photo-Fenton process with

150 ZnO as an alternative semi-conductor to TiO₂ under identical experimental conditions (TiO₂= 0.5 g/L,
151 H₂O₂=1600, Fe²⁺=40 mg/L and pH 8). Fig. 5 illustrates the results of this experiment and a comparison
152 of the effectiveness of comparative data using TiO₂-P25 and ZnO is presented. It is clear from Fig. 5
153 that, the use of ZnO resulted in a reduction of about 18% in the COD removal efficiency. This result
154 may be attributed to the difference in the surface area of the two semiconductors since TiO₂ has a larger
155 surface area than ZnO. For this reason, another set of experiments was conducted to examine the effect
156 of ZnO concentration on COD removal efficiency. Examination of Fig. 5 (and Fig. 2) shows that about
157 an 8-fold increase in the ZnO dosage, compared with TiO₂ dose of 0.5 g/L, would be required to obtain
158 the same COD removal. This observation is in accordance with previous investigations reported in the
159 literature. ^[19, 20]

160

161 **Comparison of the homogenous and the heterogeneous photo-catalytic systems**

162 The effect of the reaction time on the COD reduction rate of several AOPs tested is illustrated in
163 Fig. 6. The photo-Fenton process is a homogenous process, while the Fenton/TiO₂/UV,
164 Fenton/ZnO/UV and Fenton/TiO₂/UV/Air processes would be described as the heterogeneous
165 processes. It can be seen from Fig. 6 that the degradation graph for all these AOPs exhibited the same
166 general pattern, that is, that approximately 50% of the initial COD was degraded within the first 15
167 minutes, followed by a dramatic decrease in the conversion rate. However, the final COD reduction
168 (%) differs considerably (ranging from 61 to 84%), depending on the process adopted, as summarized
169 in Table 1.

170 If the Fenton/UV process in the absence of TiO₂ is compared to the combined system of
171 Fenton/TiO₂/UV under the optimal conditions described in Table 1, a 10% enhancement in the COD
172 removal was achieved. This reflects the role of TiO₂ and can be explained by the fact that the presence
173 of TiO₂ is not only essential for the ·OH production, but also for the adsorption of the diesel molecules
174 on the TiO₂ surface. More significantly, air bubbling as a source of O₂ can enhance the

175 Fenton/TiO₂/UV system by further increasing the degradation rate of the emulsion by 13%, as shown in
176 Table 1. When air is bubbled into solution, the O₂ can scavenge the photon-produced electrons on the
177 TiO₂ surface, thereby improving the overall reaction rate. In addition, the presence of O₂ in air
178 noticeably works as an oxidizing agent for the organic molecules present in the solution. This
179 observation is in accordance with the results reported by Pouloupoulos and Philippopoulos,^[21] Barakat,
180 et al.^[22] and Hea et al.^[23]

181 Although the Fenton/TiO₂/UV with air bubbling was found to be the optimum combination for the
182 treatment diesel oil-water emulsion compared to the other systems studied, the process has a number of
183 disadvantages. Such disadvantages include the necessity to separate the TiO₂ separation from the
184 suspension after the reaction. Additionally, some of the COD removal by its adsorption onto the TiO₂
185 surface is not a destructive process compared to the chemical oxidation, thus a further step may be
186 needed for the complete removal of the organic compounds.^[23] Moreover, there is an additional cost
187 associated with the addition of TiO₂ and bubbling air through the emulsion.^[24]

188

189 **Total iron concentration after the AOPs**

190

191 The main disadvantage of using Fenton's reagent in wastewater treatment is the presence of
192 residual iron in the effluent. The iron residual must be removed after the AOPs since the permissible
193 iron concentration is 2 mg/L in treated wastewater for direct discharge to a receiving water and 20
194 mg/L for discharge to a municipal biological treatment plant.^[25-27] An excess concentration of iron
195 may pose a threat to aquatic life.^[1] Thus, the concentration of the iron in Fenton's reagent should be
196 lowest possible to minimize the iron residuals in the wastewater effluent. Alternatively, the iron ions
197 may be recovered and recycled again into the treatment system. For this reason, measurement of the
198 iron residuals after photo-Fenton treatment of the wastewater was undertaken in this study, as
199 illustrated in Fig. 7. Examination of Fig. 7 illustrates the clear correlation between the iron

200 concentration in the Fenton's reagent and the residual iron concentration in the supernatant. An iron
201 precipitation step following the photo-Fenton reaction may be desirable to re-use the added iron and
202 minimize disposal costs. According to the literature, the re-use of iron solution after the Fenton
203 treatment has no negative consequences on its catalytic action. [25, 28]

204 **CONCLUSIONS**

205

206 The combined Fenton/UV augmented with TiO₂ and ZnO for mineralization of diesel-oil
207 wastewater emulsion has been studied. The results show that the process is sensitive to the
208 concentrations of the Fe²⁺, H₂O₂ and TiO₂ or ZnO, but the process performs well over a wide pH range.
209 The optimum conditions were found to be: 40 mg/L, 400 mg/L and 500 mg/L for Fe²⁺, H₂O₂ and TiO₂
210 respectively and a pH of about 8.0. Under such conditions, with air being bubbled through the
211 emulsion, an 84% reduction in the diesel oil-water emulsion COD concentration was achieved. The
212 Fenton/UV process (without any TiO₂ or ZnO) achieved a 61% COD reduction. However, issues
213 relating to TiO₂ and Fe residuals in the wastewater effluent require further study.

214

215

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217

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221

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LIST OF TABLE:

Table 1. Experimental conditions and final COD removals to compare and evaluate the performance of a several AOP techniques

Process	Experimental Conditions	Final COD removal (%)
Fenton/UV	Batch reactor, pH=8, H ₂ O ₂ =400 mg/L, Fe ²⁺ =40 mg/L, UV radiation (254nm)	61
Fenton/TiO ₂ /UV	Batch reactor, pH=8, H ₂ O ₂ =1600 mg/L, Fe ²⁺ =40 mg/L, TiO ₂ = 0.5g/L, UV radiation (254nm)	71
Fenton/ZnO/UV	Batch reactor, pH=8, H ₂ O ₂ =1600 mg/L, Fe ²⁺ =40 mg/L, ZnO= 0.5g/L, UV radiation (254nm)	66
Fenton/TiO ₂ /UV/Air	Batch reactor, pH=8, H ₂ O ₂ =1600 mg/L, Fe ²⁺ =40 mg/L, TiO ₂ = 0.5g/L, UV radiation (254nm), air diffused inside the solution during the reaction time	84

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FIGURE CAPTIONS:

Figure 1. Schematic diagram for the photo-chemical experimental set-up

Figure 2. Effect of the TiO_2 concentration on the Fenton/ TiO_2 /UV system (operating conditions: pH 8.0; $\text{H}_2\text{O}_2= 400 \text{ mg/L}$; $\text{Fe}^{2+} = 40 \text{ mg/L}$)

Figure 3. Effect of the Fenton's reagent concentration on the Fenton/ TiO_2 /UV system

(a) Effect of H_2O_2 concentration (operating conditions: pH 8.0; $\text{TiO}_2= 0.5 \text{ g/L}$; $\text{Fe}^{2+}= 40 \text{ mg/L}$)

(b) Effect of the Fe^{2+} concentration (operating conditions: pH 8.0; $\text{TiO}_2= 0.5 \text{ g/L}$; $\text{H}_2\text{O}_2= 400 \text{ mg/L}$)

Figure 4. Effectiveness of the pH on the Fenton/ TiO_2 /UV system (operating conditions: $\text{TiO}_2= 0.5 \text{ g/L}$; $\text{H}_2\text{O}_2= 400 \text{ mg/L}$; $\text{Fe}^{2+}= 40 \text{ mg/L}$)

Figure 5. Effectiveness of the ZnO and TiO_2 -P25 on the photo-Fenton/semiconductor combined system (operating conditions: semiconductor= 0.5 g/L ; $\text{H}_2\text{O}_2= 1600 \text{ mg/L}$; $\text{Fe}^{2+}= 40 \text{ mg/L}$; pH 8)

Figure 6. Comparison of the effectiveness of different AOPs and the reaction time on the oil-water emulsion

Figure 7. Iron ions concentration measurement before and after photo-Fenton treatment

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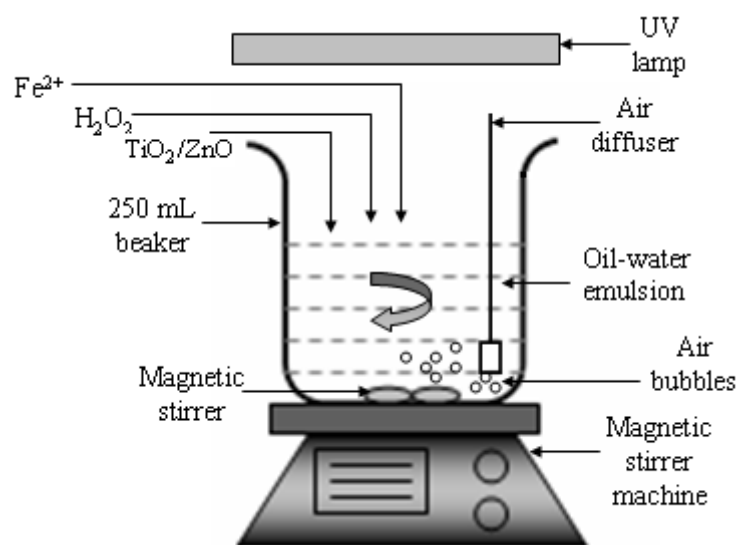
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359 **LIST OF FIGURES:**

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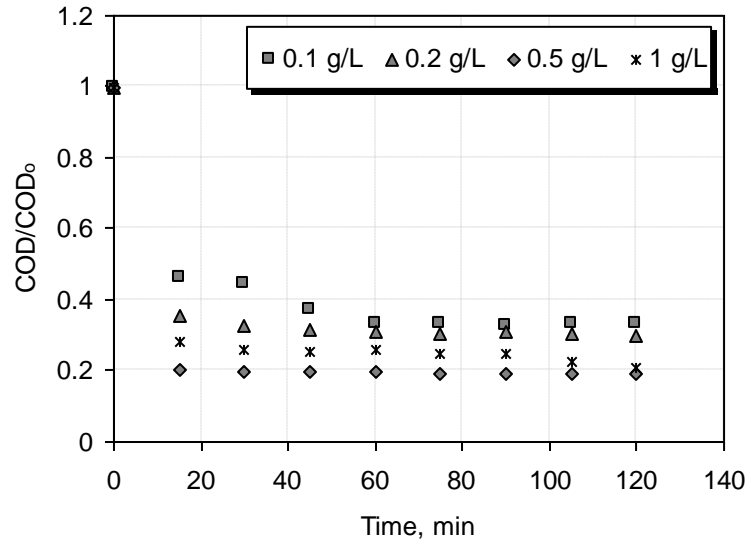
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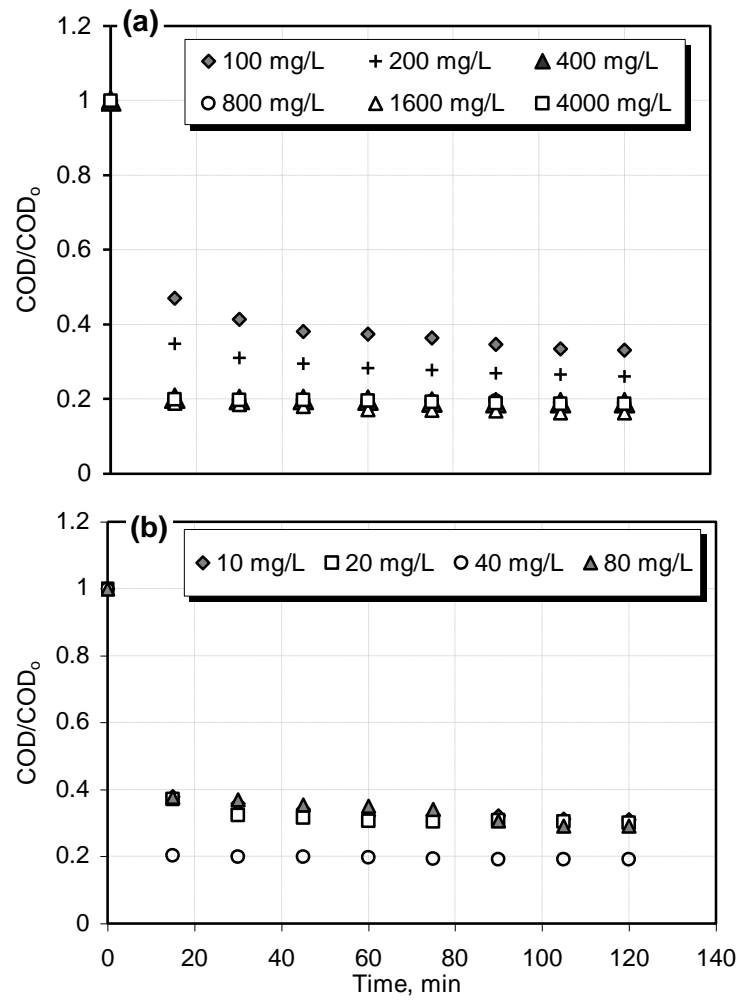
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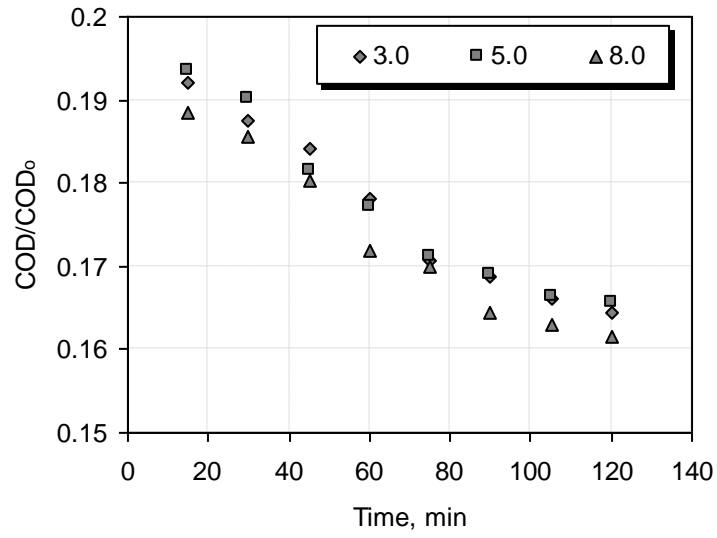
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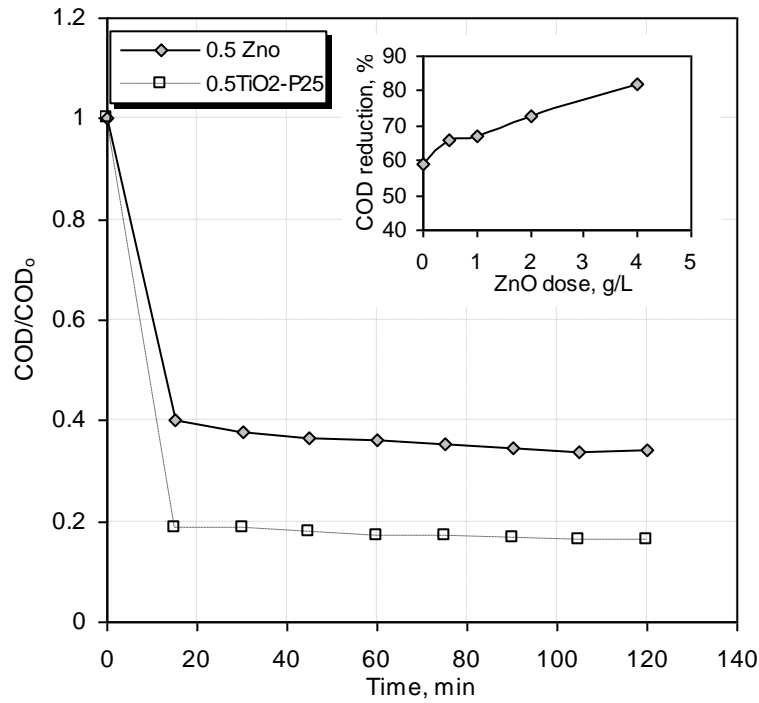
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377 Fig. 3
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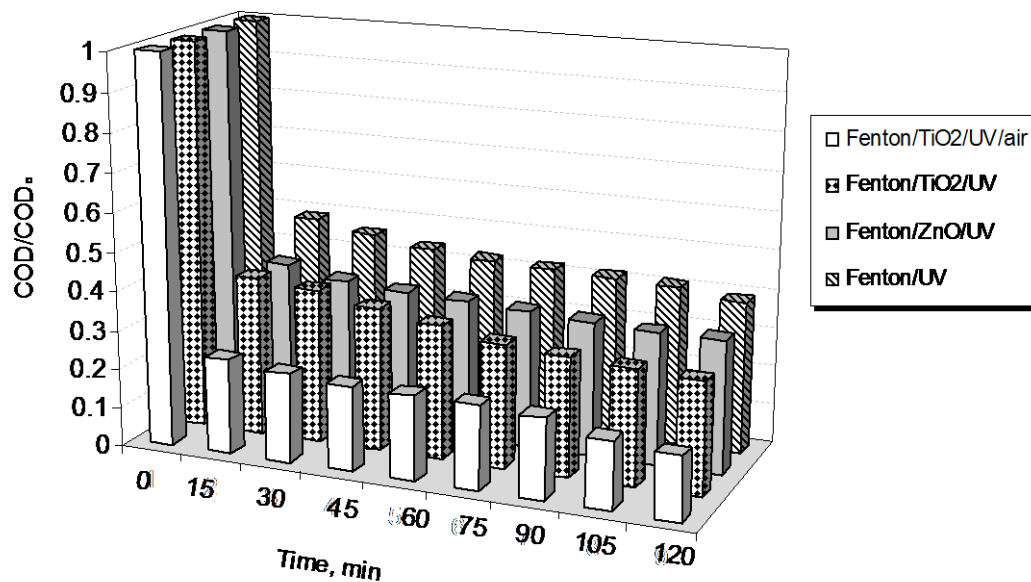


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380 Fig. 4



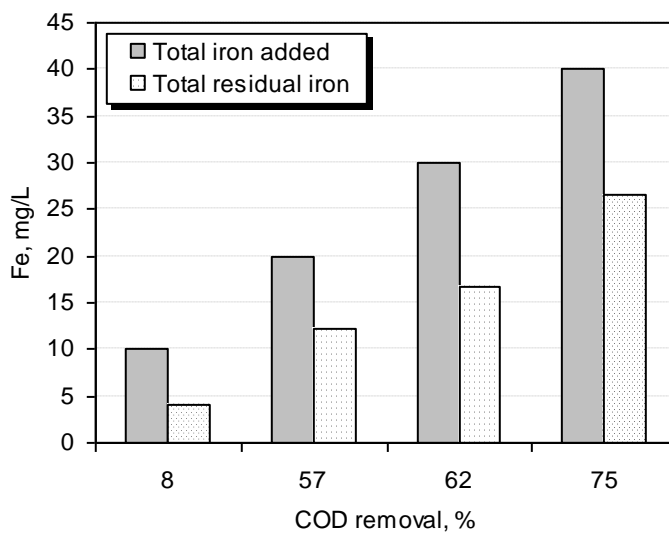
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400 Fig. 5
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