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Authors(s)	Tony, Maha A., Zhao, Y.Q., Purcell, Patrick J., El-Sherbiny, M.F.
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Evaluating the Photo-catalytic Application of Fenton's Reagent Augmented with TiO_2 and ZnO for the Mineralization of an Oil-water Emulsion

MAHA A. TONY[1, 2], Y.Q. ZHAO[1]*, P.J. PURCELL[1], M.F. El-SHERBINY[2]

[1] *Centre for Water Resources Research, School of Architecture, Landscape and Civil Engineering, University College Dublin, Newstead, Belfield, Dublin 4, Ireland*
[2] *Basic Engineering Science Department, Faculty of Engineering, Minoufiya University, Minoufiya, Egypt*

ABSTRACT

In the present work, homogenous (photo-Fenton) and heterogeneous photo-assisted systems (Fenton/TiO_2/UV, Fenton/ZnO/UV and Fenton/TiO_2/UV/Air) were investigated for the treatment of a diesel-oil wastewater emulsion. The augmentation of the photo-Fenton process by heterogeneous TiO_2 increased the reaction rate, in terms of COD reduction efficiency from 61% to 71%. Furthermore, the COD removal efficiency was increased to 84% when air was bubbled through the reactants. However, if the Fenton/TiO_2/UV/Air process is to be utilized as a treatment for this wastewater, the separation of the TiO_2 from the treated effluent would need further consideration.

Keywords: photo-catalytic mineralization; diesel oil; ultraviolet radiation; photo-Fenton; TiO_2; ZnO

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* Address correspondence to Y.Q. Zhao, Centre for Water Resources Research, School of Architecture, Landscape and Civil Engineering, University College Dublin, Newstead, Belfield, Dublin 4, Ireland; Phone: +353 1 7163215, fax: +353 1 7163297; E-mail address: yaqian.zhao@ucd.ie

INTRODUCTION

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

Advanced Oxidation Processes (AOPs) have the advantage of rapid oxidation of pollutants to harmless end products. Such processes include heterogeneous photo-catalysis using semiconductors such as TiO_2 and ZnO and homogenous processes such as Fenton's reagent, H_2O_2 and ozone. Amongst these processes, Fenton's reagent and TiO_2 have received much attention especially when induced by the ultraviolet radiation. [5- 9]

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

The application of UV/Fenton/TiO_2 has been reported extensively in the literature, though there is a scarcity of literature published in the case of oily wastewater treatment. For example, Duran and Monteagudo [11] studied the application of the UV/Fenton/TiO_2 for the mineralization of the reactive blue 4 dye using solar light as the source of the UV radiation. They found that the pH and TiO_2 concentration were the main factors that affected the de-coloration process and an acidic pH was recommended. Nogueira et al. [12] reported the effect of the combination between the photo-Fenton's reagent and TiO_2 in the photodegradation of 4-chlorophenol and dichloroacetic acid in aqueous medium and they concluded that the iron and H_2O_2 played a more important role than the presence of TiO_2.

The aim of this study was to explore the effectiveness of photo-Fenton with TiO_2 or ZnO for treating oil-water emulsion. Comparison of the three processes of Fenton/UV, Fenton/TiO_2/UV and Fenton/ZnO/UV is presented in detail. The role of the process parameters (initial concentrations of Fe^{2+}, H_2O_2 and TiO_2 or ZnO as well as pH) for the mineralization of diesel oil wastewater emulsion was studied. In addition, the iron residual following the treatment of the wastewater was evaluated.

EXPERIMENTAL METHODOLOGY

Materials

Ferrous chloride tetrahydrate ($FeCl_2.4H_2O$) and hydrogen peroxide (H_2O_2; 30 wt %) from Sigma-Aldrich were used as the source of the Fenton's reagent. TiO_2-P25 (supplied by Degussa) and ZnO (supplied by Alfa Aesar) were used as semiconductors. TiO_2-P25 has a surface area of 50 ± 15 m^2/g while the surface area of ZnO is 10-25 m^2/g. Diesel oil was provided by a petrol station in Dublin city and chemical emulsifier was used to prepare the synthetic model oil-water emulsion pollutant.

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

Artificial oily wastewater

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

Experimental method

The experiments were performed in a batch mode test by pouring 200 mL of the emulsion solution into a 250 mL beaker. The Fenton reagent was then introduced to the solution by adding the ferrous solution (40 mg/L) and hydrogen peroxide (400 mg/L), these dosages having been determined in previous work. [10] For the experiments in which TiO_2 or ZnO were used, these reagents were added to the oil-water emulsion prior to the addition of Fenton's reagent. In the case of the experiments where the effect of the pH was examined, the pH of the emulsion was adjusted before all the reagents were added. After the addition of the reagents, the solution was then subjected to stirring with a magnetic stirrer for 120 minutes in the presence of UV radiation (placed 9 cm above the solution surface) for photo-chemical reaction (see Fig. 1). An air diffuser was used to bubble air inside the beaker. The treated model wastewater was then sampled at regular time intervals to determine the COD removal efficiency.

Analysis

A DR/2400 HACH spectrophotometer was used for COD measurement following the standard procedure of sample digestion. This instrument was also used to determine the total iron (FerroVer method) in the final solution at the end of the treatment. The pH of the emulsion was measured using a digital pH-meter (model PHM62 Radiometer, Copenhagen). For the TiO_2 and ZnO experiments, the samples were subjected to the centrifugation before COD measurement.

RESULTS AND DISCUSSION

Effect of TiO_2 concentration

Fig. 2 shows the effect of TiO_2 initial concentration at given conditions (H_2O_2= 400 mg/L, Fe^{2+}= 40 mg/L and pH 8). The results illustrate that increasing the catalyst concentration from 0.1 to 0.5 g/L has a positive influence on the degradation rate. This may be explained by the increase in the number of diesel-oil molecules that were adsorbed by the TiO_2, as been reported by Lee et al. [13] Moreover, when TiO_2 is exposed to UV light, the light induction generates a hole in the valence band and an electron in the conduction band. The oxidation of adsorbed water or hydroxyl ions by holes in the valence band at the excited surface produces the hydroxyl radicals. [14] The resultant radicals degrade the diesel oil molecules which increases the mineralization rate of wastewater. However, increasing the TiO_2 dosage beyond an optimal value has a negative effect on the mineralization process. This is due to the fact that excess TiO_2 particles increases the opacity of the suspension thereby decreasing the light penetration into the solution, resulting in a reduction in the number of $^{\cdot}OH$ radicals.

Effect of Fenton-reagent concentration

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

Effect of pH

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

Effect of ZnO

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

ZnO as an alternative semi-conductor to TiO_2 under identical experimental conditions (TiO_2= 0.5 g/L, H_2O_2=1600, Fe^{2+}=40 mg/L and pH 8). Fig. 5 illustrates the results of this experiment and a comparison of the effectiveness of comparative data using TiO_2-P25 and ZnO is presented. It is clear from Fig. 5 that, the use of ZnO resulted in a reduction of about 18% in the COD removal efficiency. This result may be attributed to the difference in the surface area of the two semiconductors since TiO_2 has a larger surface area than ZnO. For this reason, another set of experiments was conducted to examine the effect of ZnO concentration on COD removal efficiency. Examination of Fig. 5 (and Fig. 2) shows that about an 8-fold increase in the ZnO dosage, compared with TiO_2 dose of 0.5 g/L, would be required to obtain the same COD removal. This observation is in accordance with previous investigations reported in the literature. [19, 20]

Comparison of the homogenous and the heterogeneous photo-catalytic systems

The effect of the reaction time on the COD reduction rate of several AOPs tested is illustrated in Fig. 6. The photo-Fenton process is a homogenous process, while the Fenton/TiO_2/UV, Fenton/ZnO/UV and Fenton/TiO_2/UV/Air processes would be described as the heterogeneous processes. It can be seen from Fig. 6 that the degradation graph for all these AOPs exhibited the same general pattern, that is, that approximately 50% of the initial COD was degraded within the first 15 minutes, followed by a dramatic decrease in the conversion rate. However, the final COD reduction (%) differs considerably (ranging from 61 to 84%), depending on the process adopted, as summarized in Table 1.

If the Fenton/UV process in the absence of TiO_2 is compared to the combined system of Fenton/TiO_2/UV under the optimal conditions described in Table 1, a 10% enhancement in the COD removal was achieved. This reflects the role of TiO_2 and can be explained by the fact that the presence of TiO_2 is not only essential for the $^{\cdot}OH$ production, but also for the adsorption of the diesel molecules on the TiO_2 surface. More significantly, air bubbling as a source of O_2 can enhance the

Fenton/TiO_2/UV system by further increasing the degradation rate of the emulsion by 13%, as shown in Table 1. When air is bubbled into solution, the O_2 can scavenge the photon-produced electrons on the TiO_2 surface, thereby improving the overall reaction rate. In addition, the presence of O_2 in air noticeably works as an oxidizing agent for the organic molecules present in the solution. This observation is in accordance with the results reported by Poulopoulos and Philippopoulos, [21] Barakat, et al. [22] and Hea et al. [23]

Although the Fenton/TiO_2/UV with air bubbling was found to be the optimum combination for the treatment diesel oil-water emulsion compared to the other systems studied, the process has a number of disadvantages. Such disadvantages include the necessity to separate the TiO_2 separation from the suspension after the reaction. Additionally, some of the COD removal by its adsorption onto the TiO_2 surface is not a destructive process compared to the chemical oxidation, thus a further step may be needed for the complete removal of the organic compounds. [23] Moreover, there is an additional cost associated with the addition of TiO_2 and bubbling air through the emulsion. [24]

Total iron concentration after the AOPs

The main disadvantage of using Fenton's reagent in wastewater treatment is the presence of residual iron in the effluent. The iron residual must be removed after the AOPs since the permissible iron concentration is 2 mg/L in treated wastewater for direct discharge to a receiving water and 20 mg/L for discharge to a municipal biological treatment plant. [25-27] An excess concentration of iron may pose a threat to aquatic life. [1] Thus, the concentration of the iron in Fenton's reagent should be lowest possible to minimize the iron residuals in the wastewater effluent. Alternatively, the iron ions may be recovered and recycled again into the treatment system. For this reason, measurement of the iron residuals after photo-Fenton treatment of the wastewater was undertaken in this study, as illustrated in Fig. 7. Examination of Fig. 7 illustrates the clear correlation between the iron concentration in the Fenton’s reagent and the residual iron concentration in the supernatant. An iron precipitation step following the photo-Fenton reaction may be desirable to re-use the added iron and minimize disposal costs. According to the literature, the re-use of iron solution after the Fenton treatment has no negative consequences on its catalytic action. [25, 28]

CONCLUSIONS

The combined Fenton/UV augmented with TiO_2 and ZnO for mineralization of diesel-oil wastewater emulsion has been studied. The results show that the process is sensitive to the concentrations of the Fe^{2+}, H_2O_2 and TiO_2 or ZnO, but the process performs well over a wide pH range. The optimum conditions were found to be: 40 mg/L, 400 mg/L and 500 mg/L for Fe^{2+}, H_2O_2 and TiO_2 respectively and a pH of about 8.0. Under such conditions, with air being bubbled through the emulsion, an 84% reduction in the diesel oil-water emulsion COD concentration was achieved. The Fenton/UV process (without any TiO_2 or ZnO) achieved a 61% COD reduction. However, issues relating to TiO_2 and Fe residuals in the wastewater effluent require further study.

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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_2O_2=400 mg/L, Fe^{2+}=40 mg/L, UV radiation (254nm)	61
Fenton/TiO_2/UV	Batch reactor, pH=8, H_2O_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_2O_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_2O_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

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; H_2O_2= 400 mg/L; Fe^{2+}= 40 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; TiO_2= 0.5 g/L; Fe^{2+}= 40 mg/L)

(b) Effect of the Fe^{2+} concentration (operating conditions: pH 8.0; TiO_2= 0.5 g/L; H_2O_2= 400 mg/L)

Figure 4. Effectiveness of the pH on the Fenton/ TiO_2/UV system (operating conditions: TiO_2= 0.5 g/L; H_2O_2= 400 mg/L; Fe^{2+}= 40 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; H_2O_2= 1600 mg/L; Fe^{2+}= 40 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

LIST OF FIGURES:

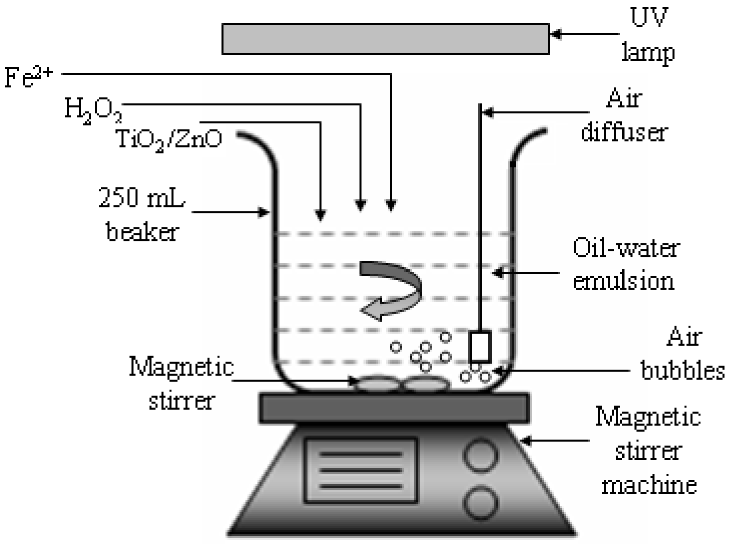
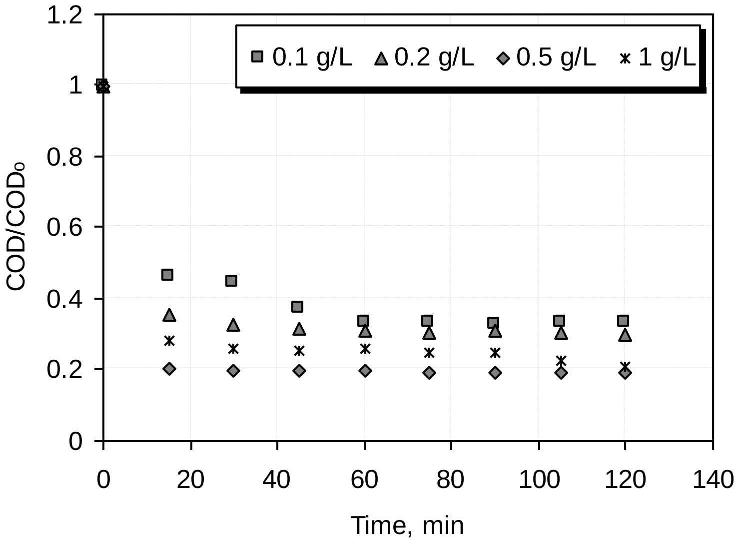


Fig. 1



0.1 g/L
0.2 g/L
0.5 g/L
1 g/L
COD/COD₀
1.2
1
0.8
0.6
0.4
0.2
0
0
20
40
60
80
100
120
140
Time, min

Fig. 2

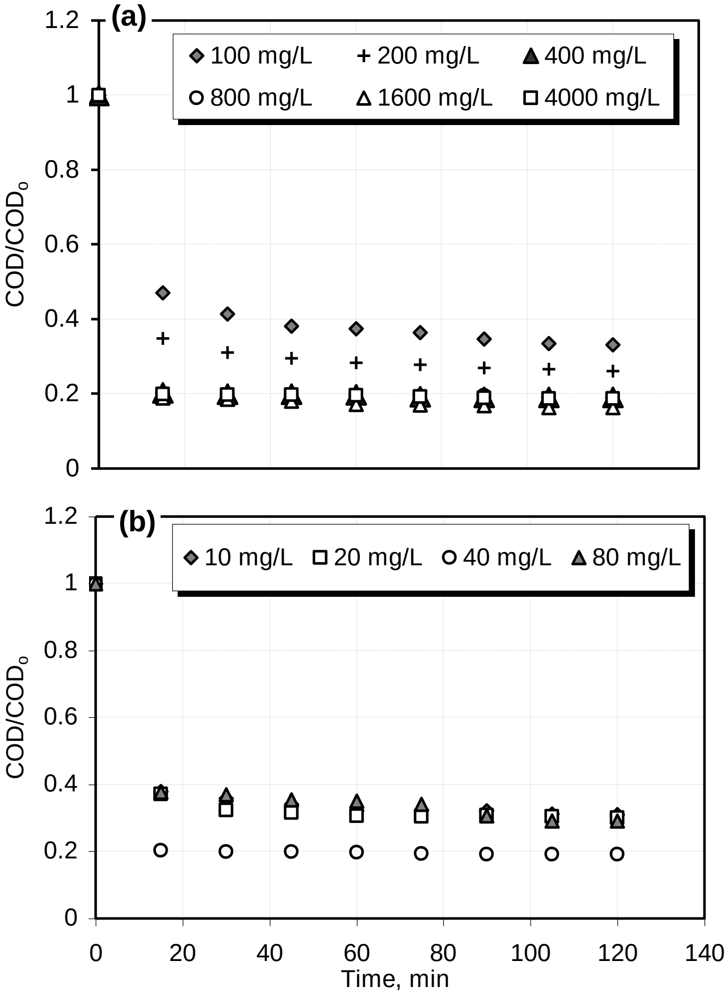

(a)
100 mg/L
200 mg/L
400 mg/L
800 mg/L
1600 mg/L
4000 mg/L
COD/COD$_o$
1.2
1
0.8
0.6
0.4
0.2
0
(b)
10 mg/L
20 mg/L
40 mg/L
80 mg/L
COD/COD$_o$
1.2
1
0.8
0.6
0.4
0.2
0
0
20
40
60
80
100
120
140
Time, min

Fig. 3

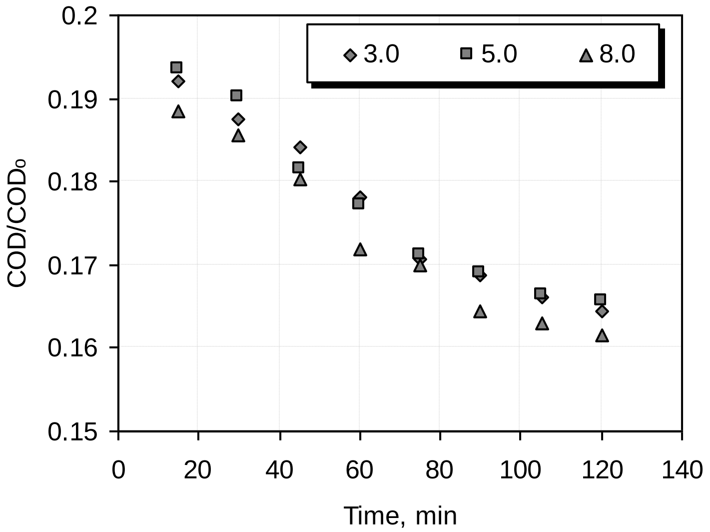

3.0
5.0
8.0
COD/COD₀
0.2
0.19
0.18
0.17
0.16
0.15
0
20
40
60
80
100
120
140
Time, min

Fig. 4

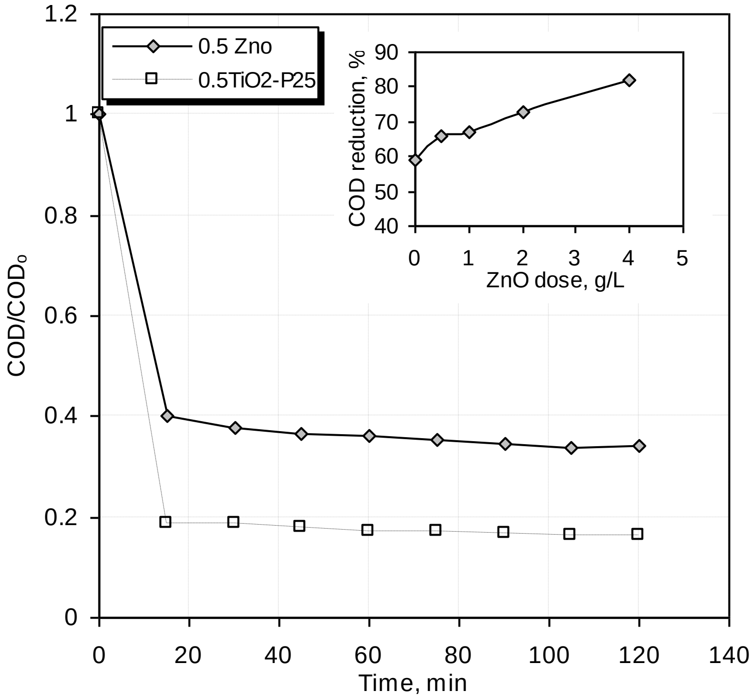

0.5 Zno
0.5TiO2-P25
COD/COD₀
1.2
1
0.8
0.6
0.4
0.2
0
0
20
40
60
80
100
120
140
Time, min
COD reduction, %
90
80
70
60
50
40
0
1
2
3
4
5
ZnO dose, g/L

Fig. 5

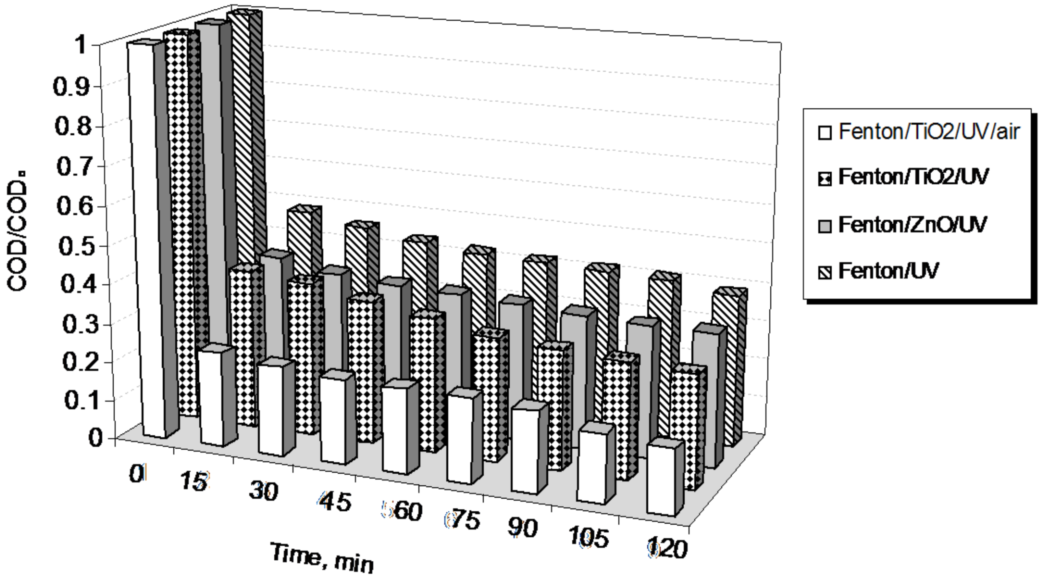

COD/COD₀
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
15
30
45
60
75
90
105
120
Time, min
Fenton/TiO2/UV/air
Fenton/TiO2/UV
Fenton/ZnO/UV
Fenton/UV

Fig. 6

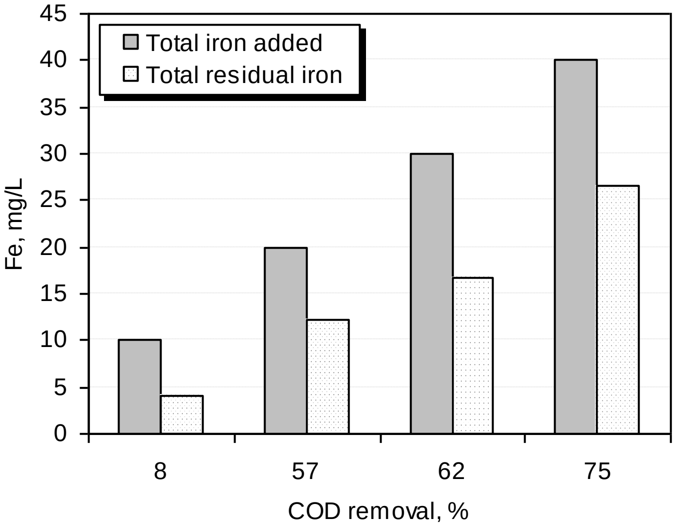

Fe, mg/L
45
40
35
30
25
20
15
10
5
0
8
57
62
75
COD removal, %
Total iron added
Total residual iron

Fig. 7