

Research Article

Photo-Fenton and Fenton Oxidation of Recalcitrant Industrial Wastewater Using Nanoscale Zero-Valent Iron

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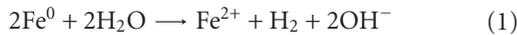
There is a need for the development of on-site wastewater treatment technologies suitable for “dry-process industries,” such as the wood-floor sector. Due to the nature of their activities, these industries generate lower volumes of highly polluted wastewaters after cleaning activities. Advanced oxidation processes such as Fenton and photo-Fenton, are potentially feasible options for treatment of these wastewaters. One of the disadvantages of the Fenton process is the formation of large amounts of ferrous iron sludge, a constraint that might be overcome with the use of nanoscale zero-valent iron (nZVI) powder. Wastewater from a wood-floor industry with initial COD of 4956 mg/L and TOC of 2730 mg/L was treated with dark-Fenton (nZVI/H₂O₂) and photo-Fenton (nZVI/H₂O₂/UV) applying a 2-level full-factorial experimental design. The highest removal of COD and TOC (80% and 60%, resp.) was achieved using photo-Fenton. The supply of the reactants in more than one dose during the reaction time had significant and positive effects on the treatment efficiency. According to the results, Fenton and mostly photo-Fenton are promising treatment options for these highly recalcitrant wastewaters. Future investigations should focus on optimizing treatment processes and assessing toxic effects that residual pollutants and the nZVI might have. The feasibility of combining advanced oxidation processes with biological treatment is also recommended.

1. Introduction

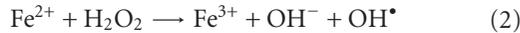
The discharge of industrial wastewaters into either municipal sewerage system or directly into recipient water bodies has raised serious concerns during decades, leading to intensive research and development of on-site treatment technologies for industrial wastewater. However, whereas investigations have been focusing on industrial sectors that have water as an important input to their manufacturing processes, “dry-process industries” such as wood-floor and wood-furniture industries that have no water requirement in their production processes have been neglected [1, 2]. These industries generate wastewaters during cleaning and washing of machinery, surfaces, and floors and regardless of their relatively low volumes these cleaning wastewaters have very high chemical oxygen demand (COD) that varies from 3200 to 50,000 mg L⁻¹ and the presence of recalcitrant organic

compounds is a limiting factor for biological treatment in conventional centralized treatment plants. Dilution of 50 times or more with drinking water has been a common practice before discharging these wastewaters into the sewage system, which is not a sustainable strategy for the 21st century. The treatment of wastewaters from the timber industry using chemical methods has shown limited efficiency [3]. The use of biological treatment [1] and sorption/filtration processes [2] has also shown limitations when the main purpose is to comply with established standards for discharges into recipient water bodies. Advanced oxidation processes (AOPs) have previously been used to treat complex wastewaters in combinations with biological and/or chemical treatment. These studies have used AOP either after biological treatments to handle the most recalcitrant substances [4, 5] or before with the purpose of reducing toxicity, when the wastewater is too toxic for biological

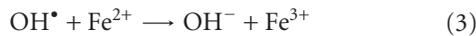
treatment [6, 7]. The Fenton reaction was first observed by H. J. Fenton in 1894 and is described as the enhanced oxidative power of H_2O_2 when using iron (Fe) as a catalyst under acidic conditions. It was later found that this enhancement was due to the generation of hydroxyl radical (HO^\bullet) [8] that is one of the strongest oxidants ($E = 2.73 \text{ V}$), and it is nonselective and capable of quickly oxidizing a broad range of organic pollutants [9]. AOPs are based on the generation of these very reactive species, which are the main oxidizing species in the Fenton process [10]. The Fenton's reagent alone or in combination has proven to be an effective way to degrade organic pollutants [11–13] and it has been used for the treatment of a wide variety of industrial wastewaters [14–16]. The Fenton process is a relatively economical method since it requires no additional energy when compared to many other AOPs. Furthermore, both iron and hydrogen peroxide are relatively cheap and safe. In the Fenton process, there is no mass transfer limitation, except during coagulation when high dose of the activator ferrous salt is needed [17]. The Fenton process is well known [18]. Iron (Fe) will in aqueous solution under acidic conditions oxidize to Fe^{2+} [19], which initiates the Fenton reaction:



The Fenton reaction is characterized by the catalytic decomposition of H_2O_2 as described below [20]:



The hydroxyl radicals created by the process can be scavenged by excess Fe^{2+} [20]:



This conventional Fenton process may be positively assisted by the application of UV-light [20]:



Photo-Fenton oxidation in the presence of short UV light (UV-C, 180–290 nm) [21] gives a faster oxidation as a consequence of the higher quantum yields [12]. When applying UV-C light, H_2O_2 can also be hydrolysed contributing to the HO^\bullet formation [8]. The disadvantages of the Fenton process include (i) the formation of a high concentration of anions in the treated wastewater and (ii) large amounts of ferrous iron sludge [22]. Recent studies have attempted to overcome these drawbacks by applying nZVI together with H_2O_2 for industrial wastewater treatment [19, 23]. This alternative process could overcome the disadvantages associated with Fe^{2+} -based AOPs by using the solid form of iron instead of Fe^{2+} as iron salts. During the last decade there has been a widespread development of nanomaterials for both industrial and domestic use. When the dimensions of a piece of solid material become very small, its physical and chemical properties become very different from those of the same material in larger bulk form [24]. Nanoparticles as a subset of nanomaterial is currently defined by consensus

TABLE 1: Wastewater characterization ($n = 3$).

Parameter	Value	Mixture*
pH	2.3 ± 0.5	2.2
Conductivity (mS/cm)	6.3 ± 0.6	5.9
COD (mg/L)	5102 ± 513	4956
TOC (mg/L)	$2,801 \pm 287$	2730

*Wastewater obtained from a mixture of these three characterized samples.

as single particles with a diameter $< 100 \text{ nm}$ [24]. The small particle size increases the proportion of atoms located at the surface increasing the possibility for the atoms to adsorb, interact, and react with other atoms and molecules [25]. The particles have also the capacity to remain in suspension [25] and, hence, aqueous slurries containing nZVI can easily be pumped and injected where needed. The nZVI has been mostly used for groundwater remediation and treatment of specific pollutants [25]. Additionally, the treatment of industrial wastewater using nZVI in Fenton and other processes has also been reported recently [26, 27].

The main objective of this investigation was two-folded: (i) to verify the technical feasibility of treating wastewaters generated in the wood-floor industry sector using Fenton with nZVI compared to photo-Fenton with nZVI and (ii) to verify the effects of the selected variables ($\text{H}_2\text{O}_2/\text{COD}$ ratio, $\text{H}_2\text{O}_2/\text{nZVI}$ ratio and dosing mode) on the treatment efficiency.

2. Materials and Methods

2.1. Wastewater Samples. The wastewater used in the current investigation was a mixture of different streams of real industrial wastewater generated during cleaning procedures in a wood-floor industry in Nybro, Sweden. The quality and quantity of these wastewaters vary in time, as they are manually and intermittently generated as a consequence of different manufacturing processes such as wood gluing, wood filling, cleaning of floors, blade sharpening, and others. These wastewaters are characterized by the presence of formaldehyde, nitrogen [1], metals [28] detergents, and, phenols [29]. At the factory, the wastewater mixture is kept in a full-scale on-site settling/sedimentation tank from where the samples for lab studies were taken. Wastewater samples were obtained at three different occasions and transported to the laboratory where they were stored at -20°C .

In order to obtain an average composition of the wastewater, a mixture of similar proportion of the three samples stored in the lab (1 : 1 : 1) was prepared. This mixture was then filtered with a Munktell OOR grade filter paper with a pore size $>10 \mu\text{m}$ to homogenize the wastewater. The characteristics of the wastewater used in the experiments are shown in Table 1. Proxy indicators such as TOC and COD were considered suitable to monitor treatability studies of this wastewater, since it is well known that these variables as well as the ratio between them are appropriate to evaluate the efficiency of treatment options [30, 31].

TABLE 2: Variable levels applied in the 2-level factorial design.

Variables	Symbol	-1	0	+1
H ₂ O ₂ : COD	χ_1	2 : 1	3.5 : 1	5 : 1
H ₂ O ₂ : nZVI	χ_2	2 : 1	8.5 : 1	15 : 1
Dosing mode	χ_3	1	2	3

Notations: +1 (high level); 0 (centre point); -1 (lower level).

2.2. Experimental Design. To have a better understanding on which independent variables play important roles on the treatment efficiency measured as percentage reduction of COD and TOC (dependent variables), it was applied a two-level full-factorial design with triplicates of the central points with the following selected independent variables or factors: (1) H₂O₂ : COD ratio; (2) H₂O₂ : nZVI ratio and; (3) the dosing mode. By dosing mode one means the procedure of adding equal aliquots of the oxidizing agent (H₂O₂) and the catalyst (nZVI) at different times throughout the experiment or adding it at once. The levels used for each factor in this investigation (Table 2) were selected according to the literature.

The AOS (average oxidation state) value was calculated using the COD and TOC data obtained by the above-described experimental design. The AOS value can attain a value between +4, for CO₂, and -4, for CH₄, the most oxidized and the most reduced state of carbon (C). The AOS value is a rough parameter to estimate the degree of oxidation in a mixed wastewater and was calculated according to the following [31]:

$$\text{AOS} = \frac{4(\text{TOC} - \text{COD})}{\text{TOC}}, \quad (5)$$

where COD and TOC values are expressed in mol O₂/L and C/L, respectively.

The statistical software Minitab 16 was used to setup the full factorial design. For statistical analysis Minitab 16 and GraphPad Prism 5 were used.

2.3. Experimental Setup. Two variations of Fenton treatment were investigated: dark-Fenton (nZVI/H₂O₂) and photo-Fenton (nZVI/H₂O₂/UV), using, in both cases, commercial nZVI. The commercial nZVI powder consisted of Fe⁰ surface stabilized nanoparticles coated with a thin inorganic surface layer, which makes it possible long-term storage as the manufacturer delivers it. The material had particle sizes ranging between 20–100 nm with an average of 50 nm according to the manufacturer (Nano Iron, s.r.o., Czech Republic). The photo-Fenton studies were carried out in a glass-jacket immersion-type UV-reactor (UV-Consulting Peschl Mainz, Germany) with a volume of 0.7 L (Figure 1). The distance between the UV-lamp and the liquid phase was 15 mm. The reactor was cooled down with distilled water to keep the liquid phase at room temperature of around 22°C. The UV-light was emitted at a 150 W in wavelengths ranging between 250 and 580 nm with the highest peaks at 310, 360, 400, 440, 550, and 580 nm.

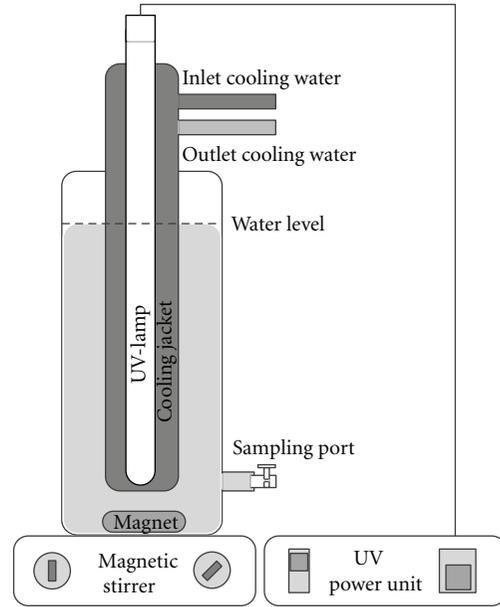


FIGURE 1: Schematic view of the UV-reactor used in the photo-Fenton experiments.

The dark-Fenton studies were conducted in 1 L glass beakers. The difference between standard glass beaker and the UV-reactor with the light in the off-mode was considered negligible according to the literature [32, 33]. Air purging was not considered in this study in order to keep treatment operational costs as low as possible. All glassware was carefully washed before each experiment.

2.4. Experimental Procedure. All runs were conducted with a volume of 0.5 L of wastewater that was agitated during 120 min by a magnetic stirrer at 400 rpm. The pH was adjusted at the beginning of each run to be kept between 2.95 and 3.05. Since this pH range has been reported to be the optimum for Fenton oxidation [13, 34], every 15 min throughout the 120 min of reaction time the pH was readjusted if needed. All pH adjustments were done with analytical grade sodium hydroxide (NaOH) and hydrochloric acid (HCl). The total amounts of nZVI and H₂O₂ were added either at the beginning of each run or in similar aliquots, at different time intervals (Table 3). The nZVI was added as slurry formed by 1 : 4 nZVI powder and water, after being stirred in a high speed shearer for 5 min, according to the manufacturer's instructions.

During the photo-Fenton treatment, the wastewater was exposed to UV-light during the treatment time of 120 min. After both Fenton and photo-Fenton treatments of 120 min, the pH of the wastewater was adjusted to 6.5 and agitated for 5 min at 400 rpm to quench the Fenton reaction [35]. In a sequence, 5 min after the agitation was stopped, the pH was raised to 8.5 to form iron precipitates [35]. The supernatant was then heated to 50°C and slowly shaken in a water bath for 30 min to expel any remaining H₂O₂. The water was then

TABLE 3: Dosing modes (the way the H₂O₂ and nZVI were added during the runs).

Sample number*	Total amount of		Number of equal doses†	0 min			40 min			60 min			80 min		120 min	
	H ₂ O ₂ (g/L)	nZVI (g/L)		H ₂ O ₂ (g/L)	nZVI (g/L)	H ₂ O ₂ (g/L)	nZVI (g/L)	H ₂ O ₂ (g/L)	nZVI (g/L)	H ₂ O ₂ (g/L)	nZVI (g/L)	H ₂ O ₂ (g/L)	nZVI (g/L)	H ₂ O ₂ (g/L)	nZVI (g/L)	
1.1; 2.1; 3.1; 4.1	24,8	1,7	1	24,8	1,7	—	—	—	—	—	—	—	—	—	—	—
1.2; 2.2; 3.2; 4.2	9,9	0,7	1	9,9	0,7	—	—	—	—	—	—	—	—	—	—	—
1.3; 2.3; 3.3; 4.3	17,3	2,0	2	8,7	1,0	—	—	8,7	1,0	—	—	—	—	—	—	—
1.4; 2.4; 3.4; 4.4	17,3	2,0	2	8,7	1,0	—	—	8,7	1,0	—	—	—	—	—	—	—
1.5; 2.5; 3.5; 4.5	9,9	0,7	3	3,3	0,2	3,3	0,2	—	—	—	—	3,3	0,2	—	—	—
1.6; 2.6; 3.6; 4.6	9,9	5,0	3	3,3	1,7	3,3	1,7	—	—	—	—	3,3	1,7	—	—	—
1.7; 2.7; 3.7; 4.7	17,3	2,0	2	8,7	1,0	—	—	8,7	1,0	—	—	—	—	—	—	—
1.8; 2.8; 3.8; 4.8	24,8	1,7	3	8,3	0,6	8,3	0,6	—	—	—	—	8,3	0,6	—	—	—
1.9; 2.9; 3.9; 4.9	24,8	12,4	3	8,3	4,1	8,3	4,1	—	—	—	—	8,3	4,1	—	—	—
1.10; 2.10; 3.10; 4.10	24,8	12,4	1	24,8	12,4	—	—	—	—	—	—	—	—	—	—	—
1.11; 2.11; 3.11; 4.11	9,9	5,0	1	9,9	5,0	—	—	—	—	—	—	—	—	—	—	—

* Treatments from 1.1 to 1.11: dark-Fenton; from 2.1 to 2.11: Photo-Fenton.

TABLE 4: COD and TOC reductions (%) with dark-Fenton and photo-Fenton experiments.

Coded variables			Dark-Fenton			Photo-Fenton		
χ_1	χ_2	χ_3	Run	% COD reduction	% TOC reduction	Run	% COD reduction	% TOC reduction
+1	+1	-1	1.1	42.6	21.4	2.1	78.4	59.4
-1	+1	-1	1.2	34.6	17.3	2.2	70.6	50.0
0	0	0	1.3	42.0	21.4	2.3	80.5	57.8
0	0	0	1.4	39.3	19.9	2.4	78.2	56.7
-1	+1	+1	1.5	35.6	19.0	2.5	77.6	56.0
-1	-1	+1	1.6	35.1	18.9	2.6	76.1	53.9
0	0	0	1.7	38.4	24.2	2.7	61.3	61.7
+1	+1	+1	1.8	43.5	23.0	2.8	60.3	61.7
+1	-1	+1	1.9	77.5	50.3	2.9	81.6	61.6
+1	-1	-1	1.10	49.2	34.9	2.10	78.5	58.0
-1	-1	-1	1.11	38.3	24.7	2.11	70.9	53.6

centrifuged at 614 g for 15 min. After this, the supernatant was separated and all samples were frozen before analysis.

2.5. Analytical Methods. COD and TOC in the wastewater samples were analysed spectrophotometrically using Hach Lange cuvette tests (Hach Lange, Dusseldorf) and measured with a Hach Lange DR 5000 spectrophotometer (Hach Lange, Dusseldorf). The pH and conductivity were measured with an HQ40d multiparameter meter.

3. Results and Discussion

3.1. Comparison between Fenton and Photo-Fenton

3.1.1. nZVI Fenton Treatment. The treatments based on dark-Fenton (Table 4 and Figures 2(a) and 2(b)) showed large variation in the responses measured as the COD and TOC removal percentages. As observed in Table 4, the removal of COD and TOC varied from 34% to 77% and from 17% to 50%, respectively, depending on the run indicating that the ranges of H_2O_2 :COD; H_2O_2 :nZVI and dosing modes combined in different ways have played an important role on the COD and TOC removal. There was a significant difference between COD and TOC reduction % within the dark-Fenton and photo-Fenton processes (paired t -test, $P < 0.05$) as illustrated in Table 4.

The highest reductions for both COD and TOC were achieved with a setup using high H_2O_2 :COD ratios and low H_2O_2 :nZVI ratio (run 1.9 in Table 4 and 9 in Figure 2(a)), indicating that higher concentrations of the oxidizing agent (H_2O_2) and the catalyst were able to oxidize a higher amount of COD and TOC, despite the fact that high concentrations of nZVI will possibly scavenge hydroxyl radicals. The stoichiometric ratio for the reduction of COD by H_2O_2 is 2.125 which is calculated assuming the complete oxidation of COD [36]:

$$\begin{aligned} 1 \text{ g COD} &= 1 \text{ g O}_2 = 0.03125 \text{ mol O}_2 \\ &= 0.0625 \text{ mol H}_2\text{O}_2 = 2.125 \text{ g H}_2\text{O}_2, \end{aligned} \quad (6)$$

(see [36]).

The results have shown that the amount of H_2O_2 to achieve the best treatment efficiency was twice as much the amounts stoichiometrically required. However such occurrences can be due to several factors that need to be further investigated. An important aspect regarding the Fenton treatment is the reduction of Fe^{3+} to Fe^{2+} making crucial the presence of reaction intermediates able to reduce Fe^{3+} and regenerate the catalyst. However, there are reaction intermediates that instead of reducing the Fe^{3+} remove it from the Fe^{2+}/Fe^{3+} cycle, due to the generation of iron complexes, delaying and/or inhibiting the oxidation process [18]. Regardless the use of higher amounts of H_2O_2 in comparison to the stoichiometric need, the H_2O_2 :COD ratio of 5:1 was in a range similar to that reported as being effective in previous studies [14, 18]. On the other hand the H_2O_2 :nZVI ratio of 2:1 was lower than the values found in literature [12, 18, 37].

When analysing the amount of oxidizing agent H_2O_2 per unit of COD removed ($g H_2O_2/g COD$ removed) used in different treatments in Figure 2(b), other treatments can be considered economically more feasible (runs 1.2, 1.5, 1.6, and 1.11 in Table 4; respectively 2, 5, 6, and 11 in Figure 2(b)). But run 1.9 was much more efficient in terms of COD removal and it was not considerably worse than the others above mentioned regarding $g H_2O_2/g COD$ removed.

3.1.2. nZVI Photo-Fenton Treatment. The results regarding COD and TOC removals with photo-Fenton have shown that the addition of the UV energy has significantly increased the treatment efficiency compared to dark-Fenton (paired t -test, $P < 0.05$) (Figures 3(a) and 3(b)). Furthermore, it was observed that during the photo-Fenton process, the reductions of COD and TOC were more homogenous in comparison to those observed for the dark-Fenton treatment (Table 4; Figures 2(c) and 2(d)).

The increase of TOC reduction was significantly higher than the increase of COD reduction by photo-Fenton (Figure 3(c)). A significant difference was observed between the reductions (in %) of COD and TOC with photo-Fenton treatment (paired t -test, $P < 0.05$).

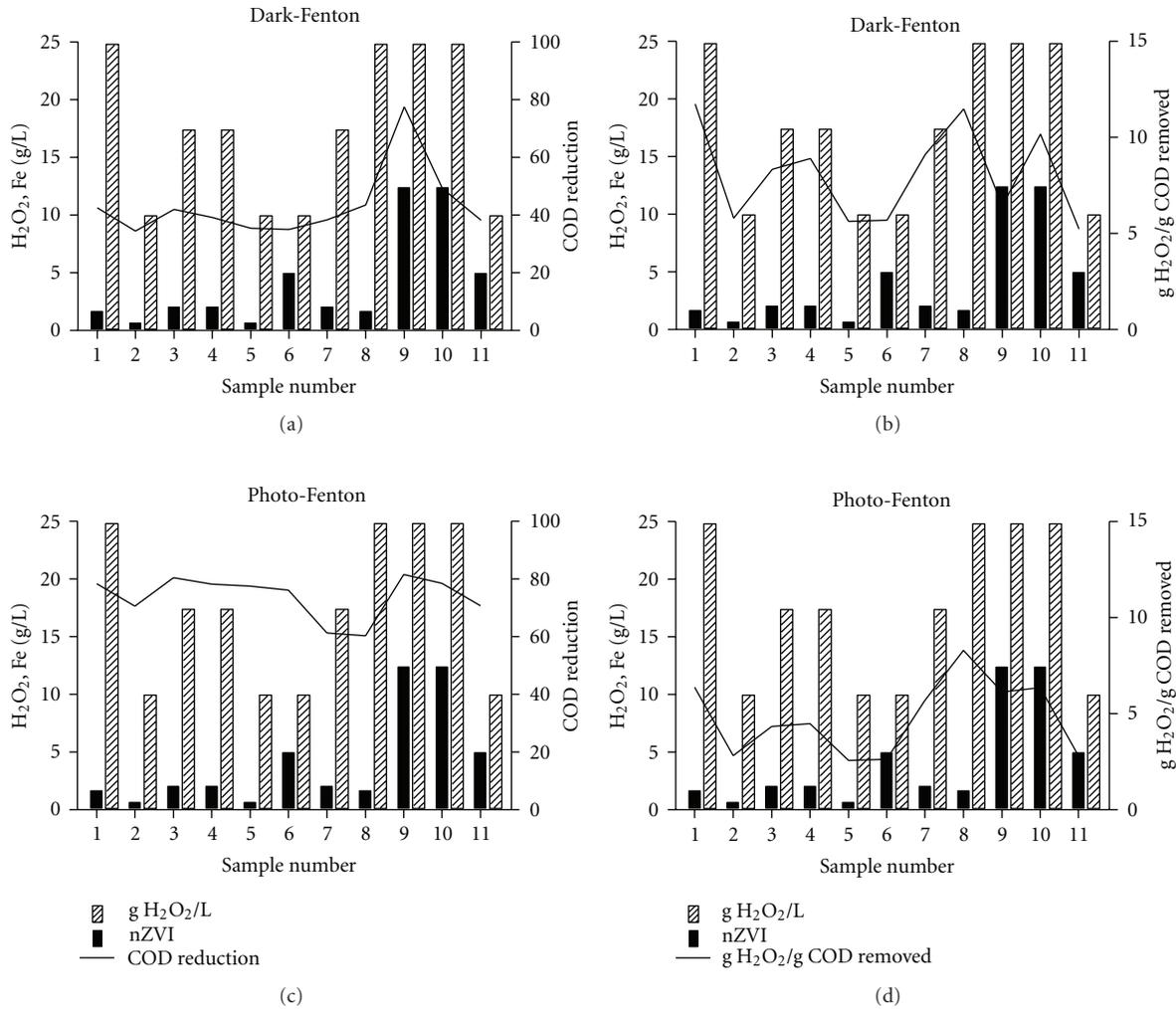


FIGURE 2: Results from dark-Fenton (a) and (b) and photo-Fenton (c) and (d) experiments using nZVI in 11 runs each. (a) and (c) Amounts of reagents (g/L) and COD removal (%); (b) and (d) amounts of reagents (g/L) and $\text{g H}_2\text{O}_2$ consumed per g COD removed.

Run 2.9 in Table 4 (equivalent to 9 in Figure 2(c)) promoted the highest removal of COD and TOC in %. However, when taking into account the amount of oxidizing agent used per amount of COD removed ($\text{g H}_2\text{O}_2/\text{g COD removed}$), another treatment was economically more effective (run 2.5 in Table 4, equivalent to run 5 in Figure 2(d)). In Figure 2, both runs 5 and 6 performed satisfactorily and with low amounts of H_2O_2 promoted COD removals of around 80%, indicating the crucial role played by the UV energy in terms of treatment efficiency. The efficiency in using the UV in combination with the Fenton reaction is confirmed in Figures 2(c) and 2(d), which illustrate that despite using a H_2O_2 :COD ratio as high as 5:1 in run 2.9 (Table 4), only a small increase in COD removal in % was observed compared to runs 2.5 and 2.6 (Table 4) where a H_2O_2 :COD ratio of only 2:1 was used. COD and TOC reductions over 75% and 55%, respectively, were achieved in runs 2.5 and 2.6 (Table 4), respectively, which corresponded to less than half of the amount of H_2O_2 applied in run 2.9 (COD and TOC reductions of 82% and 61%, resp.). Similar results were

reported [38] where an increase of H_2O_2 :COD ratio above the range of 1–3 did not improve the COD reduction related to the presence of antibiotics in the water. Furthermore, the use of high concentrations of nZVI in runs 2.6 and 2.9 (H_2O_2 :nZVI of 2:1, Table 4) did not result in a increased efficiency, in comparison to run 2.5 (H_2O_2 :nZVI of 15:1). As discussed previously, one important event for the Fenton process is the reduction of Fe^{3+} to Fe^{2+} and such reduction is enhanced when using photo-Fenton [20]. This is likely one of the reasons for the much larger reductions in general achieved with photo-Fenton, being another reason for the fact that significantly lower concentrations of nZVI can be used. It is worth noting that in all these setups the reactants were added in three doses along the treatment, reducing the risk for scavenging between the reactants. Figure 2(d) shows that when 94% less nZVI was used, only 6% less COD and TOC reductions were observed in the presence of UV. Such a large reduction of iron reduces the costs with this catalyst and the amount of spent iron that needs to be handled (see the discussion Cost Effectiveness in this paper).

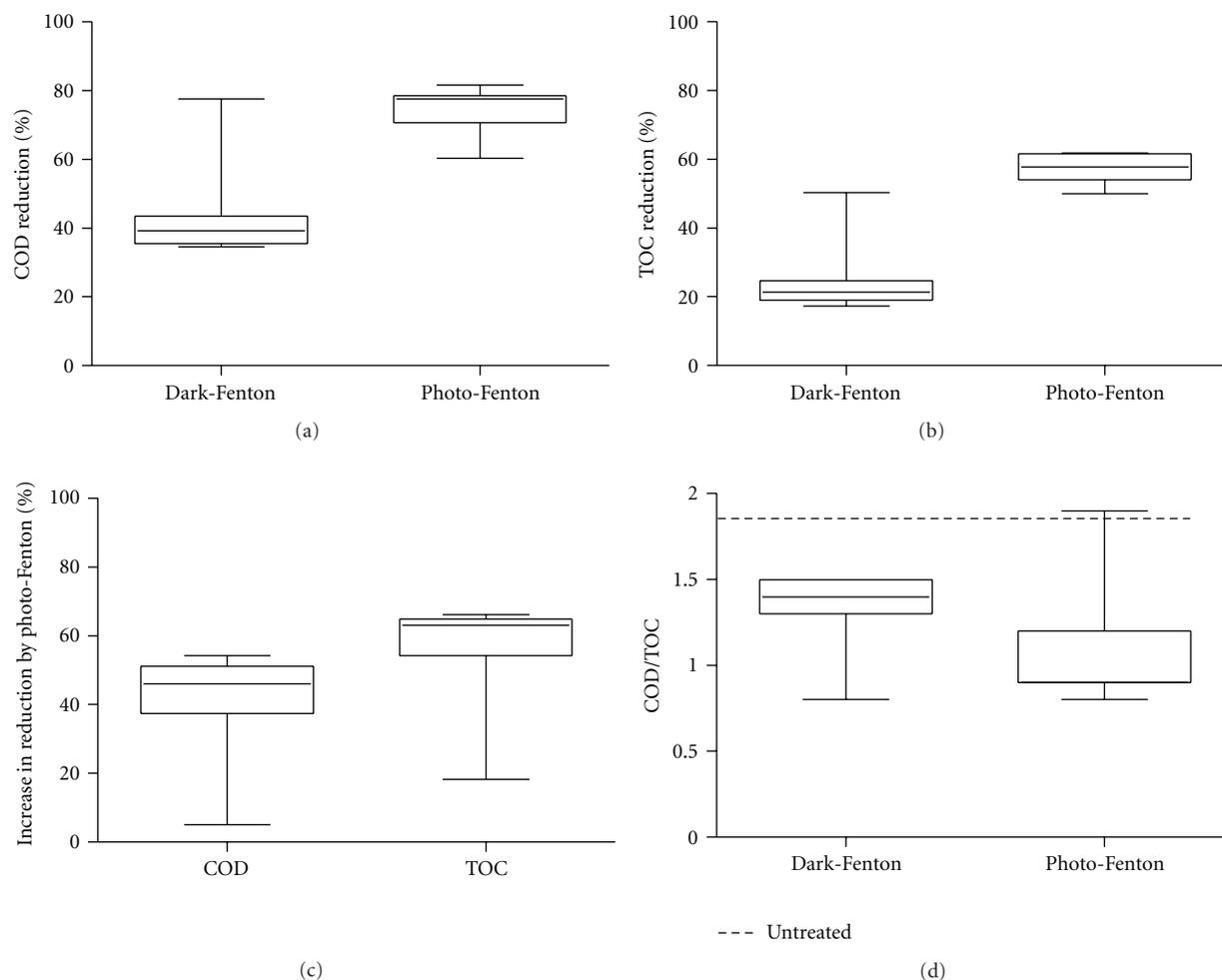


FIGURE 3: Boxplots built up with data from COD and TOC values obtained with dark-Fenton and photo-Fenton treatments. (a) COD reduction (in %) with both treatments; (b) TOC reduction (in %) with both treatments; (c) increase (in %) in the percentage of COD and TOC reduction by photo-Fenton compared to dark-Fenton; (d) changes in COD/TOC ratio due to different treatments.

3.1.3. Oxidation and Mineralisation. The results have shown that the COD and TOC values after both dark- and photo-Fenton treatments were considerably different as indicated by the COD/TOC ratios (Figure 3(d)). There was no significant difference in COD/TOC ratios when comparing photo-Fenton and dark-Fenton; however, COD/TOC ratios decreased after treatment. As illustrated in Figure 4, whereas negative correlations were found between COD and TOC reduction (in %) and COD/TOC ratio ($R^2 = 0.86$ and 0.62 , resp.) for the dark-Fenton experiments, only COD removal (in %) was correlated with COD/TOC ratio ($R^2 = 0.92$) in the photo-Fenton investigation. The correlation between TOC removal (in %) and COD/TOC for photo-Fenton had coefficient of determination as low as $R^2 = 0.18$. These results suggest that the remaining organic compounds measured as TOC were very recalcitrant and difficult to degrade as indicated by very low COD/TOC ratios after these treatments, and even with higher reductions of COD, the TOC value was not lowered. Previous studies have reported that a COD/TOC ratio below 1.3 indicates that that residual

organic carbon was mostly related to refractory organic compounds [16].

Unlike the COD value that is related to organically-bound and inorganic constituents [39], TOC is independent of the oxidation state of the organic matter and only measures organic carbon converted to CO_2 [40], suggesting that changes observed in the COD/TOC ratio can be related to the degree of changes in the structure of the organic compounds after oxidation. Figure 5 shows the AOS values before and after the treatment with dark-Fenton and photo-Fenton. It was found that by the end of the photo-Fenton treatment, the oxidation states were higher in comparison to those after the dark-Fenton treatment, confirming the stronger oxidation (higher reduction efficiency for COD and TOC) with photo-Fenton and suggesting the yield of different end products. Regarding the oxidation states in the dark-Fenton, the AOS value in the run 1.9 was considerably higher in comparison to the raw wastewater and to other dark-Fenton treatments reaching AOS value approximately as high as those obtained after the photo-Fenton process.

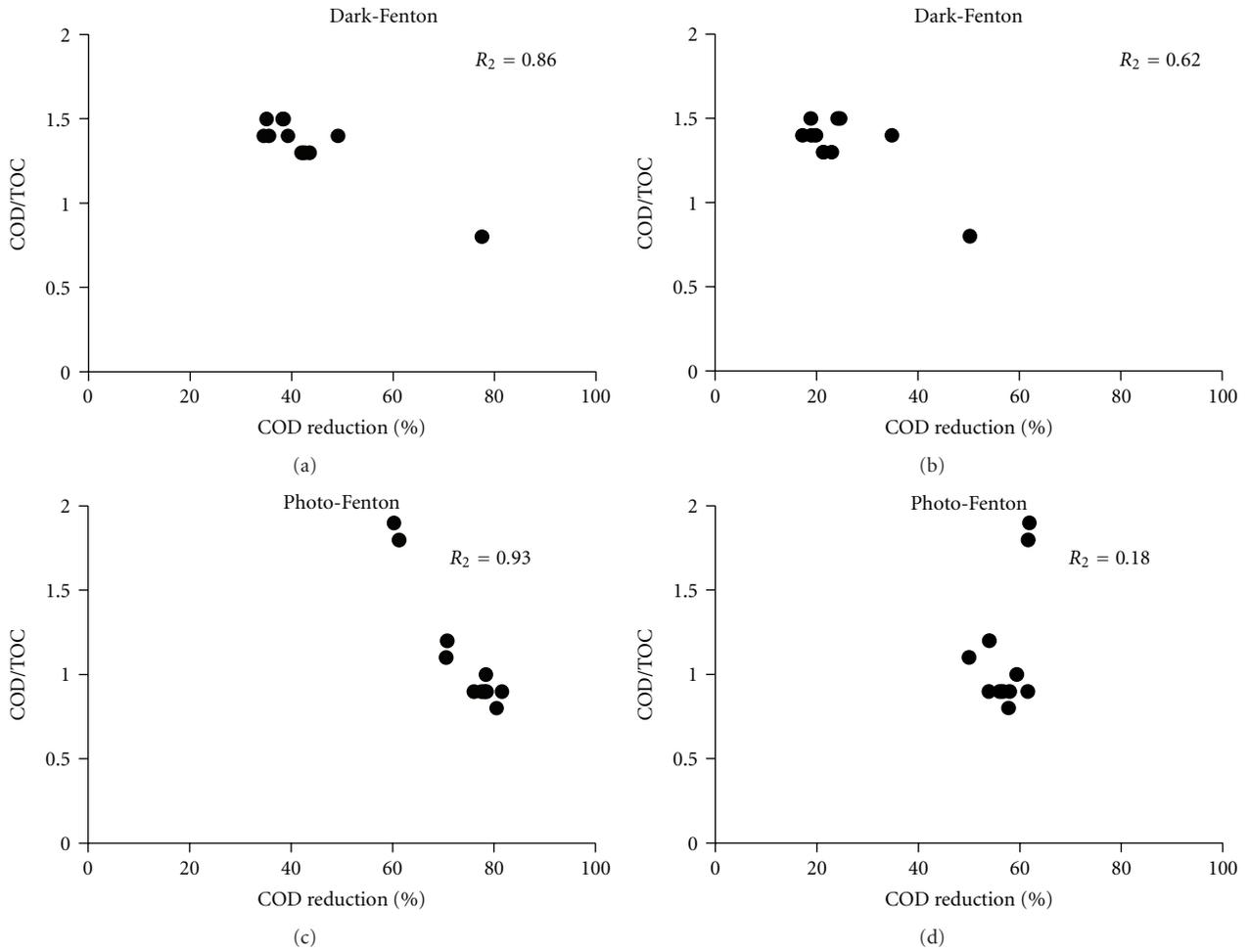


FIGURE 4: Correlation between COD and TOC reductions (in %) and COD/TOC ratios obtained with different dark- and photo-Fenton treatment setups.

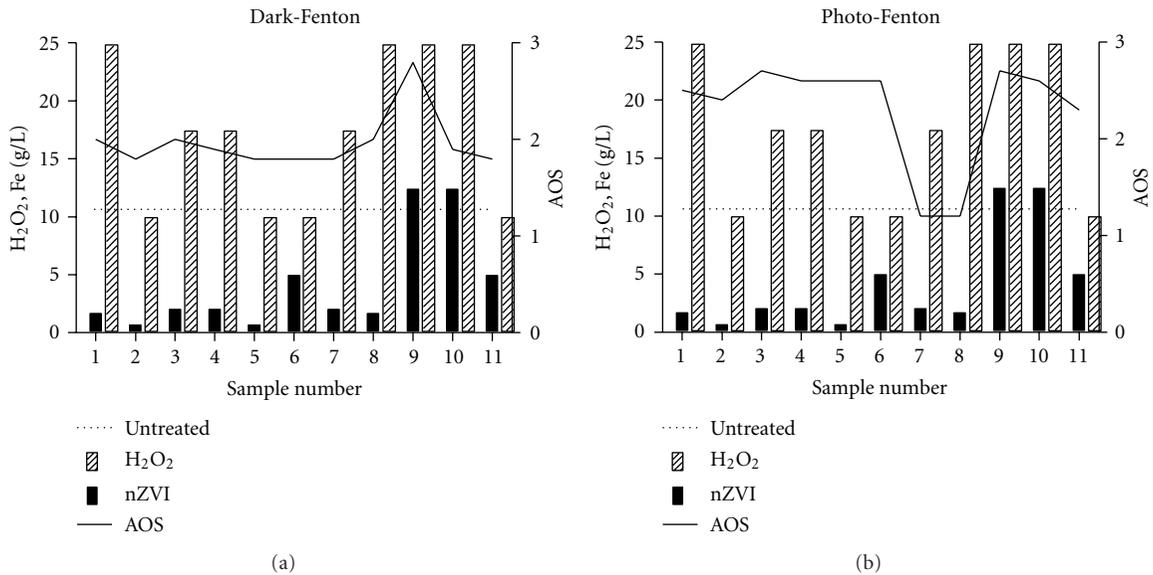


FIGURE 5: Amounts of reagents (g/L) and the AOS values obtained after each run/treatment.

TABLE 5: Results of statistical analyses of independent variables.

Term	Dark-Fenton				Photo-Fenton			
	COD reduction		TOC reduction		COD reduction		TOC reduction	
	Effect	<i>P</i>	Effect	<i>P</i>	Effect	<i>P</i>	Effect	<i>P</i>
Constant		0.00		0.00		0.00		0
H ₂ O ₂ : COD Ratio	17.3	0.01	12.4	0.02	0.9	0.91	6.8	0.07
H ₂ O ₂ : nZVI Ratio	-11.0	0.02	-12.0	0.02	-5.0	0.57	0.0	0.99
Doses	6.8	0.04	3.3	0.12	-0.7	0.94	3.0	0.24
H ₂ O ₂ : COD Ratio * H ₂ O ₂ : nZVI Ratio	-9.3	0.02	-8.4	0.03	-5.7	0.52	0.9	0.68
H ₂ O ₂ : COD Ratio * Dose	7.8	0.03	5.2	0.08	-6.8	0.46	0.0	0.99
H ₂ O ₂ : nZVI Ratio * Dose	-5.8	0.05	-1.6	0.40	-4.9	0.58	1.2	0.57
H ₂ O ₂ : COD Ratio * H ₂ O ₂ : nZVI Ratio * Dose	-8.0	0.02	-5.3	0.07	-5.7	0.52	-1.8	0.43
Ct Pt		0.07		0.01		0.91		0.39

According to Figure 5, with the exception of runs 2.7 and 2.8, AOS values after the photo-Fenton treatments were approximately +3 in all remaining runs suggesting that the oxidised chemical nature of most of the photo-Fenton treatments reached a stable AOS value and even though the treatment was to be continued, intermediates with higher oxidation state would not be formed. At the moment that AOS stabilizes, the chemical treatment is only mineralizing organic contaminants, but with no partial oxidation [41]. This together with the fact that the difference between the COD and TOC after treatment was considerably reduced by the photo-Fenton treatment (paired *t*-test, $P < 0.05$) indicates that a more complete reduction of the organic material was achieved when applying the photo-Fenton process. An increase in AOS during the treatment as observed in the current study, particularly for the photo-Fenton treatments, has been related to an increase in biodegradability [41] and reduction of toxicity [38].

This was confirmed by the fact that the reduction (in %) obtained with photo-Fenton is greater for TOC than for COD (paired *t*-test, $P < 0.05$), (Figure 3(c)). UV irradiation might have been responsible, for instance, for breaking down large aromatic molecules into aliphatic carbon chains, besides its effect on recycling Fe³⁺ back to Fe²⁺ [20].

3.1.4. Cost Effectiveness. Even though economic feasibility was not the focus of this investigation, one can mention that the main costs involved in the studied processes are related to the nZVI, the oxidizing agent H₂O₂, and the energy consumption of the UV-lamp. Photo-Fenton is reasonably more expensive than dark-Fenton treatment due to the use of a UV-lamp. However, the results have shown that when considering the overall treatment efficiency of both Fenton and photo-Fenton, the additional costs related to the UV-lamp could be compensated by the less amounts of nZVI to achieve high COD and TOC reduction %. Furthermore, the use of UV energy has brought advantages since it widened the range of reactant concentrations that could be used and still achieve very satisfactory treatment performances, making reasonable to state that is the less the amount of reactants, the more economically feasible the treatment becomes. Such

advantage becomes very important in a full scale plant, where the concentration of pollutants in the raw wastewater can vary, which would require the use of different concentrations of reactants. A clear example is the run 2.5 (Table 4), which had the most satisfactory performance observed with the photo-Fenton treatment. In run 2.5 with the lowest reactant concentrations, COD and TOC reductions of 78% and 56%, respectively, were achieved, making this the most economically feasible option in this study.

3.2. Effect of Independent Variables. The effects of the independent variables (H₂O₂ : COD; H₂O₂ : nZVI and dosing mode) and the interaction among them on the COD and TOC removal (in %) were obtained based on the data from the full-factorial design as shown in Table 5. Whereas all factors and respective two-way and three-way interactions had significant effects on the COD and TOC removal efficiency with dark-Fenton process ($P < 0.05$), no significance was found in the case of photo-Fenton (Table 5). Reasonably, H₂O₂ : COD and H₂O₂ : nZVI ratios were the factors that played the most important roles considering dark-Fenton treatment. Reasonably, negative values were obtained for the effects caused by the H₂O₂ : nZVI ratios on COD and TOC reduction in % with dark-Fenton, since the lower the ratio is, the higher the treatment efficiency will be as previously discussed. The results have shown that by reducing the H₂O₂ : nZVI ratio from 15 : 1 down to 2 : 1, the reductions (in %) of COD and TOC could be increased by 11% and 12%, respectively. The significant effect of the dosing mode on both COD and TOC reductions suggests that when large amounts of reactants are added at once, the treatment performance was not increased due to scavenging [37, 42]. On the other hand, by splitting the doses of the reactants into several steps, scavenging was avoided, an effect that has been described only very few previous studies [42, 43]. The results have shown that the studied factors and levels applied did not play any significant role in the case of photo-Fenton experiments. These results suggest that the long UV-exposure time has eliminated large differences in the results or by combining chemical oxidation and UV irradiation other factors might be involved.

4. Conclusions

The following conclusions can be withdrawn from this investigation:

- a. COD and TOC can effectively be reduced by at least 80% and 60%, respectively, from recalcitrant industrial wastewater from the wood industry using photo-Fenton;
- b. the most effective treatment setup for dark-Fenton was achieved with H_2O_2 :COD ratio of 5:1, H_2O_2 :nZVI ratio of 2:1 and with a dose mode that supplies the reactants in 3 equal aliquots added at equal time intervals;
- c. the most effective treatment setup for photo-Fenton was obtained with H_2O_2 :COD ratio of 5:1, H_2O_2 :nZVI ratio of 2:1, supplying the reactants in 3 equal aliquots added at equal time intervals; however, treatments close to the stoichiometry value (2.125) preformed almost as good;
- d. there was a significant increase in the mineralization when combining UV with Fenton (photo-Fenton).

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