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# PHOTO-FENTON AND FENTON OXIDATION OF RECALCITRANT INDUSTRIAL WASTEWATER

*Henrik Hansson<sup>a</sup>, Fabio Kazcala<sup>a</sup>, Marcia Marques<sup>a,b</sup>, William Hogland<sup>a</sup>*

*<sup>a</sup>Linnaeus University-LNU, Sweden*

*<sup>b</sup>Rio de Janeiro State University-UERJ, Brazil*

## **Abstract**

There is a need for development of on-site wastewater treatment technologies suitable to “dry-process industries”, such as the wood-floor industry. Due to the nature of their activities, these industries generate lower volumes of highly polluted and recalcitrant wastewaters after cleaning and washing activities. Advanced oxidation processes, such as Fenton and photo-Fenton are potentially good options for treatment. Wastewater from a wood-floor industry with initial COD of 4956 mg/L and TOC of 2730 mg/L was treated with Fenton (Fe/H<sub>2</sub>O<sub>2</sub>) and photo-Fenton (Fe/H<sub>2</sub>O<sub>2</sub>/UV). The highest removal of COD and TOC (80% and 60% respectively) was achieved using photo-Fenton.

**Keywords:** wastewater treatment; photo-Fenton; Fenton; wooden floor industry

## **Introduction**

Discharge of industrial wastewaters into either municipal sewerage systems or directly into recipient water bodies has raised serious concerns during decades, leading to intensive research and development of on-site treatment technologies. However, whereas investigations have focused on industrial sectors that have water as an important input to their manufacturing processes, “dry industries”, which due to the nature of their activities generate lower volumes of highly polluted wastewater after cleaning activities have been neglected. The wooden floor and furniture industries, for instance, have no water requirement for their production processes [1-2]. Even though, these industries generate wastewaters during cleaning and washing of machinery, surfaces and floors. Regardless the relatively low volumes these cleaning wastewaters contain high amounts of pollutants such as urea-formaldehyde and phenols, ammonium sulphate, wood filler, lacquer and detergents, among others. Chemical oxygen demand (COD) varying from 3200 to 50000 mg L<sup>-1</sup> are described and the presence of recalcitrant organic compounds in these cleaning wastewaters 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 into the sewage system. Such procedure cannot be seen as a sustainable strategy for the 21<sup>st</sup> century. The treatment of wastewaters from the timber industry using chemical methods has had

limited efficiency [3]. The use of biological treatment [4] and sorption/filtration processes [2] have also shown limitations considering the main purpose of complying with established standards for discharge into recipient water bodies. Advanced oxidation processes (AOP) have been used to treat complex wastewaters in combinations with biological and/or chemical treatment. These studies have used AOP after [5-6] for polishing or before [7-8] biological treatment with the purpose of reducing toxicity when the wastewater is too toxic. Hydroxyl radicals are one of the strongest oxidants ( $E = 2.73 \text{ V}$ ), it is non-selective and capable to quickly oxidize a broad range of organic pollutants[9]. These are the main oxidizing species in the Fenton process [10]. The Fenton's reagent 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 has no energy requirements compared to many other AOP. Additionally, both iron and hydrogen peroxide are relatively cheap and safe. The mechanisms that take place in the Fenton process are well-known [17] and the conventional Fenton process may be positively assisted by the application of UV-light [18]. Photo-Fenton oxidation in the presence of short-UV (UV-C) light gives a faster oxidation as a consequence of the higher quantum yields [12]. When applying UV-C light,  $\text{H}_2\text{O}_2$  can also be hydrolysed contributing to the  $\text{HO}\cdot$  formation [12].

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 compared to photo-Fenton; (ii) Verify the effects of different levels for the selected independent variables ( $\text{H}_2\text{O}_2/\text{COD}$  ratio,  $\text{H}_2\text{O}_2/\text{Fe}$  ratio) on the treatment efficiency.

## Materials and Methods

### Wastewater samples

The wastewater used in the experiments was a mixture of different streams of real wastewaters generated after manual cleaning procedures in a wood floor industry in Nybro, Sweden. The composition varied with time, as the wastewaters are generated intermittently by different processes that are running within the industry, such as gluing, filling, floor cleaning, blade sharpening and others. At the factory, the wastewater mixture is kept in a full-scale on-site 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  $-20 \text{ }^\circ\text{C}$ .

In the beginning of this investigation, with the purpose of obtaining an average composition of the wastewater, a mixture of similar proportion of 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  $>10 \text{ }\mu\text{m}$  to homogenize the wastewater. The characteristics of the wastewater used in the experiments are shown in Table 1. The characterisation based on proxy indicators such as TOC and COD was considered suitable for the type of wastewater and the selected treatability study, since it is well-known that parameters such as COD and TOC as well as the ratio between them are good indicators of the effects resulting from the treatment carried out [19-20] (table 2). The range for the concentration of reactants was chosen from a literature survey (table 1).

Table 1. Variables and levels applied in the study

Variables	Symbol	-1	0	+1
$\text{H}_2\text{O}_2:\text{COD}$ ratio	$\chi_1$	2:1	3.5:1	5:1
$\text{H}_2\text{O}_2:\text{Fe0}$ ratio	$\chi_2$	2:1	8.5:1	15:1

Table 2 Wastewater characterization (n = 3).

Parameter	Value	Mixture*
pH	2.3 ± 0,5	2.2
Conductivity (µS/cm)	6.3 ± 0.6	5.9
COD (mg/L)	5102 ± 513	4956
TOC (mg/L)	2,801 ± 287	2730

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

The statistical software Minitab 16 and GraphPad Prism 5 was used to setup the full factorial design as well all statistical analyses.

### Experimental setup

Two variations of Fenton treatment were investigated: (i) the dark Fenton (Fe/H<sub>2</sub>O<sub>2</sub>) and; (ii) the photo-Fenton (Fe/H<sub>2</sub>O<sub>2</sub>/UV), in both cases, using, Fe<sup>2+</sup>Cl as catalyst. Dark Fenton experiments were conducted in 1 L glass beakers. For the photo-Fenton experiments, a UV-reactor with a volume of 0.7 L was used. 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. All glassware was carefully washed before each experiment.

### Experimental procedure

All runs were conducted with a wastewater 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 the range from 2.95 to 3.05. The pH was controlled every 15 min throughout the 120 min of reaction time, since this pH range has been reported to be optimum for Fenton oxidation [13, 21]. All pH adjustments were done with analytical grade sodium hydroxide (NaOH) and hydrochloric acid (HCl). During the photo-Fenton treatment, the wastewater was exposed to UV light for 120 min followed by a pH adjusted to 6.5 and agitation of 400 rpm for 5 min to quench the Fenton reaction as reported in the literature [22]. In a sequence, at 5 min after the agitation was stopped, the pH raised to 8.5 to form iron precipitates [22]. The supernatant was then heated to 50<sup>0</sup>C and slowly shook in a water bath for 30 min to expel any remaining H<sub>2</sub>O<sub>2</sub>. The water was then centrifuged at 614 g for 15 min. After this, the supernatant was separated and all samples were frozen before analysis.

### 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 Multi-Parameter Meter.

## Results and Discussion

### Comparison between Fenton and photo-Fenton

#### *Dark Fenton treatment*

The treatments based on dark Fenton (Table 4 and Figure 1a-1c) showed large variation in the responses measured as the COD and TOC removal percentage. As observed in Table 4, the removal of COD and TOC varied from 33% to 83% and from 12% to 66% respectively, depending on the run. There was a significant difference between the reductions of COD and TOC (paired t-test,  $p < 0.05$ ).

Table 3 COD and TOC reductions (%) with dark-Fenton and photo-Fenton experiments.

Coded variables		Dark-Fenton			Photo-Fenton		
$\chi_1$	$\chi_2$	Sample	% COD reduction	% TOC reduction	Sample	% COD reduction	% TOC reduction
+1	+1	1.1	65.6	38.9	2.1	71.8	48.1
-1	+1	1.2	31.1	18.6	2.2	68.5	44.1
0	0	1.3	66.4	46.0	2.3	75.3	47.1
0	0	1.4	67.4	42.3	2.4	78.5	55.5
-1	+1	1.5	33.3	12.5	2.5	74.5	47.4
-1	-1	1.6	70.3	47.4	2.6	71.6	49.6
0	0	1.7	65.3	42.7	2.7	79.0	53.3
+1	+1	1.8	58.4	31.2	2.8	74.2	55.8
+1	-1	1.9	78.1	60.0	2.9	75.8	61.9
+1	-1	1.10	76.9	47.5	2.10	78.0	51.2
-1	-1	1.11	67.6	47.0	2.11	66.6	58.9

The highest reduction for both COD and TOC was achieved with a setup using high  $\text{H}_2\text{O}_2$ :COD ratios and low  $\text{H}_2\text{O}_2$ :Fe ratio (run 1.9 in Table 4 and 9 in Figure 1a). The  $\text{H}_2\text{O}_2$ :COD ratio of 5:1, were in the range that has been found to be effective in other studies [14, 17] combined with a  $\text{H}_2\text{O}_2$ :Fe ratio of 2:1, which were lower than the values found in literature [12, 17, 23]. However, when analysing the amount of oxidizing agent per unit of COD removed ( $\text{g H}_2\text{O}_2 / \text{g COD removed}$ ) for the different treatments in Figure 1c, other treatments can be considered more effective (runs 1.6 and 1.11 in Table 4; respectively 6 and 11 in Figure 1b). Considering this run 1.9 was considerably worse than the others above-mentioned regarding  $\text{g H}_2\text{O}_2 / \text{g COD removed}$ , using more than double the amount of  $\text{H}_2\text{O}_2 / \text{g COD removed}$ . Run 1.9 is an experiment with high concentrations of both  $\text{H}_2\text{O}_2$  and Fe, something that is known can cause a scavenging effect between the reactants [24].

#### **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,  $p < 0.05$ ) (Figure 2a and 2b).

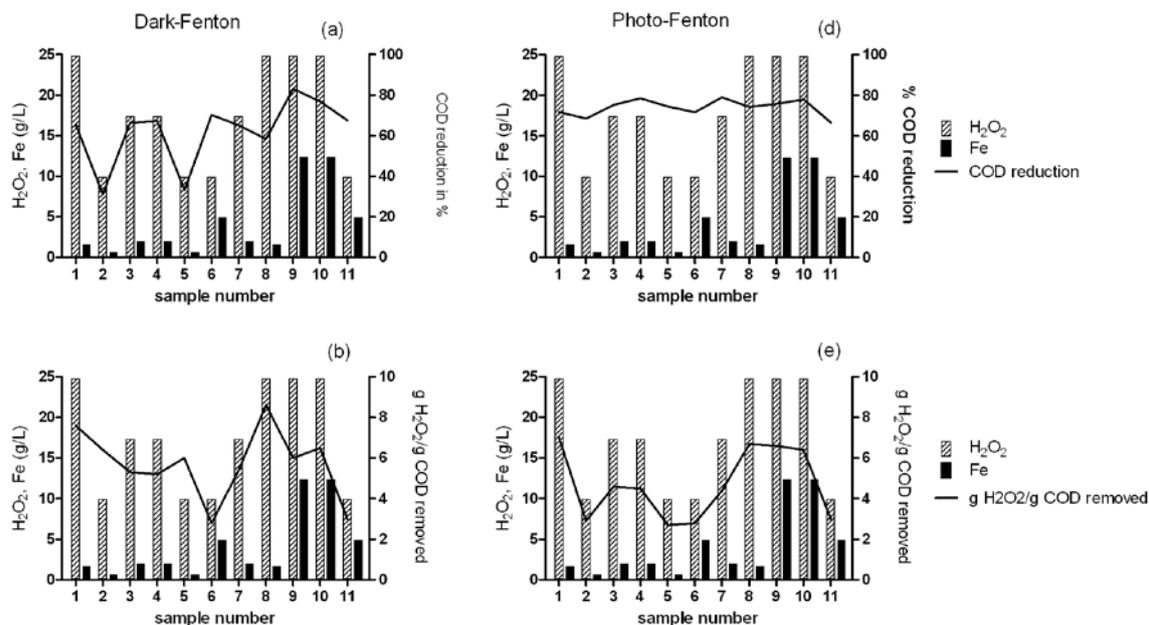


Figure 1. Results from dark-Fenton and photo-Fenton experiments in 11 runs each. (a) and (b) amount of reagents (g/L) and COD removal (%). (c) and (d) amount of reagents (g/L) and g H<sub>2</sub>O<sub>2</sub> per g COD removal.

A significant difference was observed between the reductions (in %) of COD and TOC with photo-Fenton treatment (paired t-test,  $p < 0.05$ ). Run 2.4 in Table 3 promoted the highest COD reduction and close to highest TOC reduction in %, 78.5 and 55.5 respectively. However the difference between the 7 runs with the highest reduction is less than 4 % and between all samples the difference is only 12 % for COD. This is a very small difference compared to dark-Fenton where the difference was over 45 % for COD. This increase in effectiveness when applying photo-Fenton strengthens the case for that for the waters in this study one of the major problems is inhibiting of the Fe<sup>3+</sup> Fe<sup>2+</sup> cycle, as photo-Fenton is known to assist this process [25].

### COD and TOC removal

The COD and TOC removals achieved with photo-Fenton show that the addition of UV has significantly increased the treatment efficiency (paired t-test,  $p < 0.05$ ) (Figure 2a and 2b). The results have also 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 2d). The photo-Fenton treatment had a significantly larger effect on TOC removal compared to COD removal, (paired t-test,  $p < 0.05$ ) (figure 2c). This indicates that the photo-Fenton treatment was more effective in producing a complete reduction of the organic material, since the TOC values only measures organic carbon [26] converted to CO<sub>2</sub> [27]. UV irradiation might have been responsible for instance, for breaking down large aromatic molecules into aliphatic carbon chains, besides its effect on recycling Fe<sup>3+</sup> back to Fe<sup>2+</sup> [28]. The differences regarding COD/TOC ratios are not significant between photo-Fenton and dark-Fenton, but there is a lowering of the COD/TOC ratio after compared to before treatment suggesting that the more recalcitrant compounds are left in the treated wastewater [16].

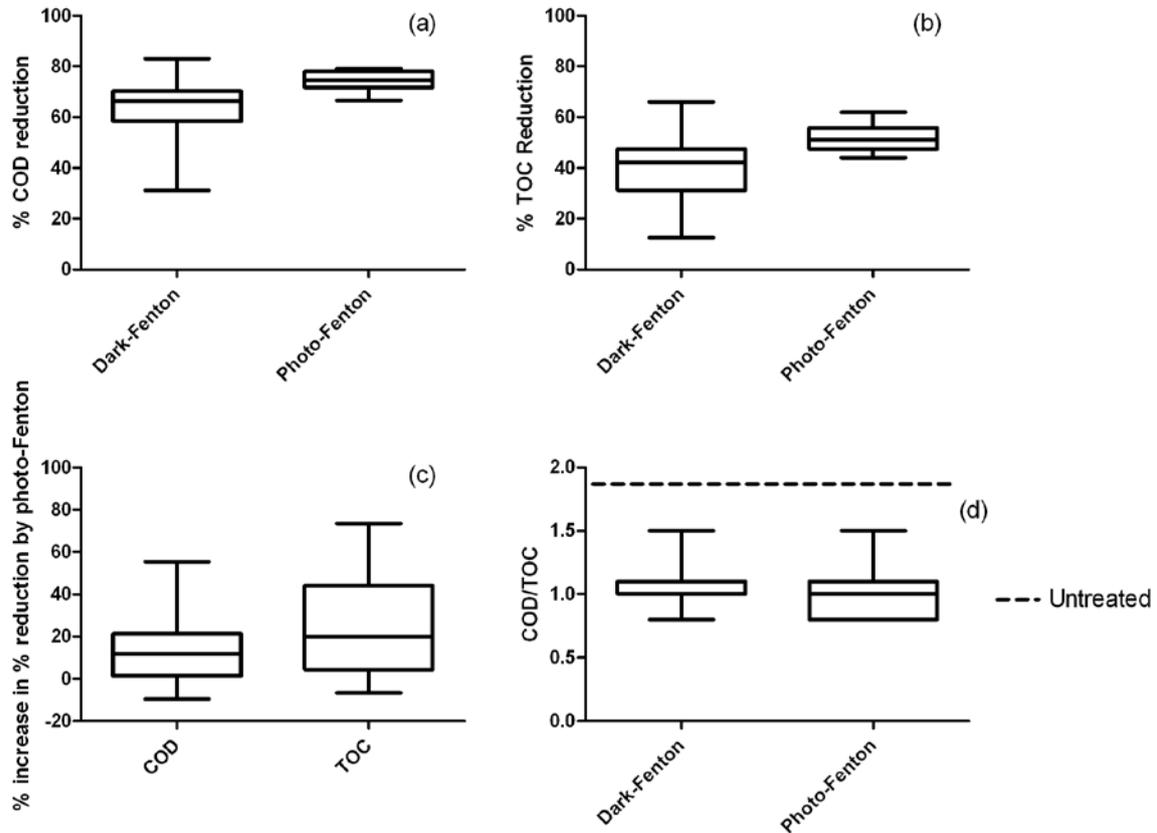


Figure 2. Boxplots built-up with data from COD and TOC values obtained with dark-Fenton and photo-Fenton treatments. (a) COD reduction (in %) with both treatments; (b) TOC reduction (in %) with both treatments; (c) Increase (in %) in the percentage of COD and TOC reduction by photo-Fenton compared to dark-Fenton; (d) changes in COD/TOC ratio due to different treatments.

A negative correlations were found between COD and the COD/TOC ratio for both Fenton and photo-Fenton ( $R^2 = 0.58$  and  $0.48$  respectively) no correlation was found for TOC and the COD/TOC ratio ( $R^2 = 0.32$  and  $0.35$  respectively). 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 treatment, 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].

## Conclusions and future research

The following conclusions can be withdrawn from this study:

- COD and TOC can effectively be reduced by at over 80% and 60% respectively from recalcitrant industrial wastewater from the wood industry using photo-Fenton;
- The most effective treatment setup for dark-Fenton for both COD and TOC reduction was achieved with H<sub>2</sub>O<sub>2</sub>:COD ratio of 5:1, H<sub>2</sub>O<sub>2</sub>:Fe ratio of 2:1
- The most effective treatment setup for photo-Fenton for reduction of COD and TOC was obtained with H<sub>2</sub>O<sub>2</sub>:COD ratio of 3.5:1, H<sub>2</sub>O<sub>2</sub>:Fe ratio of 8.5:1; however treatments close to the stoichiometry value (2.155) performed almost as good;
- There is a significant increase in the mineralization when combining UV with Fenton (photo-Fenton);
- Future investigations should focus on optimizing the process, studying the toxic effects of the residual pollutants
- The possibility of combining photo-Fenton with biological treatment (coupled systems) is recommended.

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