

Fenton and Photo-Fenton oxidation of tannery wastewater

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ABSTRACT. Fenton and Photo-Fenton processes are attractive alternatives in effluent treatment, especially when applied to recalcitrant compounds. The aim of this work was to evaluate the efficiency of Fenton and Photo-Fenton processes for the treatment of wastewater from leather industry, investigating the reduction of COD, ammoniac nitrogen concentration and toxicity in treated wastewaters. The results showed that the kinetic of degradation by Fenton and Photo-Fenton reactions can be divided in two stages: an initial fast process, where approximately 70% of the COD reduction takes place, followed, by a slow process, where a reaction takes up to 4 hours, resulting in about 90% of COD reduction. Different mass ratios of $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ were tested and the results showed that the efficiency of the Fenton and photo-Fenton reactions increases from 65 to 90% as the concentration of hydroxyl radicals ($\cdot\text{OH}$) increases. No significant difference in the ammoniac nitrogen amount reduction for the Fenton and Photo-Fenton processes was observed, either before or after coagulation. The ammonia removal was ascribed to the oxidation of nitrogen organic compounds, possibly forming N_2 and nitrate ions. The toxicity bioassays using *Artemia salina* decreased as the wastewater was degraded and increased if the hydrogen peroxide residue at the end of the reaction was high.

Key words: tannery wastewater, Fenton reaction, photo-Fenton reaction; toxicity.

RESUMO. Oxidação em processos Fenton e Foto-Fenton em efluentes de curtumes. Os processos Fenton e Foto-fenton são alternativas atraentes no tratamento de efluentes, especialmente aplicados àqueles contendo compostos recalcitrantes. Neste trabalho foi avaliada a remoção de DQO e amônia durante o tratamento de efluentes de curtumes pelos processos Fenton e Foto-Fenton. A cinética de degradação foi dividida em dois estágios, sendo um processo inicial rápido, no qual 70% da DQO inicial é removida; seguido por uma etapa lenta que acontece em até 4 horas de reação, alcançando cerca de 90% de remoção da DQO inicial. Diferentes proporções mássicas $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ foram testadas e os resultados mostraram que a eficiência dos processos Fenton e Foto-Fenton aumenta de 65 até 90% à medida que a produção de radicais livres hidroxil aumenta. Nenhuma diferença apreciável na degradação de nitrogênio amoniacal foi observada entre os processos Fenton e Foto-Fenton, mesmo após a coagulação. A remoção de amônia foi atribuída à oxidação de compostos orgânicos, formando N_2 e íons nitrato. A toxicidade do efluente tratado diminuiu até a dosagem de 9g/L de H_2O_2 e aumentou para maiores dosagens, devido ao residual peróxido de hidrogênio ou a formação de produtos oxidados mais tóxicos.

Palavras-chave: efluente de curtumes, reação Fenton, reação foto-Fenton, toxicidade.

Introduction

The leather industry is associated with the generation of huge amounts of liquid effluents (30-35L/kg of raw material processed) (Suresh *et al.*, 2001). The wastewater may be characterized by several key parameters such as sulfide, chromium, oil and grease, BOD and COD (Kabdasli *et al.*, 1993).

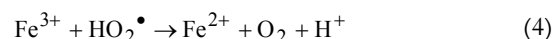
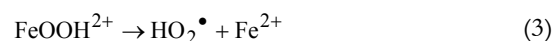
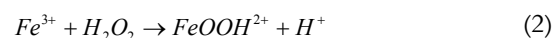
It has been demonstrated that a single treatment unit is not sufficient to achieve legal parameters. In fact, after conventional treatment (i.e., chromium precipitation, primary sedimentation, biological oxidation, secondary sedimentation), effluents still do not have the required limits, at least for some parameters, such as COD, salinity, ammonia and surfactants (Iaconi *et al.*, 2002).

Advanced oxidation processes (AOP's) based on the chemistry of hydroxyl radicals ($\bullet\text{OH}$) are currently used for destroying organic pollutants (Oturán *et al.*, 2001). These radicals react in a non-selective way on organic compounds, leading finally to mineral end products. Fenton's reagent is a system based on the generation of very reactive free radicals, especially hydroxyl radicals, which have a stronger oxidation potential than ozone (De Heredia *et al.*, 2001). Fenton's oxidation process has been successfully employed to treat textile wastewater (Kang and Hwang, 2000; Pérez *et al.*, 2002a; Kang *et al.*, 2002), paper pulp wastewater (Pérez *et al.*, 2002b) and single contaminants in aqueous solution (Maletzky and Bauer, 1998; Fallmann *et al.*, 1999; Oturan *et al.*, 2001).

In Fenton reaction, hydroxyl radicals $\bullet\text{OH}$ are produced by interaction of H_2O_2 with ferrous salts according to Equation 1.



Fe^{3+} can react with H_2O_2 in the Fenton-like reaction (Eqs. 2 to 4), regenerating Fe^{2+} and thus supporting the Fenton process (Pérez *et al.*, 2002a).



When the system is irradiated with UV illumination, the degradation rate of the organic pollutants by Fenton reaction can increase through the involvement of high valence iron intermediates, responsible for the direct attack on organic matter (Pérez *et al.*, 2002b). The absorption of visible light by the complex formed between Fe^{3+} and H_2O_2 could be the cause of these intermediates.

This paper evaluates the Fenton and Photo-Fenton processes to treat tannery wastewater, removing chemical oxygen demand and ammonia nitrogen. The possible toxicity of the reaction products was also investigated, using *Artemia salina* bioassays.

Material and methods

Ferrous sulfate $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, sulphuric acid and hydrogen peroxide (30% wt.) of analytical grade (Merck) were used. The effluent was obtained from a specific tannery (Centro de Tecnologia do Couro e

do Calçado Albano Franco - Campina Grande, Paraíba, Brazil), without any pre-treatment. The wastewater characteristics are given in Table 1. The relation COD/BOD is nearly 18, indicating that most of the contaminants are not biodegradable.

Table 1. Characterization of the tannery wastewater.

pH	8.0
COD, $\text{mg O}_2\cdot\text{L}^{-1}$	1803
BOD, $\text{mg O}_2\cdot\text{L}^{-1}$	106
Chloride, $\text{mg}\cdot\text{L}^{-1}$	2251
Total solids, $\text{mg}\cdot\text{L}^{-1}$	9961
Total fixed solids, $\text{mg}\cdot\text{L}^{-1}$	6146
Total volatile solids, $\text{mg}\cdot\text{L}^{-1}$	3815
Suspended solids, $\text{mg}\cdot\text{L}^{-1}$	526
Suspended fixed solids, $\text{mg}\cdot\text{L}^{-1}$	184
Volatile suspended solid, $\text{mg}\cdot\text{L}^{-1}$	342
Total dissolved solids (TDS), $\text{mg}\cdot\text{L}^{-1}$	9435
Dissolved solid Fixed, $\text{mg}\cdot\text{L}^{-1}$	5962
Dissolved volatile solids, $\text{mg}\cdot\text{L}^{-1}$	3473
Settleable solids, $\text{mL}\cdot\text{L}^{-1}$	23
Ammonia Nitrogen, $\text{mg}\cdot\text{L}^{-1}$	0.7

Fenton process: The Fenton reactions were carried out, at 25°C , in a 1-L batch reactor using a wastewater volume of 500mL. In the oxidation step, hydrogen peroxide and ferrous sulfate were added together in the reactor. In the coagulation step, the oxidized sample above mentioned was slowly mixed and then left still for sedimentation. The pH for Fenton oxidation was controlled at 2.5 with H_2SO_4 and the pH was adjusted to 7.0 for the coagulation step, using NaOH 6M. At the end of the process, the residual hydrogen peroxide was analyzed using the method described by Malick and Saha (2003).

Photo-Fenton process: The Photo-Fenton reactions were carried out in a 1-L batch reactor under strong solar irradiation, from 11:00 am to 02:00 p.m., at 25°C , in the city of Campina Grande, State of Paraíba, northeastern Brazil, from October 1st to February 20, 2003. The UV-B index was in the range 12.2 – 12.8 (Inpe, 2003). The pH was controlled at 2.5 using H_2SO_4 , and adjusted at 7.0 for coagulation, using NaOH 6M.

Chemical analyses: The COD was measured according to procedures described in Standard Methods (APHA, 1995). Since the residual H_2O_2 interferes with the measurement of COD (Kang *et al.*, 2002), the residual amount of H_2O_2 was also measured, using the permanganate titration with KMnO_4 0.1N. This method is suitable for measuring solutions of hydrogen peroxide in the range 0.25 to 70% wt (Morita and Assumpção, 1995). According Lin and Lo (1997), $1\text{mg}\cdot\text{L}^{-1}$ of H_2O_2 contributes $0.27\text{mg}\cdot\text{L}^{-1}$ COD concentration. Since no H_2O_2 residual concentration higher than 0.25% was measured, no correction was performed to

COD analysis. All other analyses were performed according to Standard Methods (APHA, 1995).

Artemia salina bioassays: *Artemia salina* cysts were incubated in artificial seawater illuminated by a tungsten filament light and gently sparged with air at 25°C. After 24 hours, hatched *A. salina* cysts were transferred to fresh artificial seawater and incubated for further 24h under artificial light with air sparging (Metcalf and Lindsay, 2002). Subsequently, an aliquot of 0.5mL of treated wastewater and 5mL of fresh seawater was poured into wells in polystyrene microtiter plates, and then 7 to 10 *A. salina* nauplii were placed in each well. Deaths were periodically recorded after incubating at 25°C for 24 hours.

Results and discussion

Kinetics of Fenton and Photo-Fenton processes

Previous results showed that tannery wastewater did not suffer decomposition when only hydrogen peroxide or ferrous sulfate were added (Dantas, 2003).

The COD removal/time rate by Fenton and photo-Fenton processes is shown in Figure 1, where it can be observed that the tannery wastewater is significantly oxidized by the Fenton and Photo-Fenton processes. No significant difference is apparent between Fenton and Photo-Fenton kinetics, possibly due to insufficient UV irradiation. The whole reaction can be divided into a two-stage reaction for both processes. The degradation rate in the first 20 minutes of the reaction was more rapid than after. Almost 70% of the degradation occurs in the first 20 minutes for both processes. The rest of the reaction occurs slowly, i.e., it takes 240 minutes for almost 90% of degradation.

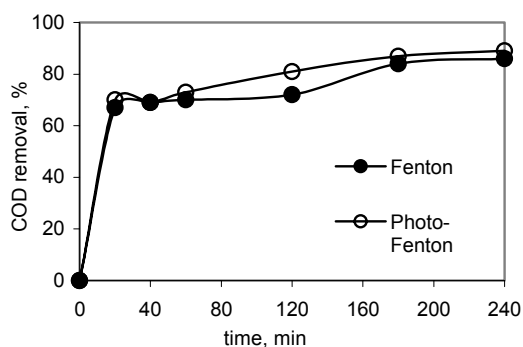


Figure 1. Kinetics of COD removal after Fenton and photo-Fenton processes ($[\text{Fe}^{2+}] = 1.0\text{g.L}^{-1}$; $[\text{H}_2\text{O}_2] = 15\text{g.L}^{-1}$; $\text{pH} = 2.5$).

These two-stage reaction can be explained considering that ferrous ions react very quickly with

hydrogen peroxide to produce large amounts of hydroxyl radicals (Malick and Saha, 2003). The hydroxyl radicals produced can react rapidly with organic matter. The ferric ions produced in the first stage react with hydrogen peroxide to produce hydroperoxyl radicals ($\text{HO}_2^\bullet$) and ferrous ions, according to reactions 2 and 3 and, finally, the reproduced ferrous ions react with hydrogen peroxide to produce more hydroxyl radicals.

The hydroxyl and hydroperoxyl radicals thus formed are apt to continue the wastewater oxidation. These two-stage reactions have been observed also by other authors (Lu *et al.*, 1999; Malik and Saha, 2003). Since the hydroperoxyl radicals have a lower oxidation capability than the hydroxyl radicals, this results in a rapid first-stage reaction, referred to as the $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ stage, followed by the slow second step, referred to as the $\text{Fe}^{3+}/\text{H}_2\text{O}_2$ stage.

Despite the high COD removal, the acute toxicity of treated wastewater for different times is high (Figure 2). The mortality of *Artemia salina* in control tubes was zero in all tests. As shown in Figure 2, the wastewater treated by the Fenton and photo-Fenton processes presented the same acute toxicity, indicating only partial oxidation or residual H_2O_2 concentration, as discussed below. In the first-stage reactions, since hydroxyl radicals were in high number, the toxicity was also measured, indicating that, for industrial applications, the reaction time should be higher than 120 minutes to achieve toxicity decreasing.

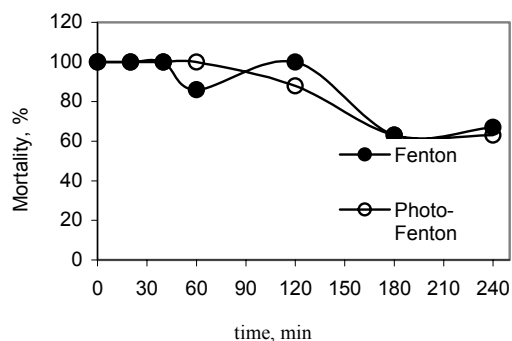


Figure 2. Mortality of *Artemia salina* in wastewater treated for different reaction times. $[\text{Fe}^{2+}] = 1.0\text{g.L}^{-1}$; $[\text{H}_2\text{O}_2] = 15\text{g.L}^{-1}$ and $\text{pH} = 2.5$.

Effect of H_2O_2 dosage on the COD removal and on the toxicity by Fenton and Photo-Fenton processes

Figure 3 shows the COD removal at different H_2O_2 dosages after Fenton and Photo-Fenton processes (oxidation + coagulation) for a reaction time of 3 hours. As the H_2O_2 dosage increased from

0 to 30 g.L⁻¹, the COD removal increased from 65% to 90% after the Fenton process. According to reaction 1, the concentration of $\cdot\text{OH}$ is expected to increase with the increasing H_2O_2 dosage, leading to increased oxidation rates of organic compounds.

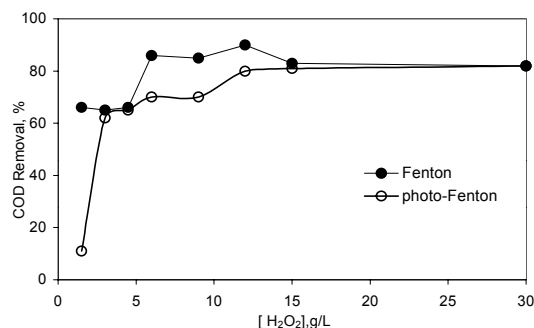


Figure 3. Effect of H_2O_2 dosage on COD removal by the Fenton and photo-Fenton processes (pH = 2.5; $[\text{Fe}^{2+}] = 1.0 \text{ g.L}^{-1}$; reaction time = 3 h).

The toxicity of the treated wastewater is shown in Figure 4 for different H_2O_2 dosages. It may be observed that the toxicity decreases as the H_2O_2 dosage increases up to 9 g.L⁻¹, and then the toxicity increases. No residual H_2O_2 concentration was measured after reaction and coagulation, although the detection limit for residual H_2O_2 concentration by permanganate titration method is 0.25% wt. However, the LC_{50} value for H_2O_2 reported by Twiner *et al.* (2001) is $2.6 \times 10^{-2} \text{ mol/L}$ (0.08% wt) and the presence of iron increases the toxicity, depending on the iron concentration. The partial oxidation of organic compounds is able to lead to less or more toxic components in the wastewater, depending on the products formed. Also, the residual H_2O_2 concentration below detection limit by permanganate titration could increase the toxicity of treated wastewater.

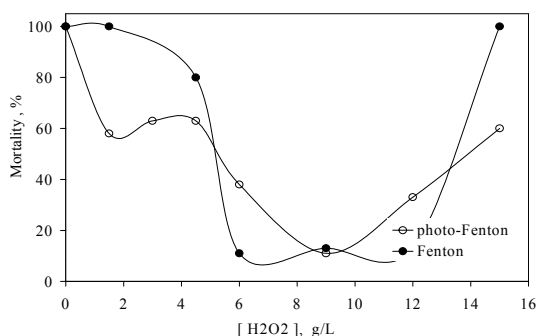


Figure 4. Effect of the dosage of H_2O_2 on the toxicity after Fenton and photo-Fenton processes (pH = 2.5; $[\text{Fe}^{2+}] = 1.0 \text{ g.L}^{-1}$; reaction time = 3 h).

Ammonia nitrogen removal

During the experiments, the ammonia concentration was measured. The ammonia removal by Fenton and Photo-Fenton processes is shown in Figure 5. No significant differences were observed for either of the processes, and the ammonia removal reached 90% after treatment.

Organic nitrogen can be decomposed to form ions and gases, for example, as nitrate, nitrite, ammonia, molecular nitrogen or nitrogen monoxide (Maletsky and Bauer, 1998). Maletsky and Bauer (1998) reported that the Fenton degradation of nitrogen contained in organic compounds produces ammonia and traces of nitrate. In this case, the ammonia concentration should increase, because ammonia can be oxidized to nitrite, but only under special conditions and in small concentrations (Meyer and Pietsch, 1996).

To H_2O_2 concentration higher than 5 g/L, Figure 5 shows that it is possible to eliminate ammonia up to 80%. Several authors have reported that only for high H_2O_2 concentration it is possible to eliminate ammonia nitrogen and the main byproducts are gaseous N_2 and nitrate (Zoh and Stenstrom, 2002; Goi and Trapido, 2002). Then it should be expected that the ammonia concentration should decrease continuously as the wastewater is oxidized.

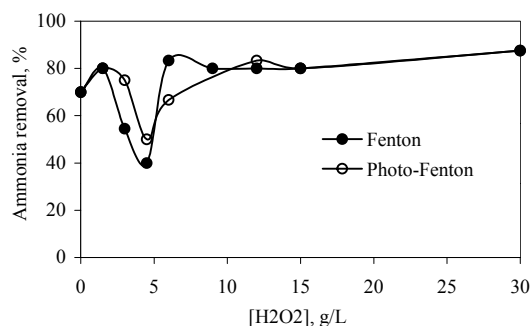


Figure 5. Ammonia removal after 3h reaction and coagulation by Fenton and Photo-Fenton process at different H_2O_2 initial concentration (pH = 2.5; $[\text{Fe}^{2+}] = 1.0 \text{ g.L}^{-1}$; reaction time = 3 h).

Conclusion

No significant differences were observed after Fenton and photo-Fenton processes for the treatment of tannery wastewater, in relation to kinetics, toxicity or ammoniac nitrogen removal. The kinetic of COD removal for both processes showed similar results. The degradation reaction can be divided in two periods for both processes and the degradation rate in the first 20 minutes is much faster than it is after this period. About 70% of the degradation occurs in the first 20 minutes for the

two processes and the remainder of the reaction occurs slowly. Thus 4 hours are necessary for a degradation of 90% of the organic matter.

Using ferrous ions at a dosage of 1g.L^{-1} and a concentration of 15g.L^{-1} of hydrogen peroxide, the Fenton process reached 83% of COD removal and the Photo-Fenton process reached 87% of COD removal for 3 hours of reaction. No appreciable difference in the reduction of the ammonia nitrogen amount for the two processes was found and the removal of ammonia can be ascribed to the oxidation reaction.

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