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Fenton oxidation treatment of tannery wastewater and tanning agents: synthetic tannin and nonylphenol ethoxylate based degreasing agent

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ABSTRACT

In the present experimental work, the degradation and detoxification of two commercially important products being widely used in the tannery industry as synthetic tannin (ST) and degreasing agent (EP) containing 0.1% of nonylphenol ethoxylate (NPE) as well as degreasing wastewater from re-tanning was investigated using Fenton (FO) and Photo-Fenton (PFC) oxidation processes. FO and PFC oxidation experiments were performed in batch reactors for 30 min at pH 3 ± 0.2 and 40–45 °C, considering the actual temperature and pH values of re-tanning bath effluents. For the FO experiments the effect of varying Fe^{2+} and H_2O_2 concentrations and UV-C light irradiation on oxidation measured by the parameters COD, UV_{254} and UV_{280} absorbancies was studied. Toxicity of untreated and FO, PFC-treated synthetic solutions to the freshwater cladoceran *Daphnia magna* was also tested. PFC provided appreciably high COD (>80%) and UV_{254} and UV_{280} (>90%) removals for ST. The toxicity could be drastically reduced in the PFC-treated ST samples. A maximum COD removal of 57% for FO and 77% for PFC was obtained for EP samples. However, the FO process resulted in 90% toxicity even after 30 min of oxidation, while the effluent of PFC exhibited 10% of immobilization to *D. magna*. FO carried out on degreasing wastewater allowed resulted in 72% COD removal as well as 86% and 77% of UV_{254} and UV_{280} removals, respectively.

Keywords: Advanced oxidation processes; Fenton's and photo-fenton oxidation; Leather tannery wastewater; Synthetic tannin; Nonylphenol ethoxylate; *Daphnia magna*

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1. Introduction

Typically, as shown in Fig. 1, re-tanning bath procedure is composed by four phases: degreasing, chrome re-tanning, neutralization and re-tanning. More then 3 thousand chemicals are used in leather tanning processes, most of them are organic compounds which can be classified as priority and persistent substances [1–5]. However, there are few studies related with the toxic impact of chemicals released by leather tannery industry [6–7]. They are not completely fixed by skins and remain partially (up to 50%) in the effluent, therefore, the effluent from re-tanning phase contains high amounts of xenobiotic compounds such as cresol based synthetic tannins (STs) representing a class of phenolic compounds classified by U.S. EPA [7] as persistent, priority and toxic pollutants and found to accumulate in fish or meat [8]. Besides, nonylphenol ethoxylates (NPEs) based degreasing agents (EP) used for preparing the leather to the successive operations yields a high COD equivalent to be considered for the priority pollution source. Nonylphenol is a hydrophobic compound consisting of

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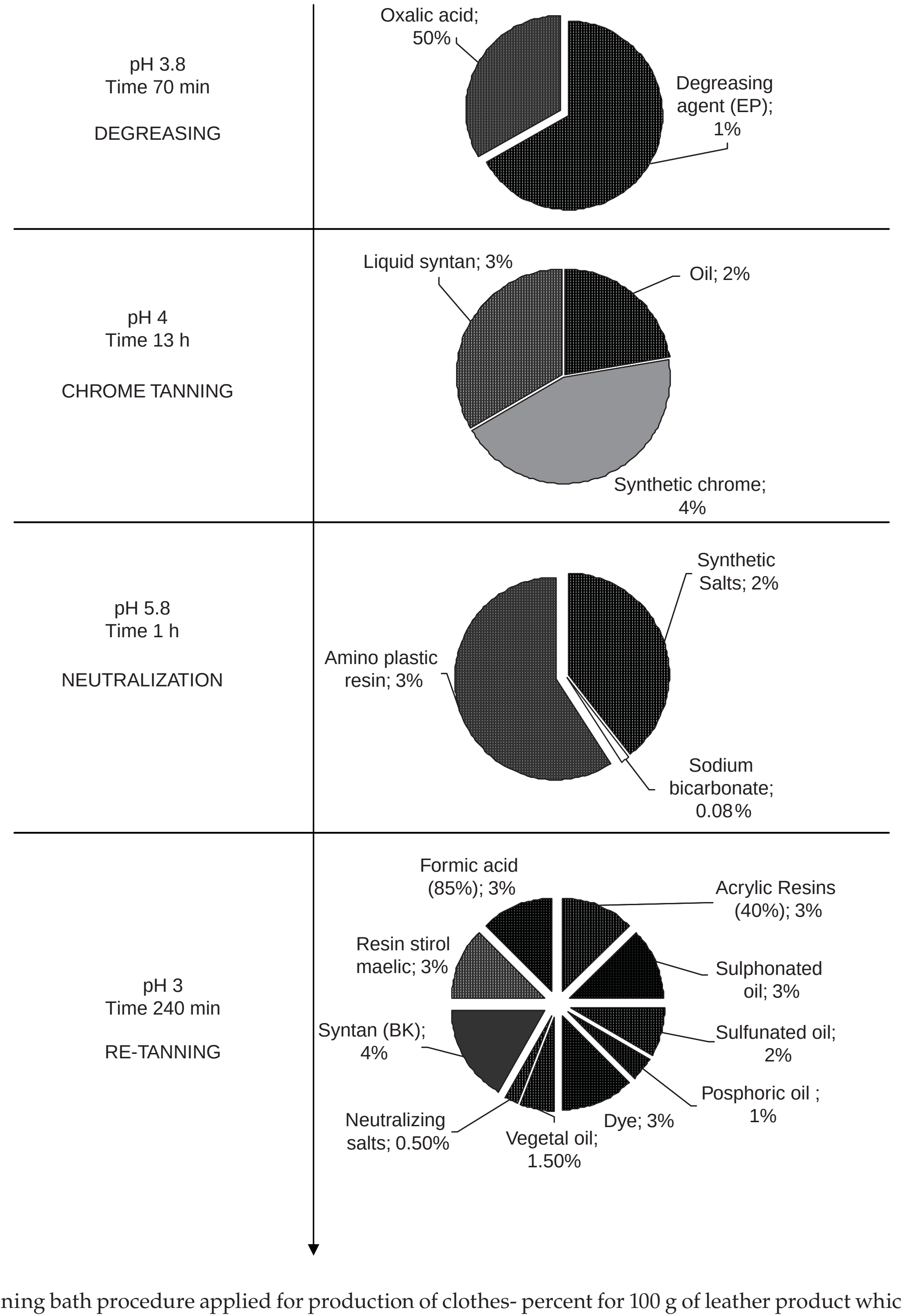

Fig. 1. A re-tanning bath procedure applied for production of clothes- percent for 100 g of leather product which is proceeded in the tumbler (6 l of water is used for production of 1–2 kg raw prepickled leather (600% of water for 100% of leather).

a phenol ring and a nine-carbon branched chain on the para-position, with a log K_{ow} value of 4.48 and low solubility in water [9]. While there are just few applications of the nonylphenols themselves, nonylphenol ethoxylates, which are the main source of nonylphenol to the environment, are used as industrial surfactant formulations in metal, textile and leather processing [10].

Although the biological treatment processes are at present the cheapest and the most environmental friendly, their potential for removal non-biodegradable

COD and micro-pollutants is limited [5,11,12]. Therefore there is an increasing need to focus on new treatment technologies. Advanced oxidation processes (AOPs) are promising methods for wastewater decontamination. AOPs are based on the generation of highly reactive hydroxyl radicals (HO•) which are powerful oxidants (E = 2.8 V) that are able to mineralize quickly and unselectively a broad range of organic compounds [13–15]. They have been successfully applied on tannery effluent [16–19] as well as synthetic and natural tanning materials [7,20,21]. Among them, the Fenton (Fe^{2+}/H_2O_2) and Photo-Fenton ($Fe^{2+}/H_2O_2/UV$) processes are very promising since they achieve high reaction yields with a relatively low treatment cost.

Fenton's oxidation (FO) is achieved by the catalytic decomposition of H_2O_2 with ferric (Fe^{3+}) and ferrous (Fe^{2+}) iron in acidic aqueous solutions which are among the most common homogeneous advanced oxidation systems and potential sources of HO generation. The $Fe^{2+}/Fe^{3+}/H_2O_2$ system has its maximum catalytic activity at pH = 2.8 –3.0. As such, an increase or decrease in the pH sharply reduces the catalytic activity of iron. At elevated pH (>5), the ferric ion precipitates as ferric hydroxide and at lower pH, the complexation of Fe^{3+} with H_2O_2 is inhibited [15].

UV light radiation can improve the Fenton's reaction. The reasons for the positive effect of UV light on the degradation rate include the photolysis of Fe^{3+} that leading to the production of HO• and Fe^{2+}. Moreover, •OH are also produced via direct H_2O_2/UV-C photolysis (slow reaction) and the reaction of H_2O_2 with Fe^{2+} produced by photoreduction of Fe^{3+} according to the following reaction:

$$Fe^{3+} + h\cdot + H_2O \cdot Fe^{2+} + \bullet OH + H^+ \qquad (1)$$

As indicated in our previous study the optimum ratio of H_2O_2/ $FeSO_4$ concentrations (resulting in 80–90% of COD removal) were determined as 600/500 (w/w) at pH 3.0, 40–45 °C and 30 rpm mixing for 30 min for STs while 600/750 (w/w) ratio of $H_2O_2/FeSO_4$ resulted in the highest COD removal under the same oxidation conditions for oils used in the tannery industry [21]. However, when AOPs are applied on tannery wastewater some problems occur due to: (i) the presence of free radical scavenger compounds which can reduce the kinetics of advanced oxidation reactions to uneconomical values, (ii) the oxidation of trivalent chromium to hexavalent chromium is well known to be more toxic than the previous one [22]. For both reasons, AOPs should be applied more properly to segregated effluents containing high amount of aromatic compounds.

This study aims to evaluate Fenton (FO) and Photo Fenton (PFC) oxidation processes for the pre-treatment of two re-tanning agents (as cresol-based synthetic tannin, ST and nonylphenol ethoxylates (NPEs) based degreasing agent, EP) which are added in the first (degreasing) and fourth (re-tanning) phases of the re-tanning bath procedure (Fig. 1). In the second phase, the effluent of the first phase (degreasing) of retanning bath was introduced to Fenton oxidation process. The low pH, relatively high temperature (43–45°C) and the high presence of aromatic compounds are attractive to use FO processes in these kind of streams. The optimum process conditions were comparatively evaluated in terms of COD and absorbance (UV_{254}, UV_{280}) removal. The UV absorbance is to measure in particular, double bonds and aromaticity which can be characterized by UV_{254} and UV_{280} respectively. For that purpose of the presence of aromatic structured organic compounds in leather tanning wastewater such as syntans and degreasing agents UV_{254} and UV_{280} were used in this study. The toxicity of untreated and treated samples to *D. magna* which is one of the main species to monitor discharges in Italy was evaluated [23].

2. Materials and methods

2.1. Chemicals

Ferrous sulphate hepta-hydrate ($FeSO_4{\cdot}7H_2O$) used as source of Fe^{2+} was of analytical grade and purchased from Merck. H_2O_2 solution (30% w/w) in stable form was provided from Carlo Erba. MilliQ ultrapure deionised water was used through the experiments.

2.2. Samples

2.2.1. Synthetic solutions

By considering the COD contribution of syntan (ST) and degreasing agents (EP) to re-tanning bath effluent as reported in our previous studies [4,21,24], a range of 100 mg/l–350 mg/l of COD equivalent was prepared for both chemicals investigated.

2.2.2. Degreasing wastewater (DGW)

A-8 h composite sample was taken from a tumbler in degreasing phase where the skins react with the degreasing agent (EP) investigated and oxalic acid in aqueous solutions as shown in Fig. 1.

2.3. Experimental

FO experiments were performed in batch reactors using different $H_2O_2/FeSO_4$ w/w ratios of 600/750, 600/600, 600/500, 150/500 w/w for EP and 600/750, 600/1000, 1200/750 w/w for DGW by mixing the reactors for 30 min at pH 3 ± 0.2 and 40–45°C considering the actual temperature of re-tanning bath effluent and treatment conditions according to our previous study [21]. Following the mixing step, the samples were left to settle for 30 min, then the supernatants were drawn from each one beaker and pH was readjusted to over 9 using 2 N NaOH to avoid further oxidation (to cease the reaction). Besides these samples were heated for 30 min at 40–45°C [25]. After that, the samples were left to settle for further 30 min. If the colour of the supernatant was not transparent another pH adjustment was done with 0.01 N H_2SO_4 to decrease pH below to 8 in order to achieve the maximum amount of $Fe(OH)_3$ precipitation. Than, the samples were filtered through 0.45 µm cut-off Millipore filters before submitting to the analyses.

PFC experiments were carried out in a manufactured, stirred, cylindrical photoreactor as described in Lofrano et al. [24], using following $H_2O_2/FeSO_4$ ratio of 150/500 w/w for 100 mg/l and 300 mg/l of ST and 350 mg/l of EP; 150/400 for 100 mg/l of ST. All experiments were run at 40–45 °C and pH 3 by mixing the reactors for 30 min under irradiation by 16 W low-pressure mercury vapour lamp emitting UV-C light in the wavelength range of 100–280 nm with a broad maximum light emission at 254 nm (Novus, Italy).

Potassium ferrioxalate actinometry was performed to measure the light intensity in the reaction medium as described in literature [27]. The incident light flux of the lamp was found as $5{,}515\cdot10^{-9}$ einstein per seconds (1 l volume reactor).

Control tests (H_2O_2 only, UV-C only) were carried for both oxidation processes too.

2.4. Chemical analysis

COD was measured according to Standard Methods [26]. Absorbance values at 254 and 280 nm were determined by UV spectrophotometry (Perkin Elmer, Lambda 12 model), using 1 cm quartz cuvettes.

2.5. Toxicity assessment

The toxicity of untreated and treated solutions was measured using 24 h new born *D. magna* at different dilutions according to Standard Methods [25,28]. Test animals were grown by a 16 h light (with 1000 lx), 8 h dark cycle. They were regularly fed with the algae *Selenastrum capricornutum* (300,000 cells/ml) and *Schizosaccharomyces cerevisiae* (200,000 cells/ml). Toxicity tests were performed quadruplicate using 5 daphnids in each test beaker with 100 ml effective volume. The results were expressed as a percentage of immobilised animals after 24 h exposure.

3. Results and discussion

3.1. Control experiments

As first step the influence of direct UV-C photolysis was evaluated. After 30 min of treatment no degradation was observed for both compounds as well as for the degreasing wastewater. Direct UV-C photolysis is therefore not recommended for the treatment of chemicals and wastewater investigated. For all H_2O_2 concentrations, blank experiments were performed in parallel (in the absence of light and catalyst). In this study no degradation of ST and EP was observed as well as for degreasing wastewater. On the contrary in some cases the COD removal was negatively affected by the progressive increase of H_2O_2 (data not shown) which causes excessive consumption of $K_2Cr_2O_7$ leading to an increase of inorganic COD [29].

3.2. Synthetic solutions

The physicochemical characteristics of the investigated compounds are reported in Table 1. The raw ST solutions with 100 and 300 mg/l COD equivalent resulted in 80% and 100% immobilization of *D. magna*, respectively [21]. A 350 mg/l COD equivalent of EP solution resulted in 100% of immobilization of *D. magna*.

In order to decrease the amount of catalyst and oxidant concentrations used during FO of various STs as reported in our previous studies [21,24], PFC oxidation was performed as priority because our previous findings on similar synthetic tannin indicated that the Photo-Fenton process (add with UV_C light) is more suitable

Table 1
Chemical characteristics of synthetic tannin and degreasing agent investigated

Tanning agents	Colour	pH	Density 20 °C [kg/m^3]	Solubility 20 °C [g/l]	COD equivalent g:g	BOD/COD	UV$_{254}$ [cm^{-1}]	UV$_{280}$ [cm^{-1}]
Syntan (ST)	White	5.5–6	700	100	1	0.098	1.32	1.48
Degreasing agent (EP)	White	6.5	–	–	1.2	0.075	0.467#	0.256#

Ten times diluted.

than Photo-Fenton in the presence of UV-A light to be applied for removing STs [24]. UV-C has been recently used for the photocatalytic degradation of Orange II in a ferrioxalate-assisted photo-Fenton process [30] as well as for the oxidation of organic fluorinated organic compounds [31].

According to Fig. 2a, a 82% of COD removal for 100 mg/l of ST solution was achieved by PFC oxidation using 150/500 (w/w) of $H_2O_2/FeSO_4$ after 5 min. The COD removal reached 85% after 30 min of oxidation. While the UV_{280} removal increased gradually from 89% to 96% after 5 and 30 min of oxidation. In parallel to COD and UV_{280} removal, the toxicity to *D. magna* was drastically reduced as seen in Fig. 2a. The reduction in immobilization of *D. magna* was recorded as 88% after 5 min and 100% after 15 min of oxidation. It was noticeable that no toxicity increase was observed due to any toxic intermediate formation after 15 min of oxidation (100% of toxicity reduction after 30 min). When the ratio 150/400 w/w of $H_2O_2/FeSO_4$ was applied to 100 mg/l of ST a maximum COD removal of 75% could be achieved after 30 min (Fig. 2b).

The PFC oxidation was also performed for 300 mg/l of ST using a ratio of 150/500 w/w $H_2O_2/ FeSO_4$ which resulted in a maximum 70% of COD removal during 30 min (Fig. 3). No toxicity of the treated solutions tested at 50% dilution, due to their higher initial COD contents, was observed starting from 15 min of oxidation.

As displayed in Fig. 4a, both FO and PFC oxidation were applied to 350 mg/l of EP using the ratio of

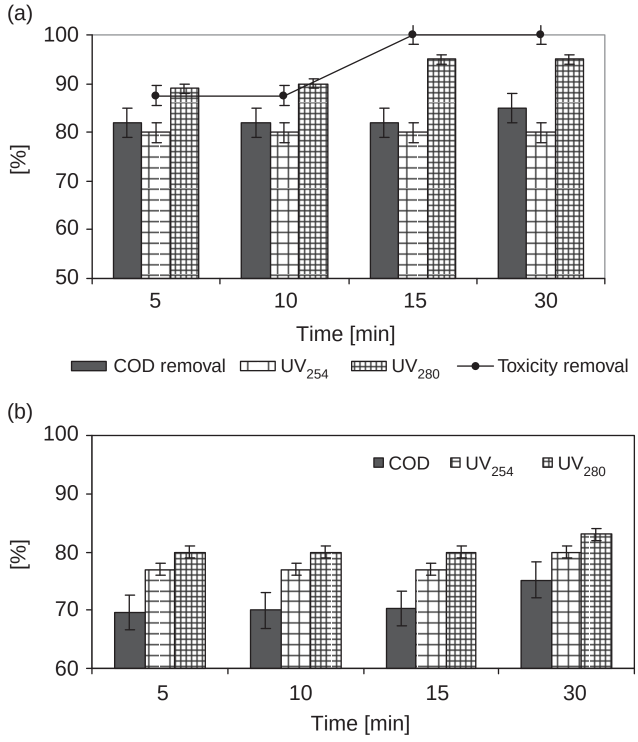

Fig. 2. (a) Immobilization of *D. magna* , COD and UV removal for 100 mg/l of synthetic tannin (ST) solution by Photo-Fenton process (UVC) using 150/500 (w/w) of $H_2O_2/FeSO_4$ at 30 rpm, 3.0 pH, 45°C, 30 min; (b) COD and UV removal for 100 mg/l of ST solution by PFC using 150/400 (w/w) of $H_2O_2/FeSO_4$ at 30 rpm, 3.0 pH, 45 °C, 30 min.

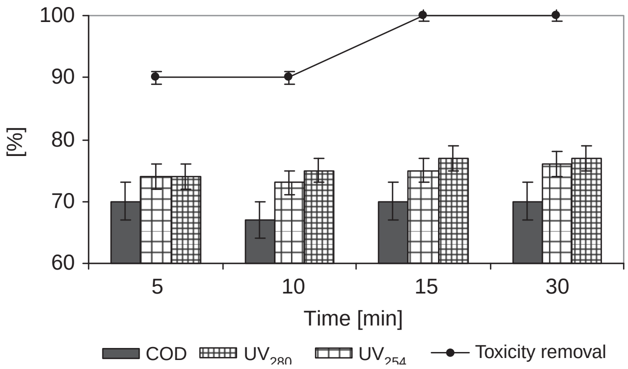

Fig. 3. Immobilization of *D. magna* and COD removal for 300 mg/l ST solution by Photo-Fenton process using 150/500 (w/w) of $H_2O_2/FeSO_4$ at 30 rpm, 3.0 pH, 45 °C, 30 min (Fenton process did not function at this ratio, data not shown).

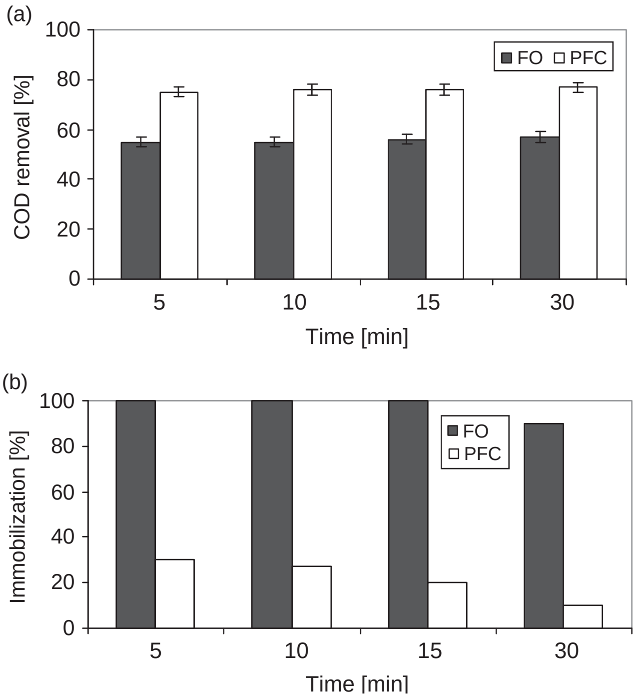

Fig. 4. (a) COD removal for 350 mg/l of of nonylphenol ethoxylate based degreasing agent (EP) solution treated by Fenton and Photo-Fenton processes using 150/500 ratio of $H_2O_2/FeSO_4$ at 30 rpm, 3.0 pH, 45 °C, 30 min; (b) Immobilization of *D. magna* for 350 mg/l EP solution treated by Fenton and Photo-Fenton processes using 150/500 ratio of $H_2O_2/FeSO_4$ at 30 rpm, 3.0 pH and 45 °C, 30 min.

150/500 w/w $H_2O_2/FeSO_4$. Although the COD removal was improved by applying PFC; a maximum range of COD removal 57% for FO and 77% for PFC treatments could be obtained after 30 min with respect to the EP oxidation. In fact, as seen in Fig. 4b, the FO-treated sample resulted in 90% toxicity to *D. magna* even after 30 min of oxidation while the effluent of PFC treated EP solution displayed the toxicity reduced to 10% of immobilization after 30 min.

As it can be observed in Fig. 5a, the FO process proved a range of 68%, 48% and 51% for COD, UV_{280} and UV_{254} removals respectively for EP (COD 350 mg/l) at the ratio of 600/750 $H_2O_2/FeSO_4$ w/w after 30 min. When the concentration of $FeSO_4$ was reduced to 500 mg/l the efficiency of the process slightly decreased to 50%, 40% and 43% for COD, UV_{280} and UV_{254}. This trend was exactly on the contrary of ST as can be seen by comparing these results with our previous findings (Fig. 5b).

3.3. Degreasing wastewater

The initial COD of degreasing wastewater was 6300 mg/l, its pH was 3.5 and temperature around 40–45°C. As described above, a series of FO experiments were carried out at relatively higher ratios of $H_2O_2/FeSO_4$ as 600/750, 600/1000, 1200/750 w/w due to fact of initial high COD. Among these ratios applied, that one of 600/1000 $H_2O_2/FeSO_4$ resulted in the maximum COD (72%), UV_{254} and UV_{280} (86% and 77%, respectively) removals (Fig. 6a).

As shown in Fig. 6b, the toxicity of treated DGW samples was not removed as they were tested without dilution or after 50% v/v dilution. When the treated DGW samples were tested at further dilutions (75% and 87.5%) the apparent reduction in toxicity was obtained at the optimum $H_2O_2/FeSO_4$ (600/1000) ratio which provided the highest COD and UV absorbance removals.

As a comparison, when FO treatment was applied to DGW and EP samples using the ratio of 600/750 w/w $H_2O_2/FeSO_4$, a reduction in COD removal (47%) was observed in DGW, due to the high concentration of free radical scavengers such as chlorides and chromium (III) derived from hides and skin [12,22]. However, these results are not easily to be comparable with the

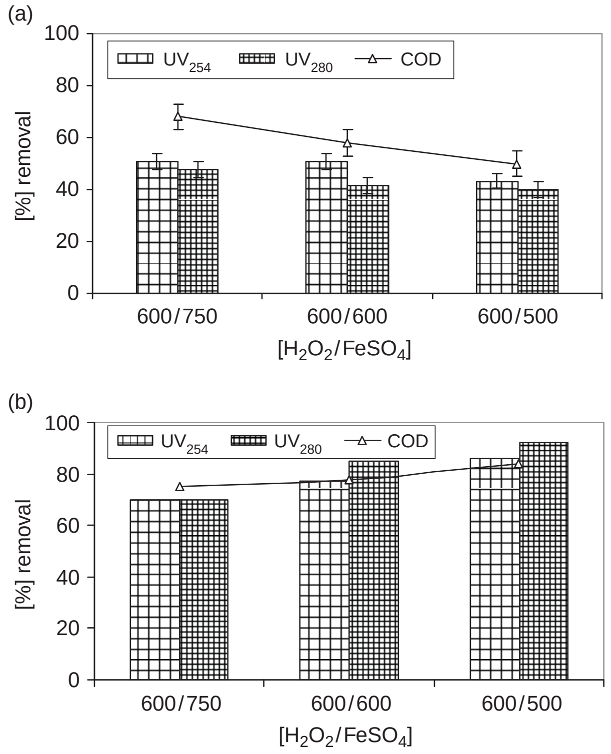

Fig. 5. (a) COD (initial value 350 mg/l) and UV (UV_{254} 0.467; UV_{280} 0.256 1/cm) removal for EP using 600/750, 600/600 and 600/500 w/w ratios of $H_2O_2/FeSO_4$ at 30 rpm, pH 3.0, 45 °C, 30 min. (b) COD (initial value 350 mg/l) and UV removal for ST using 600/750, 600/600 and 600/500 w/w ratios of $H_2O_2/FeSO_4$ at 30 rpm, pH 3.0, 45 °C, 30 min [21].

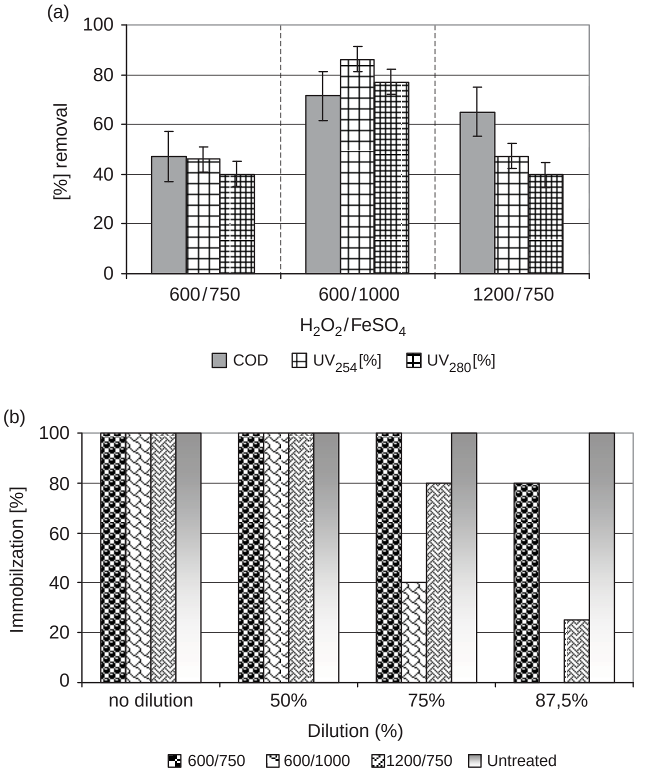

Fig. 6. (a) COD (initial value 6300 mg/l) and UV (UV_{254} 2.44; UV_{280} 1.52 1/cm ten times diluted) removal for degreasing wastewater (shown in Fig. 1) using 600/750, 600/1000 and 1200/750 w/w ratios of $H_2O_2/FeSO_4$ at 30 rpm, pH 3.0, 45 °C, 30 min; (b) Immobilization of *D. magna* for degreasing wastewater treated by FO.

related scientific literature which were performed at the different experimental conditions (reagent dosages, reaction time and COD values) to carry out the AOPs to leather tanning wastewater. Schrank et al. [18] evaluated the applicability of FO in the treatment of coagulated tannery wastewater having an initial COD of 130 mg/l, which was very low compared to the initial COD value of wastewater used in this study. They run the experiments for 2 h at varying $FeSO_4$ $7H_2O$ (in the range 50–240 mg/l) and H_2O_2 (in the range 100–500 mg/l) doses. Optimum results were achieved at the H_2O_2/Fe^{2+} ratio of 500/100 w/w which provided 80% of COD removal. In a recent study Kurt et al. [19] reported that a 70% of COD removal was obtained using electro-Fenton process during 10 min at pH 3 to oxidize wastewater collected from the equalization tank of the Organized Tannery District in Istanbul, Turkey. Accordingly they obtained an effluent complying with the Discharge Limit set by the Water and Sewerage Administration of Istanbul (800 mg/l). However, the initial COD value of 2810 mg/l. The same authors [19] underlined that COD reduction changed from 41% to 99% based on different variables such as wastewater type, electrical energy consumption, reaction time, etc.

According to all data obtained within this and our previous studies [24] a general treatment schedule as shown in Fig. 7 could be proposed to integrate a Fenton/Photo-Fenton (Solar-driven) process to treat re-tanning bath effluents to operate sewage treatment works at higher efficiency. For highly polluted wastewaters pretreatment is required prior to the application of AOPs. In a treatment scheme, AOPs should follow other primary physicochemical treatment processes (coagulation, filtration, etc.) to remove colloids, suspended solids, inorganics, etc.

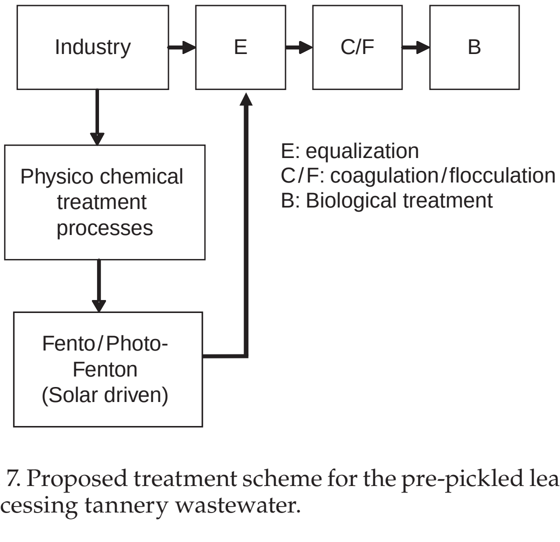

Fig. 7. Proposed treatment scheme for the pre-pickled leather processing tannery wastewater.

5. Conclusion

This study evaluated the removal of a synthetic tannin cresol based (ST) and a degreasing agent containing nonylphenol ethoxylate (EP) which are commonly present in tanning bath effluents by Fenton (FO) and Photo-Fenton C (PFC) processes. FO experiments were carried out on degreasing wastewater to evaluate the treatment of segregated effluents. The maximum removal of COD (83% and 77% for ST and NPE respectively) was obtained by using PFC treatment at ratio 150/500 (w/w) of $H_2O_2/FeSO_4$. The organic matter was significantly reduced in degreasing wastewater: 72% COD removal and 86% and 77% of UV_{254} and UV_{280} removals, respectively, were achieved by using FO at a ratio mass ratio of 600/1000. At optimized study conditions a reduction of toxicity to *D. magna* could be achieved.

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