Fenton and photo-Fenton treatment of a synthetic tannin used in leather tannery: a multi-approach study

G. Lofrano*, S. Meric*, V. Belgiorno*, A. Nikolaou** and R.M.A. Napoli***

*University of Salerno, Sanitary and Environmental Engineering Division (SEED), Department of Civil Engineering, via Ponte don Melillo, 1, 84084 Fisciano (SA), Italy (E-mail: glofrano@unisa.it; msureyya@unisa.it; v.belgiorno@unisa.it)

**University of the Aegean, Faculty of the Environment, Department of Marine Sciences, University Hill, 81100, Mytilene, Greece (E-mail: nnikol@aegean.gr)

***University of Parthenope, Faculty of Engineering, Naples, Italy (E-mail: university@rodolfonapoli.it)

Abstract
The aim of this work was to compare the behaviour of Fenton and photo-Fenton (UV-A, UV-C) processes to treat synthetic tannin (syntan) used in leather tannery which is one of the most polluting industries, releasing many xenobiotics. Both oxidation processes were performed at pH 3.0 and temperature 40–45°C, which is the original temperature of the re-tanning process, in synthetic solutions containing 100 and 300 mg/L of COD equivalent of syntan. The efficiency of the applied oxidation processes was monitored by chemical oxygen demand (COD), oxidation redox potential (ORP) and aromaticity (UV280) and double bond (UV 254) absorbance measurements. Acute toxicity test on Daphnia magna was performed to monitor toxicity in untreated and treated syntan solution. Gas chromatography–mass spectrometry (GC-MS) was applied to identify by-products of partial oxidation occurring in treated samples. The effective ratio of H2O2/FeSO4 for photo-Fenton processes was found to be feasible in terms of reagents used in the process.

Keywords
Acute toxicity; Fenton and photo-Fenton oxidation; gas chromatography-mass spectrometry (GC-MS); leather tanning industry; synthetic tannin; xenobiotics

Introduction
The leather industry is considered to be one of the major pollutant sources with its waste streams containing high organic content and salinity as well as many xenobiotic compounds such as biocides, synthetic tannins, metals (Kabdasli et al., 1993, Jochimsen and Jekel, 1997). Therefore, there have been numerous studies on toxicity evaluation of the leather tannery industry (Cotman et al., 2004; Meric et al., 2005a; Lofrano et al., 2006). Many toxic organic compounds were also recorded in raw and oxidised leather tannery wastewater (Schrank et al., 2005). Many natural phenols (vegetable tannins) or their condensation products such as synthetic tannins (Syntan, ST) which are used in the re-tanning process in chromium tannery industry, have been recognised as a concern of global interest because they are present in the waste stream of several agro-industries (Gernjak et al., 2003; De Nicola et al., 2007). Conventional treatments are not enough to remove xenobiotic compounds from the effluents of many industrial plants. Due to inhibition property of STs on bacteriological populations, in particular nitrifiers (Jochimsen and Jekel, 1997), alternative treatment methods such as ozone oxidation (Jochimsen and Jekel, 1997), photocatalysis (Schrank et al., 2004) and Fenton oxidation (Lofrano et al., 2007) have been investigated to avoid their exposure to humans and the environment. Cresol, which represents a class of chemical phenolic compounds and is classified by USEPA as a persistent, priority and toxic pollutant and found to accumulate in fish or meat (ATSDR, 1995), was individually removed by Fenton oxidation
process (Kavitha and Palanivelu, 2005). Lofrano et al. (2007) optimised the Fenton process for four origins of STs (cresol-based, poly-condensed formaldehyde and disulphane with sulphonic aromatic acids, phenol-based, condensed phenol-based) and >85% of COD removal was obtained for each type. Six model phenolic compounds (vanillin, protocatechuic acid, syringic acid, p-coumaric acid, gallic acid and L-tyrosine were successfully oxidised by the photo-Fenton process (Gernjak et al., 2003).

The Fenton oxidation process is an advanced oxidation technology in which iron (II) reacts with hydrogen peroxide to form hydroxyl radicals able to oxide a wide range of organic compounds. The Fenton oxidation process has been performed for treatment of various xenobiotics containing wastewater such as dye wastewater (Liu et al., 2007), pharmaceutical wastewater (Alaton-Arslan and Gurses, 2004), olive oil wastewater (Ahmadi et al., 2005) and tannery wastewater (Schrank et al., 2004). The key features of the Fenton system are believed to be its reagent conditions, such as [Fe²⁺], [Fe³⁺], [H₂O₂] and the reaction characteristics (pH, temperature and the quantity of organic and inorganic constituents) (Neyens and Baeyens, 2003). When hydrogen peroxide is irradiated with UV light at visible wavelengths lower than 400 nm (UV-A, UV-C), the degradation rate of pollutants can be increased (Kusic et al., 2006). The photo-Fenton process has been reported to be a very promising technique to treat leather tanning wastewater (Schrank et al., 2005). Both processes should be effectively optimised also in regard to the toxicity of the intermediate products (Meric et al., 2005b).

The present study aimed to comparatively assess the treatability of a widely used cresol-based ST used in soft open leather production before dying leather by Fenton and photo-Fenton processes. Gas chromatography-mass spectrometry (GC-MS) was applied to determine by-products of partial/complete oxidation of the ST by each treatment processes. The toxicity of raw and treated ST was monitored by Daphnia magna as a standard and reliable test (Meric et al., 2005b) to obtain immobilisation end-point.

Methods
Solutions
The colour of the syntan was white, pH between 5.5 and 6, density at 20°C: 700 kg/m³, solubility at 20°C: 100 g/L, COD equivalent was measured 1 g/g, the ratio BOD₅/COD: 0.098, UV₂₅₄: 1.32 L/cm UV₂₈₀: 1.48 L/cm. Synthetic tannin (BK) solutions containing 100 and 300 mg/L of COD equivalent were prepared for optimising Fenton and photo-Fenton processes. These concentrations were estimated according to a re-tanning bath procedure as previously explained elsewhere (Lofrano et al., 2007).

Treatment procedures
Fenton (FK) and photo-Fenton (PFKC/A) experiments were performed in batch reactors during 30 minutes of oxidation at pH 3 ± 0.2 and 40–45°C, considering the actual temperature of re-tanning bath effluent according to our previous study (Lofrano et al., 2007). Different doses of FeSO₄ and H₂O₂, varying from 150 to 750 mg/L and from 300 to 600 mg/L, respectively, were used to optimise the processes.

PFKC (H₂O₂/FeSO₄/UVC) experiments were performed in a manufactured, stirred, cylindrical photoreactor with a total volume of 2.0 L (Figure 1a). The reactor was made of glass and was covered with an aluminium sheet during functioning. At the top, the reactor was equipped with inlets for feeding reactants and ports for measuring temperature and withdrawing samples. The UV irradiation source was a 16 W low-pressure mercury vapour lamp (UV emission 5.3 W/55.2 μW/cm² per metre, Novus, Italy) encased in a quartz tube. The UV-C lamp was axially centred and immersed in the solution.
The PFKA (H₂O₂/FeSO₄/UVA) process was performed with a 125 W black light fluorescent lamp (BLF). The photo-Fenton A process was identical to the system used for photocatalytic treatment of humic acids and drinking water samples in a previous study by Bekbolet et al. (2005). As control experiments, each UV lamp was tested alone on the BK solutions.

Analysis
The efficiency of each treatment schedule was subjected to multi-parameter evaluation. As measurement of double bonds and aromaticity, absorbances at 254 and 280 nm, respectively, were determined by UV spectrophotometer (Perkin Elmer, Lambda 12 Model), using a 1 cm quartz tube. COD analyses were performed according to Standard Methods (1998). The redox potential (ORP) was monitored during oxidation (Hanna Instruments, Model 8314). All chemicals used were of analytical reagent grade (Carlo Erba, Italy). H₂O₂ solution (30%) was of medical extra pure grade (Merck). Ultra-pure was prepared by a Milli-Q system (Millipore, Milford, MA, USA) to be used in synthetic solutions. Residual H₂O₂ was measured before and after pH adjustment of the supernatants using CHEMets Kit as explained in Lofrano et al. (2007). Because the pH of the supernatants was adjusted over 7.5 immediately, no additional chemical was used to destroy any residual H₂O₂ in the solution.

The determination of the organic by-products was performed by liquid-liquid extraction gas chromatography-mass spectrometry (LLE-GC-MS), using a Hewlett Packard 5890 Series II gas chromatograph connected to a Hewlett Packard HP5971 MSD, supported from the HP G1034C software (Nikolaou et al., 2005). The column used for the chromatographic separation of the compounds was 30 m × 0.32 mm i.d. × 0.25 μm i.d. fused silica capillary DB-5MS. Helium (ECD) was used as the carrier gas and the injection technique was split/splitless operated in SCAN mode. The oven temperature programme was 50°C for 4 min, 20°C/min to 170°C, 8°C/min to 270°C. The carrier gas flow was 0.9 mL/min and the injector temperature 280°C. The sample preparation procedure included addition of sodium sulphate (Merck) (5 g) in 50 mL of sample, liquid-liquid extraction for 5 minutes initially with dichloromethane (Merck, for organic trace analysis) (20 mL) and afterwards with n-pentane (Merck, for organic trace analysis) (20 mL). The extracts were combined and, after addition of sodium sulphate (5 g) for drying, were evaporated to dryness in a water bath at 50°C. The analytes were reconstituted with 1 mL of dichloromethane. One microlitre of the final extract was injected into the GC (Nikolaou et al., 2002).
**Daphnia magna** acute toxicity

The toxicity of untreated and treated ST solutions was measured using 24 hour-old *D. magna* at different dilutions according to standard methods (ISO, 1996; Merić et al., 2005b). Toxicity tests were performed in quadruplicate using five daphnids in each test beaker with 100 mL effective volume. The results were expressed as a percentage of immobilised animals after 24 hours.

**Results and discussion**

The aromatic structure of ST studied in this work (BK) was effectively destroyed at 600/500 (mg/mg) ratio of H$_2$O$_2$/FeSO$_4$ at 3.0 pH and 45 $^\circ$C after 15 minutes of oxidation as seen in Figure 2. As continuation of the previous work, here the ratio between [H$_2$O$_2$] and [Fe$^{2+}$] was varied to optimise photo-Fenton processes (PFKA, PFKC). With the aim to decrease the amount of H$_2$O$_2$, FeSO$_4$ concentration (500 mg/L) was kept constant while the concentration of H$_2$O$_2$ was varied from 500 to 300 mg/L. However, no evident reactions occurred at those amounts of H$_2$O$_2$.

During the next step, experiments to reduce reagents needed at the reactions, 300/750 (mg/mg) of [H$_2$O$_2$]/[FeSO$_4$] ratio increased degradation of ST and mineralisation efficiency was observed as shown in Figure 3.

Although it was reported that UV radiation itself has the ability to destroy organic molecules (Schrank et al., 2005), no effect of it alone was observed during experiments. Because the efficiency of photolysis of some organics was proved depending on their reactivity and photosensitivity (Kusic et al., 2006), we can suppose that the organic structure of ST is not able to be destroyed by UV alone.

As seen in Figure 3, after 15 minutes of oxidation by FK, PFKA and PFKC the COD removal efficiency of the initial 300 mg/L equivalent of BK (ST) was 62, 78 and 76%, respectively. However, after the first 5 minutes of oxidation, the maximum COD removal was obtained using PFKC (82%). As shown in Figure 1, the decreasing COD removal efficiency vs. time can be attributed to the competition of high amounts of Fe$^{2+}$ in the solution with the organics for consuming hydroxyl radicals (Benitez et al., 2001), according to the following reaction.

Fe$^{2+}$ + OH$^-$ → OH$^-$ + Fe$^{3+}$

![Figure 2](https://iwaponline.com/wst/article-pdf/55/10/53/439131/53.pdf)

**Figure 2** Time interval removal for 300 mg/L of BK using 600/500 (mg/mg) of H$_2$O$_2$/FeSO$_4$ at 3.0 pH and 45 $^\circ$C (Lofrano et al., 2007)
Although high COD removal was improved by oxidation for 300 mg/L of BK, the GC-MS spectral analyses of treated solutions displayed a number of intermediates still remaining after 30 minutes of oxidation (Table 1). Few studies have been performed to identify the by-products of AOPs using GC-MS such as photocatalysis (Schrank et al., 2004) and Fenton oxidation (Schrank et al., 2005) processes applied on pre-coagulated leather tannery wastewater. Moreover, Arana et al. (2001) reported catechol and hydroquinone were the dominant by-products in the phenol solutions treated by photo-Fenton process. Hence, the results shown in this study have the bonus of being the first findings in this field. However, further considerations such as chemicals used in the extraction procedure or combining GC-MS with further MS or LC-MS steps should be the next stage of this study for identifying the species accordingly.

As indicated in Figure 4, it was possible to quantify a significant amount of some by-products of 300 mg/L BK-treated solution after 5 minutes of oxidation with PFKC (4a) and PFKA (4b), respectively. A higher frequency of 1,3,5-trimethyl-2-octadecyl-benzene, ethyl benzaldehyde, bis-(2-ethylhexyl) phthalate by-products were found in the effluent of PFKA. Compared to the result obtained on the 300 mg/L solution, this result confirms that the H2O2 requirement seems to be related mainly to initial COD of the sample.

Table 1 GC-MS spectra of Fenton and photo-Fenton (A/C) treated BK solution after 30 minutes of oxidation (> 90 recovery percentile) using 600/500 (mg/mg) of H2O2/FeSO4 at 3.0 pH and 45°C

<table>
<thead>
<tr>
<th>Ions</th>
<th>Identification (&gt; 90% hits in the GC-MS library)</th>
</tr>
</thead>
<tbody>
<tr>
<td>133,147</td>
<td>1,3,5-trimethyl-2-octadecyl-benzene</td>
</tr>
<tr>
<td>183, 198, 128, 153, 168, 141</td>
<td>1,4-dimethyl-7-(1-methylethyl)- azulene</td>
</tr>
<tr>
<td>149, 167</td>
<td>bis-(2-ethylhexyl) phthalate</td>
</tr>
<tr>
<td>133, 119</td>
<td>ethyl benzaldehyde</td>
</tr>
<tr>
<td>94, 95, 66, 65, 55, 39</td>
<td>phenol</td>
</tr>
<tr>
<td>121, 136, 93, 65, 39</td>
<td>4-hydroxyacetophenone</td>
</tr>
<tr>
<td>110, 81, 55, 53, 39, 27</td>
<td>hydroquinone</td>
</tr>
<tr>
<td>108, 84, 80, 82, 26</td>
<td>p-benzoquinone</td>
</tr>
<tr>
<td>60, 73, 41, 29</td>
<td>pentanoic acid</td>
</tr>
<tr>
<td>74, 57, 55, 45, 28, 29, 27</td>
<td>propanoic acid</td>
</tr>
<tr>
<td>124, 123, 78, 77, 79, 106, 105</td>
<td>3-methyl-1,2-benzenediol</td>
</tr>
<tr>
<td>121, 122, 65, 66, 63, 39, 38, 40, 65, 66, 76</td>
<td>2-hydroxy-benzaldehyde</td>
</tr>
<tr>
<td>138, 137, 120, 92, 81, 53</td>
<td>2,5-dihydroxy-benzaldehyde</td>
</tr>
<tr>
<td>124, 123, 125, 95, 107, 78, 77</td>
<td>3,5-dihydroxyltoluene</td>
</tr>
<tr>
<td>57, 69, 111, 152, 194, 236</td>
<td>hexadecanoic acid eicosyl ester</td>
</tr>
<tr>
<td>257, 239</td>
<td>9-eicosene</td>
</tr>
</tbody>
</table>
As seen in Figure 5, the ST solution with 100 mg/L COD equivalent resulted in 80% of immobilisation of Daphnia magna while the effluent of PFKC resulted in 30% toxic even after 30 minutes of oxidation for 100 mg/L of BK. However, differing from FK and PFKA the toxicity of PFKC effluent did not vary from 10 to 30 minutes of oxidation. This increase in toxicity after 10 minutes, due to treatment schedules by FK and PFKA, can be associated with the higher amounts of by-products formed at that time, and their concentrations as well as the composition (complex mixture) changed with time, thus affecting the toxicity more significantly than PFKC effluent (Schrank et al., 2005; Meric et al., 2005b).

Among the treatment processes applied, a complete COD removal was obtained for PFKC (H2O2/FeSO4/UVC) after 10 minutes for 100 mg/L (Figure 6) using 600/500 (mg/mg) of H2O2/FeSO4.

The toxicity results for 100 mg/L oxidation were in accordance with the absorbance removal. As seen in Figures 7 and 8, UV254 and UV280 measurements after 10 minutes of oxidation with PFKC process showed that BK was almost completely mineralised. Thus, the intermediates formed after 10 minutes at essential levels were...
Figure 6 COD removal for 100 mg/L BK solution using 600/500 (mg/mg) of H2O2/FeSO4 at 3.0 pH and 45°C

Figure 7 Compariance of absorbances in 100 mg/L of BK solution by FK, PFKA and PFKC treatment schedules during 30 min oxidation and using 600/500 (mg/mg) of H2O2/FeSO4 at 3.0 pH and 45°C

Figure 8 Absorbance variation in 100 mg/L of BK solution by PFKC treatment during 30 min oxidation and using 600/500 (mg/mg) of H2O2/FeSO4 at 3.0 pH and 45°C
almost stabilised and they were not affected by the oxidation with PFKC after 30 minutes of oxidation. Taking into account the differences between the lamps used the results shown in Figure 7 indicate that the photo-Fenton C process is more suitable than photo-Fenton A to be applied for degrading syntans.

Conclusions
In this study, the removal of a synthetic tannin (BK) was studied by Fenton (FK) and photo-Fenton (PFKA and C) processes at two initial syntan (BK) concentrations of 100 mg/L and 300 mg/L which are the most frequent concentrations in tanning bath effluents. These oxidation processes were chosen considering the original low pH value of these effluents (<4.0 pH) which are favourable for Fenton oxidation at a relatively low cost. However, considering the higher cost of hydrogen peroxide used in the process the use of UV irradiation additionally was expected to make this process an economic one for full-scale application. In fact, the comparative treatment studies on BK solutions indicated that photo-Fenton processes are more appropriate AOP technologies for removing xenobiotic compounds from wastewater, however, the oxidation time and the oxidant dose must be optimised according to toxicity of by-products formed during oxidation.

Acknowledgements
The authors gratefully thank Carmine Lettieri for supplying synthetic tannin, Paolo Napodano, Antonio Serino and M. Gallo for their technical support and Dr Giovanni Pagano for his suggestions.

References


