Comparison of different advanced oxidation process to reduce toxicity and mineralisation of tannery wastewater

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Abstract Many organic compounds contained in wastewater are resistant to conventional chemical and/or biological treatment. Because of this reason different degradation techniques are studied as an alternative to biological and classical physico-chemical processes. Advanced Oxidation Processes (AOPs) probably have developed to become the best options in the near future. AOP while making use of different reaction systems, are all characterised by the same chemical feature: production of OH radicals (*OH). The versatility of AOPs is also enhanced by the fact that they offer different possibilities for OH radical production, thus allowing them to conform to specific treatment requirements. The main problem with AOPs is their high cost. The application of solar technologies to these processes could help to diminish that problem by reducing the energy consumption required for generating UV radiation.

In this work, different AOPs (O3, TiO2/UV, Fenton and H2O2/UV) were examined to treat tannery wastewater or as a pre-treatment step for improving the biodegradation of tannery wastewater, at different pH and dosage of the chemicals. Under certain circumstances retardation in biodegradation and/or an increase in toxicity may be observed within these treatment steps. Two different bioassays (*Daphnia magna and Vibrio fischeri*) have been used for testing the progress of toxicity during the treatment. In parallel other objectives were to analyse and identify organic compounds present in the untreated wastewater and arising degradation products in AOP treated wastewater samples. For this purpose substance specific techniques, e.g., gas chromatography – mass spectrometry (GC-MS) in positive electron impact (EI+) mode and atmospheric pressure ionisation (API) in combination with flow injection analysis (FIA) or liquid chromatography – mass and tandem mass spectrometry (LC-MS or LC-MS-MS) were performed.

Keywords Advance oxidation process (AOP); Daphnia magna; mass spectrometry (MS); substance specific determination; toxicity; Vibrio fischeri

Introduction

The tannery productive cycle includes a series of chemical treatments using a large number of chemicals which after use are found in wastewater. Among these organic compounds e.g., surfactants, acids, dyes, natural or synthetic tanning agents, sulfonated oils, salts, etc. are tannins (polyphenolic compounds) that are difficult to degrade and are considered to be highly toxic. Inorganic compounds , such as ammonia, sulfide and chromium ions are also present in high concentrations, so any kind of biological treatment is inhibited (Vlyssides and Israilides, 1997).

Considering the large amounts and the low biodegradability of such chemicals, tannery wastewater treatment represents a quite serious environmental and technological problem. In fact, after conventional treatment (i.e., chromium precipitation ∅ primary sedimentation biological oxidation ∅ secondary sedimentation) effluents still do not meet the required limits at least for some parameters such as COD (Chemical Oxygen Demand), salinity, ammonia and surfactants (Di Iaconi et al., 2002).

According to Kabdasli et al. (1993) pollutants analysed using these parameters cannot be removed in a single treatment unit. So advanced treatment steps become necessary to
remove persistent pollutants determinable by COD. The application of the advanced treat-
ment, if it is considered together with the high cost of preceding conventional use, is very
expensive.

Biological wastewater treatment is able to remove 90% of non-polar pollutants con-
tained in untreated wastewater. Elimination happens by biochemical conversion or degra-
dation, incorporation into or adsorption onto the activated sludge or by stripping with waste
air. For wastewater, however, containing mainly polar organic compounds it is impossible
to obtain such elimination rates, because to remove polar organic compounds by adsorption
is more difficult and expensive than to adsorb unpolar compounds (Schröder, 1996).

A lot of compounds, e.g., benzothiazoles and more polar organics were identified as
major toxic compounds in tannery effluents (Reemtsma et al., 1999). The number of chem-
icals applied is larger, since the data sheets of tanning agents give only a rough description
of the main components (Reemtsma and Jekel, 1997).

Several reports deal with the pretreatment of industrial process water containing
benzothiazole. Since biodegradation of toxic compounds only occurs below a certain
threshold concentration, and since MBT (2-mercaptobenzothiazole) is known to exert
antimicrobial effects, it is not surprising that several proposals for biological purification of
MBT manufacturing process waters include a dilution step or a preliminary elimination
of certain compounds before entering the activated sludge process. However, after high
energy γ-radiation treatment of a synthetic MBT solution, the COD, the biological oxygen
demand (BOD) and the total organic carbon (TOC) content remained unchanged (Wener
and Verachtert, 1997). Other methods have been studied as an alternative to biological and
physico-chemical processes from which AOPs will probably become the best option in the
near future (Esplugas et al., 2002).

AOP are all characterized by the same chemical feature: production of OH radicals
(·OH). The versatility of AOPs is also enhanced by the fact that they offer different possi-
bilities in ·OH radical production, thus allowing them to be conform to specific treatment
requirements (Alba et al., 2002).

According to Schröder (1996) the application of physico-chemical methods using O₃ or
O₃/UV as very strong and, moreover, unspecific oxidizing agents, leads to the development
of a large number of new compounds. Little information on partially oxidized compounds
are available, except results from sum parameter analysis, due the difficult detection.
According to their pollutant spectrum the toxicological potential of the reaction products in
treated wastewater could change when they arrive in the receiving waters.

In this work we have studied the oxidation of the organic compounds present in tannery
wastewater applying O₃, TiO₂/UV, Fenton and H₂O₂/UV. The efficiencies of these AOPs
for the treatment of such wastewater and improving the biodegradation was determined.
The degree of elimination of pollutants contained in tannery wastewater was evaluated by
GC-MS and LC-MS while the toxicity testing was performed using Daphnia magna and
Microtox bioassays.

Material and methods
Reagents
The tannery effluent was obtained from an industrial treatment plant in Brazil that was pre-
treated by coagulation, with Al₂(SO₄)₃, and decantation. For preservation the wastewater
was acidified by adding H₃PO₄ (pH = 2) while it was kept at 4°C.

Aqueous suspensions with 1g/L of titanium dioxide (Degussa, Germany (80% anatase and
20% rutile; specific area 59 m²/g)) were used in photocatalytic examinations. Ferrous sulfate
(7 H₂O) was of reagent grade and hydrogen peroxide (30%) for medical use were both pur-
chased from Merck (Germany). The rest of the chemicals used were, at least, of reagent grade.
**Photocatalytic treatment**

A volume of 2 L of effluent (pH = 3) and 2 g of TiO$_2$ were placed in a batch reactor. The reactor was equipped with a 15W low-pressure mercury lamp, surrounded by a quartz thimble and the reactor was water-jacketed to maintain constant temperature (28°C). The treatment time was 120 min. For analytical control, samples were taken and centrifuged at (JOUAN; 23,500 g/30 min) to remove TiO$_2$ particles.

**Treatment by ozone**

All ozonation experiments were performed in a 2,000 mL capacity batch reactor. Ozone was produced in an ozone generator from commercially available oxygen, and the resulting mixture was fed to the reactor through a porous plate gas sparger located at the bottom at rate 2.6 g O$_3$/h. The reaction mixture inside the reactor was maintained in suspension by means of a magnetic stirrer. Tannery wastewater were submitted to the ozonation at pH 11 and at room temperature. The treatment time was fixed to 120 min.

**Photochemical treatment using H$_2$O$_2$/UV**

H$_2$O$_2$/UV oxidation of the tannery wastewater was performed in the same batch reactor of 2,000 mL as used for ozone treatment. A 15W low-pressure mercury lamp was used as the UV source. At the beginning of the reaction 0.018 mol H$_2$O$_2$/L were added at pH 3.

**Fenton reaction**

The Fenton process was carried out in a thermostatic cylindrical Pyrex cell. The reaction mixture inside the reactor consisted of 2,000 mL of tannery effluent (pH 3.5). After addition of the precise amounts of ferrous sulfate and hydrogen peroxide the mixture was continuously stirred with a magnetic bar for 2 hrs. After reaction the pH was elevated to pH 7 to precipitate ferrous hydroxide while a supernatant sample was submitted to analyses.

**Analytical methods**

All chemical analyses and the luminescence inhibition test with *Vibrio fischeri* were performed applying German standard methods (DEV, 2002). TOC was analysed by a Ströhlein C-MAT 5500 (Ströhlein Instruments, Düsseldorf, Germany). *Daphnia magna* bioassays were determined by ISO (1994) methods. The $G_L$ value indicates the dilution rate with a luminescence inhibition lower than 20%.

A Finnigan MAT GCQ gas chromatograph (GC) equipped with an ion trap mass spectrometric detector (MS) that was operated in the positive electron impact mode (EI+) was used for the analyses of volatile compounds extracted from wastewater samples using hexane or dichloromethane. The GC-MS conditions have been previously described by Meesters et al. (2002) while FIA-MS and LC-MS conditions for the analysis of the SPE methanol eluates had been reported by Schröder (1996, 2001).

**Results and discussion**

The relation of BOD and COD can be used to judge biodegradability of a wastewater. Mixtures of pollutants with a BOD$_5$/COD ratio of < 0.4 may be considered to be hardly biodegradable. The reduced biodegradability of tannery wastewater (cf. Table 1) is due to its high content of dyestuffs, surfactants and additives (Moraes et al., 2000). Several papers have reported a decrease of biodegradability of AOP treated wastewater (Balcıoglu and Ötker, 2003; Contreras et al., 2003; Hörsch et al., 2003; Rodriguez et al., 2002; Schröder, 1996) while from examinations of Chamarro et al. (2001) applying different oxidation technologies to various substrates led to partial chemical oxidation of toxic wastewater with an increase of biodegradability up to high levels in parallel.
From our results marginal or no increased biodegradability of the wastewater after different AOP treatment steps were observed (cf. Table 1). Contreras et al. (2003), however, have found in pre-ozonation experiments applied to an aqueous solution of 2,4-DCP (100 ppm) that BOD<sub>5</sub>/COD ratio could be increased from 0 to 0.25 while the TOC in our examinations was reduced during all treatment steps (Table 1) with an in-parallel decrease in biodegradability.

For toxicity testing of tannery wastewater *Vibrio fischeri* and *Daphnia magna* bioassays were applied. With both methods a slight decrease of toxicity after application of different AOP treatment steps was observed with the exception of the application of H<sub>2</sub>O<sub>2</sub>/UV (Table 2).

For substance specific analyses GC-MS, FIA- or LC-MS and LC-MS-MS were applied as already described (Schröder, 1996). For monitoring of oxidation results under AOP the volatile compounds in the liquid/liquid extracts of the untreated tannery wastewater and the AOP treated wastewater applying TiO<sub>2</sub>/UV, O<sub>3</sub>, Fenton and H<sub>2</sub>O<sub>2</sub>/UV were determined by GC-MS. The total ion current traces (TIC) of these extracts are presented in Figure 1 and could be used for pattern recognition judging elimination efficiencies.

The application of the pattern recognition approach to the TICs to judge the oxidation results meant information could be obtained that under AOP treatment the quality of compounds recognisable by shift of retention times as well as the concentration of oxidation products outlined by the peak areas had been modified. So qualitative analysis proved that the compounds present in the untreated wastewater, e.g., phenol or benzothiazole, were reduced dramatically in concentration, i.e., had been degraded or even mineralised. The concentration of volatile compounds in parallel was reduced to one tenth of the precursor concentration.

FIA- or LC-MS and LC-MS-MS analyses of SPE eluates using atmospheric pressure ionisation (API) proved that nonylphenolethoxylates (NPEO) and polyethylene glycols (PEG) as polar compounds predominantly were present in the untreated wastewater. For screening of results obtained under AOP conditions FIA-MS was performed which presented the molecular ions or ammonia adduct ions of pollutants contained in untreated tannery wastewater with their mass/charge ratios (m/z) (Figure 2a). For recognition of oxidation results spectra of the pollutants after AOP treatment were recorded and are

### Table 1 Biodegradability (BOD<sub>5</sub>/COD) and TOC results after AOP treatment

<table>
<thead>
<tr>
<th>Treatment of wastewater</th>
<th>BOD&lt;sub&gt;5&lt;/sub&gt;/COD</th>
<th>BOD&lt;sub&gt;5&lt;/sub&gt;/TOC</th>
<th>TOC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated wastewater (pH = 11)</td>
<td>0.36</td>
<td>1.03</td>
<td>45</td>
</tr>
<tr>
<td>TiO&lt;sub&gt;2&lt;/sub&gt;/UV (pH = 3)</td>
<td>0.15</td>
<td>0.4</td>
<td>30</td>
</tr>
<tr>
<td>O&lt;sub&gt;3&lt;/sub&gt; (pH = 11)</td>
<td>0.39</td>
<td>0.5</td>
<td>30</td>
</tr>
<tr>
<td>Fenton (pH = 3.5)</td>
<td>0.34</td>
<td>1.0</td>
<td>18</td>
</tr>
<tr>
<td>H&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;2&lt;/sub&gt;/UV (pH = 3)</td>
<td>–</td>
<td>0.78</td>
<td>19</td>
</tr>
</tbody>
</table>

### Table 2 Toxicity testing using *Vibrio fischeri* (LID<sub>L</sub>)* and *Daphnia magna* (LID<sub>D</sub>)*<sup>*</sup>

<table>
<thead>
<tr>
<th>Treatment of wastewater</th>
<th>LID&lt;sub&gt;L&lt;/sub&gt;</th>
<th>LID&lt;sub&gt;D&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated wastewater</td>
<td>8</td>
<td>1</td>
</tr>
<tr>
<td>TiO&lt;sub&gt;2&lt;/sub&gt;/UV</td>
<td>4</td>
<td>1</td>
</tr>
<tr>
<td>O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>10</td>
<td>1</td>
</tr>
<tr>
<td>Fenton</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>H&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;2&lt;/sub&gt;/UV</td>
<td>8</td>
<td>4</td>
</tr>
</tbody>
</table>

*<sup>*</sup>LID = Lowest Ineffective Dilution (ISO, 1994)
shown in Figure 2b, c, d and e for comparison. Pattern recognition was easy because of the characteristic $\Delta m/z$ 44 ratios of polyether compounds such as NPEO ($m/z$ 502, 546...). A chemical degradation of NPEO by AOP could be observed resulting in mainly polyethylene glycol (PEG; $m/z$ 300, 344...; $\Delta m/z$ 44), carboxylated PEG and carboxylated NPEO (PNEC) but the reduction of carbon content was not worth mentioning.

**Conclusion**

The use of AOP as a pre-treatment in order to increase the biodegradability of the tannery wastewater failed. All treatment steps applied (TiO$_2$/UV, O$_3$, Fenton and H$_2$O$_2$/UV)
resulted in partial oxidation and mineralization reactions with an in-parallel decrease in BOD$_5$. Despite this partial degradation, the toxicity remained unchanged. The substance specific analyses applying GC- or LC-MS proved the presence of phenol, benzothiazole (BT), nonylphenolethoxylates (NPEO) and polyethyleneglycols (PEG). A complete degradation during different AOP treatment steps could be observed applying the pattern recognition approach.

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References


