ELECTRO-FENTON-BASED TREATMENTS OF REAL EFFLUENTS FROM TANNING PROCESSES AND LANDFILLS

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ABSTRACT

Leather industry uses high quantities of water, from 50 to 200 m$^3$ d$^{-1}$ and tanning processes use large quantities of tannin-based organic compounds, which with all the protein, lipids, greases and hairs, constitute high amounts of COD (chemical oxygen demand) and BOD (biological oxygen demand) with many biorefractory compounds in the tanning effluents. Effective treatment with recycling option of such large quantities of technological waters would: 1) reduce the costs of the entire tanning process (as for that of water consumption and that of salt expenses), 2) allow to easily depurate the issuing waters with lower costs, and 3) eliminate progressively the negative environmental impact of the final effluent discharge into rivers by reducing considerably (or eliminating) the remaining COD and the quantities of sludge at the end of the treatment process.

Depuration sludges are usually stocked in specially conceived landfills. Leachate from such landfills contains also high quantities of contaminants, COD from 5000-15000 ppm, and requires further treatment. Periodical recirculation of the leachate is done, which, in fact, does not always suffer subsequent treatment.

The main process presented in this work, H$_2$O$_2$-assisted electroprecipitation (AEP) with sacrificial Fe anode coupled with Ti(Pt) cathode, combines physico-chemical aspects of the treatment of water effluents with electro-Fenton(EF)-based electrochemical oxidation and partial coagulation/precipitation of the remaining compounds. The COD removal is 90% in 8 h for the desalting wastewater and in the range 60-80% in 6 h for the leachate during AEP treatment. EF and photoelectron-Fenton on boron doped diamond (BDD) anode coupled with O$_2$-diffusion cathode also allow high degradation efficiency (75-80%), limited by oxalate-complexes formation and the presence of suspended solids. BDD anodic oxidation achieves 99% destruction of COD in a longer time, more than 20 h. AEP treatment, alone or in combination with complementary treatment, allows complete COD removal from the effluents. The AEP-technology is suitable to industrial application specially for the recycling of tanning effluents and landfill leachate.

INTRODUCTION

Leather industries are large consumers of water and are, consequently, sources of potential contamination that must be treated before effluent discharge into rivers or surface waters; there has been progressive increase of organic compounds in surface and groundwater [1-5]. Therefore, regulations are adopted to avoid the critical contamination.

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When natural vegetal tanning process was traditionally used, the main problem was to ensure the degradation of the organics. In such case, the effluents have elevated COD (chemical oxygen demand) and BOD (biological oxygen demand) value, but are relatively easier to treat biologically. The necessary treatment allowed the biodegradation of the organic part at relatively low expenses in the normally accepted range of effluents concentration, value less or
equal 10,000 ppm of COD. High biodegradability is illustrated by the high BOD/COD ratios. The higher the value is the better the effluents are treated via biological depuration processes. Later with the expansion of the chromium-based tannery process, it appears necessary to eliminate the heavy metals up to their legally authorized and accepted concentrations. Now the process has a reinforced use of colorants, which are nevertheless easy to destroy. Unfortunately, the wastewater from tanning processes has levels of COD higher than the recommended limits. Usually, before biological process begins, the wastewater is subjected to a flocculation/coagulation step, where an important part of the contaminants is precipitated. The entering concentration of COD at the head of the depurator constitutes an important criterion for the payment, by the manufacturers, of the corresponding treatment taxes. Sometimes, COD values can easily attain concentrations up to ten times or more than the normally accepted one. In modern and intensive processes of depuration, the mixing of the municipal waters with those of industrial origin (tannery one, for instance) permits to lower this concentration up to values near to the recommended before the conventional depuration process begins. It is noteworthy that a meaningful dilution is sometimes made during and at the end of the tanning process justified by cleaning proposes, even if occasionally such cleaning is exaggeratedly made to ensure lower COD concentrations in the effluents before their arrival to the entrance of the conventional depuration plant.

One other important aspect of the wastewater from industrial activities and tanning processes is the accumulation of the sludge (near 300 kt y\(^{-1}\) for the studied case). The disposal in controlled landfills yields large quantities of percolates, from 200 to 500 m\(^3\) d\(^{-1}\). The leachate shows high and variable COD (from 2,000 to 15,000 ppm), low biodegradability index and various heavy metals used during the tanning and treatment processes (see Table 1). This constitutes an indication that, in fact, during the wastewater treatment, the main part of the COD of this wastewater is imprisoned in the sludge and not completely destroyed. So with the recirculation of the derived percolates at the top of depuration plant, the result obtained is not the destruction of the contamination but mainly a “COD and other contaminants” recirculation in the technological scheme, a fact that makes the lately issuing percolates even more concentrated.

Alternative solutions to the classical chemical, physico-chemical and biological technologies are needed and are being investigated to achieve the treatment of toxic and highly loaded wastewater. Apprecciable advances are being done for the practical application of electrochemical methods to the treatment of real wastewater as reported by others [6,7]. These techniques are allowing the treatment of different wastewater with oil and fat emulsion [8-10], from galvanoplastic and metal electroplating [11-14], textile and derived [15-19], and alimentary [9] sectors.

We have focused our research on the practical solutions directly applicable to the wastewater and landfill leachate, and recently, we have presented the treatment of highly concentrated effluents from vegetal tanning process [20]. In the present paper, we report the part corresponding to the recycling and treatment of tanning and landfills leachate in the case of the desalting waters and the percolates by mainly using Electro-Fenton (EF) and photoelectron-Fenton (PEF), single and H\(_2\)O\(_2\)-assisted Electro Precipitation

### Table 1. Typical composition of the studied percolates

<table>
<thead>
<tr>
<th>Components</th>
<th>Unit</th>
<th>Arzignano tanning pool</th>
<th>Istranno</th>
</tr>
</thead>
<tbody>
<tr>
<td>Halogenated organic solvents</td>
<td>μg L(^{-1})</td>
<td>&lt; 10</td>
<td>&lt; 10</td>
</tr>
<tr>
<td>Phenols</td>
<td>mg L(^{-1})</td>
<td>1.3</td>
<td>1.06</td>
</tr>
<tr>
<td>Ni</td>
<td>mg L(^{-1})</td>
<td>0.7</td>
<td>0.67</td>
</tr>
<tr>
<td>Cd</td>
<td>mg L(^{-1})</td>
<td>&lt; 0.01</td>
<td>&lt; 0.01</td>
</tr>
<tr>
<td>Pb</td>
<td>mg L(^{-1})</td>
<td>&lt; 0.2</td>
<td>&lt; 0.2</td>
</tr>
<tr>
<td>Cu</td>
<td>mg L(^{-1})</td>
<td>&lt; 0.05</td>
<td>0.16</td>
</tr>
<tr>
<td>Zn</td>
<td>mg L(^{-1})</td>
<td>0.19</td>
<td>0.39</td>
</tr>
<tr>
<td>Mn</td>
<td>mg L(^{-1})</td>
<td>0.27</td>
<td>0.27</td>
</tr>
<tr>
<td>Fe total</td>
<td>mg L(^{-1})</td>
<td>1.08</td>
<td>1.34</td>
</tr>
<tr>
<td>Cr total</td>
<td>mg L(^{-1})</td>
<td>5.7</td>
<td>5.4</td>
</tr>
<tr>
<td>Cr(_{VI})</td>
<td>mg L(^{-1})</td>
<td>&lt; 0.1</td>
<td>&lt; 0.1</td>
</tr>
<tr>
<td>Sulfates</td>
<td>mg L(^{-1})</td>
<td>355</td>
<td>255</td>
</tr>
<tr>
<td>Chlorides</td>
<td>mg L(^{-1})</td>
<td>3215</td>
<td>2520</td>
</tr>
<tr>
<td>N-NH(_4^+)</td>
<td>mg L(^{-1})</td>
<td>8730</td>
<td>7740</td>
</tr>
<tr>
<td>Sulfurs</td>
<td>mg L(^{-1})</td>
<td>27</td>
<td>51</td>
</tr>
<tr>
<td>COD</td>
<td>mg L(^{-1})</td>
<td>6600</td>
<td>2200</td>
</tr>
<tr>
<td>Conductivity</td>
<td>μS cm(^{-1})</td>
<td>44700</td>
<td>39000</td>
</tr>
<tr>
<td>pH</td>
<td>–</td>
<td>8.30</td>
<td>7.90</td>
</tr>
</tbody>
</table>
(EP) - an EF-based process with oxidation of the organic compounds and co-precipitation and coagulation of the solids together with the residual carbon [20]. This paper emphasizes strongly on industrial scaling-up for the treatment of the studied effluents.

EXPERIMENTAL

The studied effluents were obtained from the Arzignano tanning pool of Vicenza (Italy) and from Istrana landfill (Treviso, Italy). Two of the effluents were from the same Arzignano tanning pool: desalting wastewater and part of the percolates. The desalting effluents were of vegetal and/or chromium-based tanning processes origin, obtained from Dani Leather tanning enterprise (Arzignano tanning pool), and the percolate waters were from the landfill from the corresponding depuration process of the tanning effluents. The parameters and characteristics of the percolates are illustrated in Table 1. They present a darkish brown or black colour with a very repugnant odour. The desalting waters have fewer odours and are accompanied with suspended solids, like hairs, for instance. No pre-treatment was applied prior electrochemical step.

Experiments were performed in a batch undivided laboratory cell with solution volumes of 200, 500 and 750 mL, at room temperature, at current densities 30 mA cm$^{-2}$. There was no need in adding an electrolyte support to electrochemically treat the industrial effluents since they presented a sufficient and specific conductivity (ca. 40 mS cm$^{-1}$ at 20 °C), due in particular to the high contain of sodium chloride. A 10 cm$^2$-area iron (Steel C40) or BDD (Boron Doped Diamond) sheet or titanium-platinised (Ti(Pt)) grid as anode and zirconium sheet or O$_2$ Diffusion electrode as cathode were used. For H$_2$O$_2$-assisted electroprecipitation (HAEP) method, Ti(Pt)/Fe electrolytic system was used, where Ti(Pt) is cathode and Fe is anode. The same way, for EF and PEF an O$_2$-D/BDD system was used and for anodic oxidation (AO), Zr/Ti(Pt) and Zr/BDD systems were used. An 8 W Philips black light lamp tube was used to irradiate the solution under treatment during PEF. COD measurements were carried out with a HACH DR2000 spectrophotometer prior heating of the probe-filled Hach digestive vials with a thermo-reactor at 150 °C for 2 h. The influence of possible trace of hydrogen peroxide after reaction was primarily eliminated after verification of its presence in the probe with a Ti(IV) complexation solution and a spectrophotometer at 420 nm [21]. A calibration curve allowed determining the contribution of the remaining hydrogen peroxide in the COD value. All the probes were filtrated with a 0.45-μm Whatman paper before COD determination. A 35% Fluka-made hydrogen peroxide solution was used for HAEP, 96% H$_2$SO$_4$ and 40% NaOH solutions, all purchased from Fluka, were used for pH adjustment and neutralization (iron complexes precipitation) before and at the end of the process. The treated solutions were decanted or filtrated with a 50-μm paper filter to simulate the reutilisation step of the obtained water.

RESULTS AND DISCUSSIONS

Tanning macromolecules usually present good complexing capacity with metals, specially iron-based one or Fe(II) and (mostly) Fe(III) ions [20,22], as illustrated in reactions (1) and (2). The formed iron complexes are electro active [20] and the addition/generation in the medium of an oxidant as oxygen or hydrogen peroxide allows the reaction between the oxidant and the iron complexes (reactions 3-6). The result obtained is the partial mineralization of the organic pollution (reactions scheme (7)) accompanied by coagulation of the remaining carbon under ferrioxalate red precipitate complex, which is mainly Fe(III) with very low percentiles of carbon [20,23] and can be accordingly transformed into iron during metallurgical processes. The series of reactions illustrated hereby are an extension of the Haber-Weiss mechanism [24] (reactions (3)-(4)) accompanied with the Fenton and Fenton-like reactions (reactions (5)-(6)) and the organic part (L) complementary oxidation (L$_{ox}$) up to mineralization (CO$_2$ + H$_2$O):

\[
\begin{align*}
\text{Fe(II)} + \text{L} & \rightarrow \text{Fe(II)L} \quad (1) \\
\text{Fe(III)} + \text{L} & \rightarrow \text{Fe(III)L} \quad (2) \\
\text{Fe(II)L} + \text{O}_2 & \rightarrow \text{Fe(III)L} + \text{O}_2^- \quad (3) \\
\text{Fe(II)L} + \text{O}_2^- + 2\text{H}^+ & \rightarrow \text{Fe(III)L} + \text{H}_2\text{O}_2 \quad (4) \\
\text{Fe(II)L} + \text{H}_2\text{O}_2 & \rightarrow \text{Fe(III)L} + \text{H}^+ + \text{OH}^- \quad (5) \\
\text{Fe(III)L} + \text{H}_2\text{O}_2 & \rightarrow \text{Fe(II)L} + \text{H}_2\text{O}_2 + \text{H}^+ \quad (6) \\
\text{L} + \text{OH}^- & \rightarrow \text{L}_{ox} + \text{OH}^- \rightarrow \ldots \rightarrow \text{CO}_2 + \text{H}_2\text{O} \quad (7)
\end{align*}
\]

The desalting waters of initial concentration ca. 15,000 ppm of COD were treated via HAEP at initial pH 7.5 and also adjusted to 3, to be in the range of the EF process [25-27], with the addition of ca. 1 vol% of hydrogen peroxide. The cell used had a volume of 500 mL. As illustrated in Fig. 1, when the desalting waters are treated at initial pH 7.5, COD removal is high but the final solution has a yellowish colour. Treatment under pH values 3-4 permits the complete elimination of the COD and the remaining solution is transparent and colourless after neutralisation. It is noteworthy that the transparent appearance of the solution is obtained early after 1 h of oxidation and decantation. One other important aspect, which might be taken in consideration when doing scaling-up projection, is that electrolysis is accompanied by the presence of large quantities of foam, from 0.1 to 2.25 times the
initial wastewater volume before completing the first hour of treatment (See insert in Fig. 1). After this, foam quantity is low. Foam evolution is also noted immediately when hydrogen peroxide is added to the basic solution, enhanced by O₂-evolution, when, at pH 3, foam evolution is very low. This foaming phenomenon is due to the presence in the initial wastewater of tensioactive compounds and also to oxygen and CO₂ evolution.

The studied percolates have COD values of 2200, 4800 and 6600 ppm and were obtained from Arzignano tanning pool depuration station (first, third) and from Istrana landfill (Treviso). Their destruction behaviour is represented in Fig. 2. COD is destroyed to very low values and when the process is ruled at Fenton pH, the solutions are colourless after neutralisation. Treated at initial pH (ca. 8), the resulting solutions present a yellow-reddish colour, afforded to the formation of stable iron complexes involving part of the organic contaminants.

Percolates effluents generated even more foam than desalting waters during electrolysis [see inset in Fig. 2], which is destroyed towards the end of the treatment. Foam formation must be a parameter to study and monitor when scaling-up HAEP reactor.

AO- and EF-based treatments were also performed on the highly contaminated leachate. Figure 3a illustrates the COD decay. During AO on Ti(Pt) coupled to a Zr cathode, after 6 h of treatment, just ca. 20% COD removal is attained. Afterwards COD destructions are low and equal to ca. 30 and 40% respectively after 12 and 22 h of treatment. Performed on BDD anode under the same conditions, these results are much better with ca. 50 and 70% of COD destruction respectively after 6 and 12 h. Destruction of contaminants during single AO is directly dependent on the anode capacity of discharging the water molecules of the aqueous medium and consequently generating oxidants to oxidize the pollutants. The superiority in potential of oxidation of BDD upon Pt and Ti, and consequently Ti(Pt) is previously studied and demonstrated [28]. Due to its high discharge potential, a higher amount of oxidants is generated on its surface and the oxidation reactions at the interface medium-electrode improved. As no catalysis accompanies the reactions, the process is relatively slow.

Anyway, after 22 h, AO on BDD mineralizes the organic contaminants with more than 99% COD destruction. Other electrocatalytic trials are represented in the same Fig. 3a. Catalysis is just based on the action of the Fe(II) electrogene rated in the treated medium. In the case where HAEP is performed with a sacrificial Fe anode and a Ti(Pt) cathode to electrolyse the percolate, ca. 60 and 75% in COD destruction are attained respectively after 6 and 12 h of treatment. AEP shows better performance in COD destruction with respect to AO performed with the Ti(Pt)/Zr system (Figs. 2 and 3a). AEP process is faster than AO; however, a threshold is observed after 5-6 h and the destruction trend becomes lower. EF and PEF with an O₂-D/BDD system show faster rates of COD destruction than both AEP and AO processes. COD destruction during EF is ca. 55 and 60% respectively after 6 and 12 h and is higher than that of AO with Zr/Ti(Pt). PEF also improves the rate of destruction observed for EF. COD destruction is ca. 75 and 80% after 6 and 12 h of treatment, respectively. For the last two processes,
Fig. 3. Evolution (a) and foam evolution (b) of the COD of the percolate during various anodic oxidation and Electro-Fenton treatments in a laboratory cell of 200 mL, at room temperature, at pH 3-4 and current density of 30 mA cm$^{-2}$; (a) (─■─) and (─♦─) represent anodic oxidation respectively on Ti(Pt) and BDD anodes with a Zr cathode and (─•─, ─▲─, ─○─) represent respectively HAEP with Fe anode, Electro- and photoelectro-Fenton on BDD anode trials; (b) (─□─) and (─♦─) represent anodic oxidation respectively on Ti(Pt) and BDD anodes with a Zr cathode and (─•─, ─▲─, ─○─) represent respectively H$_2$O$_2$-assisted EP, and Electro- and photoelectron-Fenton on BDD anode trials.

A stationary state is observed where destruction of COD is so low that it seems the process has stopped. Two facts explain this phenomenon. The formation of iron complex and Fe(III) oxalate (typical of EF [29-30]) together with the high quantities of suspended solids contributes to slower rate. As for the synthetic wastewater [31-33], PEF achieves more than 95% destruction of the contaminant, due to the ability of UV light to break the iron oxalate bonds and to enhance the Fenton reaction by completing its cycle (reactions (5) and (6)) and by generating more hydroxyl radicals. This high yield was not observed in the case of this percolate due to the presence of high contents of suspended solids and also to foam evolution that both do not permit a deep irradiation of the electrolysed medium.

Foam evolution is observed in all processes and is more intense in the case where hydrogen peroxide is added in the medium of HAEP (Fig. 3b). This can be explained by the fact that during AO just the anode’s discharge potential of the water molecules is used to generate hydroxyl radicals and to destroy the organic matters. O$_2$ evolution at the anode and CO$_2$ evolution from the low mineralization of organics slowly enhance the foaming process. When iron catalyst and oxidation promoters (hydrogen peroxide and oxygen) are present in the medium, the anodic destruction of the contaminants is accompanied by bulk reactions (4) and (7) that favour the evolution of foam. This latter progressively dissolves back in the medium and is oxidized again.

With the good performance obtained with the destruction of the COD during electroprecipitation, high degree of metal removal is attained; more than 90% for the reported metals in Table 1, even if their initial concentrations were very low. Nitrogen is also eliminated with ca. 70% removal. Phenols and halogenated organic solvents are eliminated from the medium with removal higher than 99.9% and a good appropriation for its reuse in the tanning sector. For irrigation use, a subsequent removal of salts, up to electric conductivity lower than 5 mS cm$^{-1}$, is necessary.

**CONCLUSIONS**

Fenton-based electrochemical treatments of real wastewater from tanning processes and landfills percolates were performed under various experimental conditions and concentrations. The results obtained show that EP is suitable for the treatment of tanning solutions, percolates and consequently industrial effluents, specially at initial pH 3-4. For industrial projections, prevision of foam evolution must be done by using a cell/wastewater volume-ratio of ca. 3:1 or foam recirculation must be done from an intermediary liquefaction reservoir and the obtained liquid sent ahead to treatment with the raw wastewater. The treated solutions are transparent, colourless and ready for use in the same process, specifically in tanning industries, or for agricultural purposes after removal of the sodium chloride salt up to acceptable value. The obtained precipitate contains principally iron and non-toxic carbon (principally oxalate), with Fe easily recuperated via metallurgical processes. HAEP followed by sludge/solids and salt separation is a promising technology for most sustainable use of waters in a
closed cycle. Such concept of wastewater treatment provides an integral treatment of industrial effluents that has very positive impacts on the environment as it converges to the zero-wastes' approach

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This work is dedicated to the loving memory of Maam Ndéyy Mbogne Ndoye, 1897-1996 (www.maamndéyy.org).

REFERENCES


Discussions of this paper may appear in the discussion section of a future issue. All discussions should be submitted to the Editor-in-Chief within six months of publication.

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