

# Electrochemical Removal of Tannins from Aqueous Solutions

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The applicability of electrochemical methods to remove tannins from wastewater was investigated. Gallotannic acid was used as the reference substance. Electrochemical experiments were performed using platinum electrodes. Macroscale potentiostatic or galvanostatic electrolyses were carried out with sodium sulfate or sodium chloride as supporting electrolytes, to analyze direct and indirect oxidation processes. Operating variables such as pH and chloride concentration were considered to determine their influence on the efficiency and energy consumption of the process. The simulation of a pilot plant was carried out with a mathematical model, the parameters of which were determined by fitting of experimental profiles. The results of a preliminary investigation on the oxidation–coagulation process using sacrificial electrodes are also reported.

## Introduction

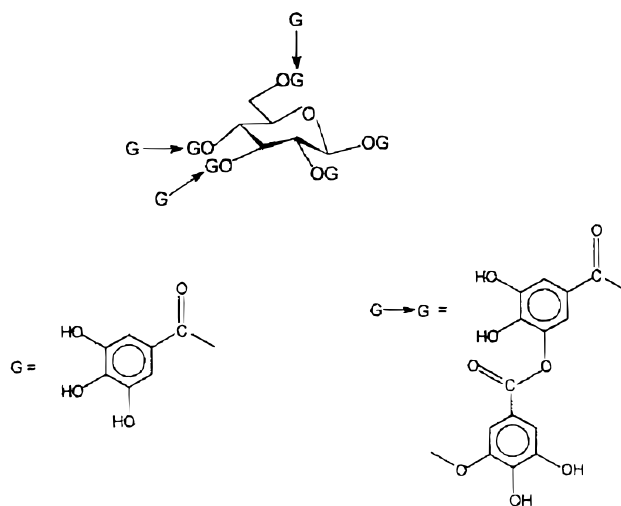
Today, natural and synthetic tannins are used not only for direct tanning but also together with chromium-(III) salt as retanning agents. These biorefractory and toxic pollutants present in tannery wastewater sometimes make traditional treatments ineffectual, whereas more sophisticated technologies have the disadvantages of high cost and low efficiency. Electrochemical processes have attracted a great deal of attention because direct and indirect electrolysis, electrocoagulation, and electroflotation can destroy not only tannins but also other pollutants present in solution or in suspension, such as inorganic salts, surfactants, etc., which are difficult to eliminate.

Although the removal of tannins from wastewater is an environmental problem of great concern, because of the difficulty of meeting prescribed quality standards for discharged effluents, only a few papers are available in the literature.

Recently, Chiang<sup>1</sup> has shown that electrochemical oxidation is a promising method to destroy refractory and toxic high molecular weight organic substances. Vlyssides<sup>2</sup> has analyzed the detoxification of tannery waste liquors, evaluating the efficiency of electrolytic oxidation with reference to the main organic pollutants present in wastewater and investigating the effect of sodium chloride.

Although previous papers have highlighted the fact that electrochemical methods may be successfully used for wastewater treatment and pretreatment, industrial applications are not currently widespread. In previous works, the authors analyzed the performance of a new electrochemical reactor<sup>3,4</sup> and evaluated the possibility of using electrochemical techniques for textile wastewater.<sup>5</sup>

The aim of the present paper is to investigate the feasibility of electrochemical methods for removing



**Figure 1.** Molecular structure of gallotannic acid.

tannins from wastewater. To develop the process, first on a pilot plant and subsequently on an industrial scale, attention was focused on various phenomena occurring at the electrodes and in solution (direct and indirect oxidation, electrocoagulation, etc.). The effects of operating variables were also defined, and energy consumption was quantified.

## Experimental Section

**Chemicals.** The solutions investigated in this study were prepared using pure chemicals. Gallotannic acid,  $C_{76}H_{52}O_{46}$  (Aldrich, Milwaukee, WI), was selected as the reference substance (Figure 1), because it is widely used as a tanning and retanning agent.

Synthetic wastewater was prepared using gallotannic acid with concentrations from 0 to 4 g/L. The chemical oxygen demand (COD) of these solutions varied from 0 to 5 g/L and the biological oxygen demand (BOD<sub>5</sub>) from

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0 to 1 g/L, indicating that the selected substance is poorly biodegradable.

Sodium sulfate or sodium chloride was used as the supporting electrolyte, and the pH was adjusted by supply of an appropriate acid (HCl or H<sub>2</sub>SO<sub>4</sub>) or a base (NaOH).

**Apparatus.** Cyclic voltammograms were obtained using an AMEL 494 cell equipped with a saturated calomel reference electrode (SCE), a working platinum microelectrode (surface area =  $3 \times 10^{-2}$  cm<sup>2</sup>), and a platinum counter electrode. During the experiments, the solution was deaerated by bubbling purified nitrogen. A dc power supply [Princeton Applied Research (PAR) model 173] was employed to provide electric power. The electrode potential could be varied using a potential programmer (PAR model 175). A digital oscilloscope (Nicolet model 3091) monitored voltammetric data, which were subsequently processed using dedicated software (Nicolet PC31).

Macroscale galvanostatic and potentiostatic experiments were conducted in two batch electrolytic cells of 200 and 500 cm<sup>3</sup> capacity, respectively; stirring was provided by a magnetic bar. Titanium-platinized grids were used as both the anode and cathode; both electrodes had an approximate geometric surface area of 25 cm<sup>2</sup> and were placed vertically and parallel to each other in the electrolytic cell. In some experiments, stainless steel AISI 316L rods (10 × 1 × 0.5 cm) were used as the cathode and anode instead of titanium-platinized grids. An SCE, equipped with a Luggin capillary, was used as the reference electrode. Electric power was provided by a potentiostat/galvanostat (AMEL model 2051) equipped with a function generator (AMEL model 568) and an integrator (AMEL model 731). During the experiments, current and voltage values were monitored continuously by a potentiometric recorder (BBC model SE420) and then processed by dedicated software. A schematic view of the laboratory apparatus is reported in a previous work.<sup>3</sup>

Each experiment was carried out at least three times, but no appreciable differences were revealed in the results.

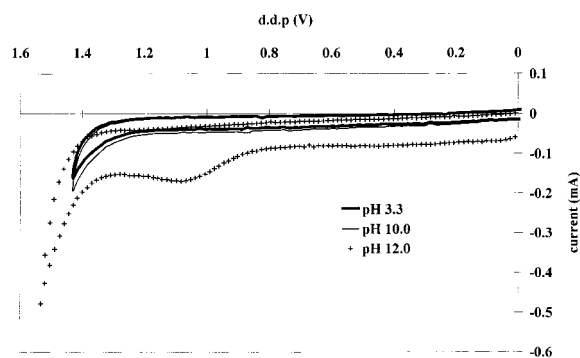
**Methods of Analysis.** A UV-vis spectrophotometer (Perkin Elmer model Lambda 11), interfaced with a PC equipped with dedicated PECCS software for data acquisition and analysis, was used for analytical procedures. Electrolysis samples were always analyzed at the same pH value (pH = 5).

COD was determined in test tubes with predosed reagents (HACH). The concentration of residual Cr<sup>3+</sup> in sample solutions was evaluated by measuring absorption at 620 nm.

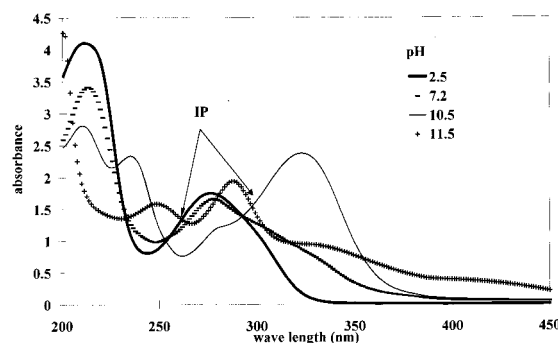
BOD was determined by the manometric method (WTW model Oxitop Control OC100). Because of the high biorefractoriness of organic compounds in the solutions, aerobic bacteria were selected starting from commercially available strains (BOD<sub>5</sub> Bioseed capsules, Supelco Sigma Aldrich), increasing quantities of gallotannic acid being added to the solution for 1 week.

## Results and Discussion

Cyclic voltammetry experiments indicate that a (chemically irreversible) oxidation peak of gallotannic acid is detectable, at potentials lower than those corresponding to oxygen evolution, only when operating conditions are



**Figure 2.** Cyclic voltammograms (sweep rate = 0.5 V/s) of gallotannic acid in aqueous solutions (2 g/L) at various pH values. Working electrode: Pt. Supporting electrolyte: Na<sub>2</sub>SO<sub>4</sub>, 0.05 M.



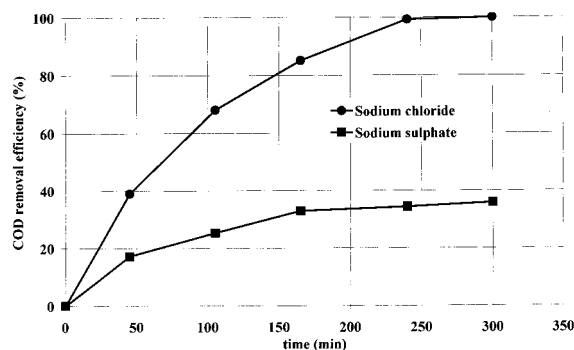
**Figure 3.** UV-vis spectra of gallotannic acid solutions (40 mg/L) at various pH values. IP = isosbestic points.

actually alkaline (see Figure 2). This peak corresponds to the direct electrochemical oxidation of gallotannic acid anions generated by deprotonation of OH groups, as indicated by the variations in UV-vis spectra with pH (see Figure 3).

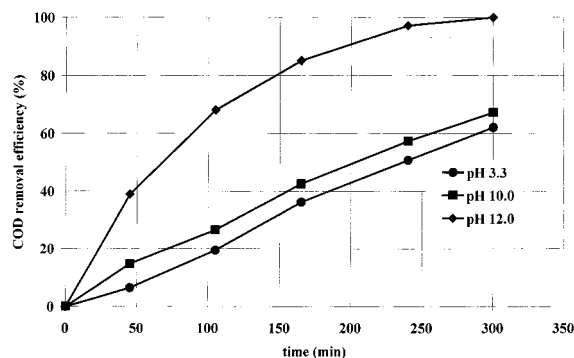
In particular, the detection of two isosbestic points at which pH values were lower than 11 and their disappearance at higher pH indicate the occurrence of several acid-base equilibria with the formation, at pH > 11, of anionic species responsible for the direct oxidation process detected.

Macroscale electrolysis runs were thus carried out using sodium sulfate as the supporting electrolyte, at pH = 12, and choosing potential values focusing only on the direct oxidation of gallotannic acid, as suggested by the data of Figure 2. The UV-vis spectra changed shape during electrolysis. In particular, first absorbance peaks rose and then began to fall gradually, confirming the occurrence of polymerization reactions, as observed by other authors.<sup>1,6,7</sup> For this reason, UV-vis spectroscopy is not suitable for quantitative analysis. Because it was not the aim of this study to detect intermediate and final substances produced during the process, parameters such as BOD and COD were used to quantify the efficiency of organic matter reduction. In particular, with reference to the previously mentioned operating conditions, COD values did not significantly decrease during macroscale electrolysis, although spectra did change shape.

Indirect oxidation of gallotannic acid due to substances generated at the electrode was therefore studied by increasing the potential to involve oxygen evolution. Experiments carried out using sodium sulfate as the supporting electrolyte highlighted the fact that, when pH values were lower than 12, there was no significant



**Figure 4.** COD removal efficiency during electrolysis of gallo-tannic acid in aqueous solution (2 g/L). Effect of type of supporting electrolyte. Sodium chloride: 2000 mg of  $\text{Cl}^-/\text{L}$ . Sodium sulfate: 0.05 M. Working electrode: Pt grid. Electrolysis potential: +3.0 V. pH: 12. Agitation level: 100 rpm.



**Figure 5.** COD removal efficiency during electrolysis of gallo-tannic acid in aqueous solution (2 g/L). Effect of pH. Working electrode: Pt grid. Electrolysis potential: +3.0 V. Supporting electrolyte: sodium chloride (2000 mg of  $\text{Cl}^-/\text{L}$ ). Agitation level: 100 rpm.

variation in COD, whereas when pH was increased to over 12, a significant decrease of COD was observed (Figure 4).

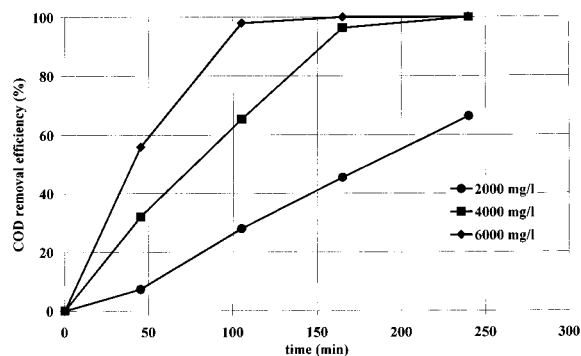
However, a limited value of COD removal efficiency seems to be reached (lower than 40%), which should indicate a situation in which neither direct nor indirect oxidation of organic substrates takes place.

The data obtained with  $\text{Na}_2\text{SO}_4$  were then compared with results of experiments carried out using sodium chloride as the supporting electrolyte.

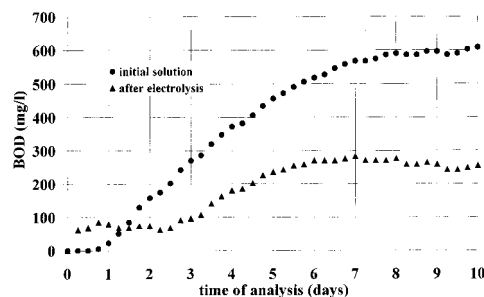
Figure 5 shows the trend of COD removal efficiency, at various pH values, obtained using sodium chloride as the supporting electrolyte and the same potential values as those in previous experiments.

The results shown in Figures 4 and 5 reveal that the presence of chloride ions in the solution not only increases COD removal efficiency; in addition, "activated" substances produced at the electrode react with gallo-tannic acid. In fact, even when the pH values were lower than 12 (when tannin oxidation was not observed to work without  $\text{Cl}^-$ ), the removal efficiency values were already high, although they were lower than those obtained at pH 12.

The effect of sodium chloride concentration on COD removal efficiency was also analyzed. To test the applicability of the method even in unfavorable experimental conditions, macroscale electrolyses were carried out with  $\text{Cl}^-$  concentrations varying from 2000 to 6000 mg/L, although chloride concentrations in tannery wastewater often exceed 15 000 mg/L, and at the lowest pH values generally detected in tannery wastewater



**Figure 6.** COD removal efficiency during electrolysis of gallo-tannic acid in aqueous solution (2 g/L). Effect of chloride concentration. Working electrode: Pt grid. pH: 3.3. Imposed current: 1.9 A. Agitation level: 100 rpm.



**Figure 7.** Electrolysis of gallo-tannic acid in aqueous solution (2 g/L). Thierault diagrams. Working electrode: Pt grid. Imposed current: 1.9 A. Supporting electrolyte: sodium chloride (2000 mg of  $\text{Cl}^-/\text{L}$ ). pH: 3.3. Electrolysis time: 190 min. Agitation level: 100 rpm.

**Table 1. Electrolysis of Gallo-tannic Acid (2 g/L): Biodegradability of Solution (Experimental Conditions as in Figure 7)**

parameters	electrolysis	
	initial values	final values
COD (mg/L)	2483	1227
$\text{BOD}_5/\text{COD}$	0.184	0.192
$\text{BOD}_{10}/\text{COD}$	0.245	0.207

(about 3 units). In this case, electrolyses were carried out in galvanostatic rather than potentiostatic conditions. Comparison of data was more meaningful because, for the same time, the same charge is produced.

As may be seen in Figure 6, after a limited period, total removal of tannin is possible, even when pH conditions are not favorable.

At the end of removal efficiency analysis, the biodegradability of the solution expressed as the BOD/COD ratio was evaluated.

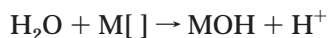
Figure 7 shows the trend of biochemical oxygen demand satisfied as a function of time.

These data, used to obtain the values listed in Table 1, confirm literature findings, i.e., that the initial solution is highly biorefractory and that the BOD/COD ratio does not change during treatment.

There are few reports in the literature concerning the direct and indirect electrochemical oxidation mechanisms of gallo-tannic acid, although there are descriptions of the indirect oxidation mechanism of aromatic compounds due to radicals produced by electrochemical oxidation of water or chloride.<sup>2,8-10</sup>

The following scheme summarizing reactions in the anodic zone is proposed, in accordance with the experimental results described above.

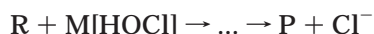
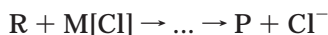
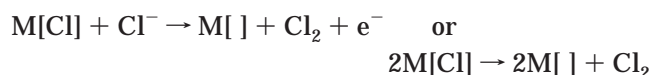
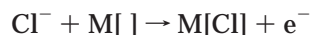
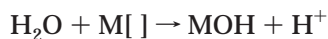
## Case 1. Supporting Electrolyte: Sodium Sulfate.



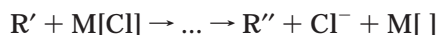
pH = 12



## Case 2. Supporting Electrolyte: Sodium Chloride.



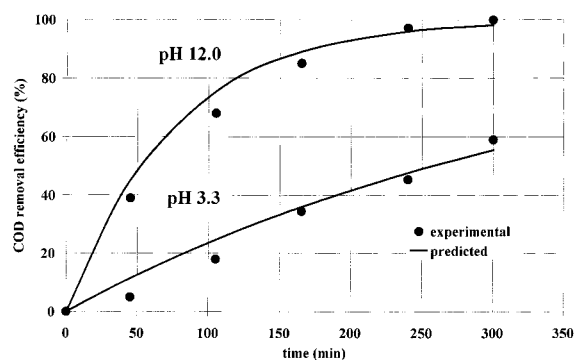
pH = 12



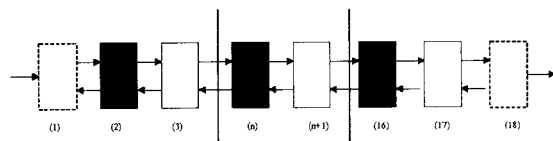
where R = gallotannic acid; R', R'', P = oxidation/degradation products; and M[ ] = active sites of the anode surface.

According to the above mechanisms, without taking into account losses due to the formation of gaseous chlorine and chloride ions, even though they participate in oxidation reactions, the chlorides remain practically constant, as found in previous studies.<sup>9</sup> To simulate the behavior of the pilot plant, already described,<sup>3</sup> a first-order kinetic law with respect to tannin describes the above mechanisms. Of course, the presence of chlorides in wastewater does mirror case 2 reported above. In acid conditions, therefore, the consumption rate of the pollutant may be presumed to be proportional to the product of the concentrations of tannin and oxidation products of  $\text{Cl}^-$ , the latter forming at the electrode. Because the concentrations of these products are functions of current, which remains almost steady throughout the process, it may first be assumed to be incorporated in the kinetic constant.

In alkaline conditions, the direct oxidation of gallotannic acid and its attack by hydroxyl radicals should be taken into account. It has already been mentioned (see Figure 4) that this phenomenon is negligible when compared with attack by "chlorine radicals". Therefore, the above kinetic model may be applied to various values of the kinetic constant, independently of the pH value. Referring to the experiments carried out at pH 3.3 and 12, when the corresponding COD value is substituted for the tannin concentration, Figure 8 shows the good simulation capacity of the first-order kinetic expression, which uses the constants obtained by fitting the experimental data.



**Figure 8.** COD removal efficiency during electrolysis of gallotannic acid (2 g/L). Comparison of experimental data and theoretical curves at various pH values. Experimental conditions as in Figure 5.



$$\begin{cases} \text{inlet cell} & 0 = \dot{V}C_0 + \beta \dot{V}C_2 - \dot{V}(1 + \beta)C_1 & n = 1 \\ \text{anodes} & K \dot{V}_r C_n = \dot{V}(1 + \beta)C_{n-1} + \beta \dot{V}C_{n+1} - \dot{V}(1 + 2\beta)C_n & n = 2, \\ \text{cathodes} & 0 = \dot{V}(1 + \beta)C_{n-1} + \beta \dot{V}C_{n+1} - \dot{V}(1 + 2\beta)C_n & n = 3, \\ \text{outlet cell} & 0 = \dot{V}(1 + \beta)C_{n-1} - \dot{V}(1 + \beta)C_n & n = 18 \end{cases}$$

$C_n$  = tannin concentration in the  $n$ -th cell,  $\text{mol cm}^{-3}$

$C_0$  = initial tannin concentration,  $\text{mol cm}^{-3}$

$\dot{F}$  = backflow rate,  $\text{cm}^3 \text{s}^{-1}$

$K$  = kinetic constant,  $\text{s}^{-1}$

$\dot{V}_r$  = reactor volume,  $\text{cm}^3$

$\dot{V}$  = volumetric flow rate,  $\text{cm}^3 \text{s}^{-1}$

$\beta = \frac{\dot{F}}{\dot{V}}$  = backflow ratio, adim

**Figure 9.** Backflow cell model: diagram of reactor and balance equations. Black cells: anodic zones. White cells: cathodic zones. Dotted cells: inlet and outlet sections.

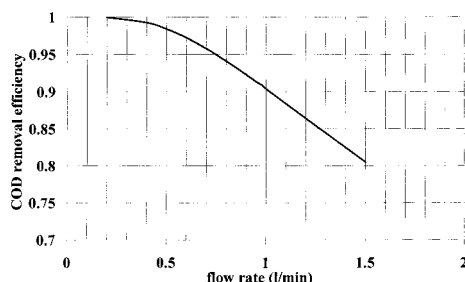
**Table 2. Details of RPC Reactor and Operating Conditions**

reactor length (m)	0.97
interelectrode gap (m)	0.05
flow area ( $\text{m}^2$ )	0.889
no. of cells	17
amplitude (m)	0.001
frequency (rpm)	120
$\beta$ factor	0.25
initial tannin concentration ( $\text{mol m}^{-3}$ )	77.62
pH of solution	12
kinetic constant ( $\text{min}^{-1}$ )	0.004

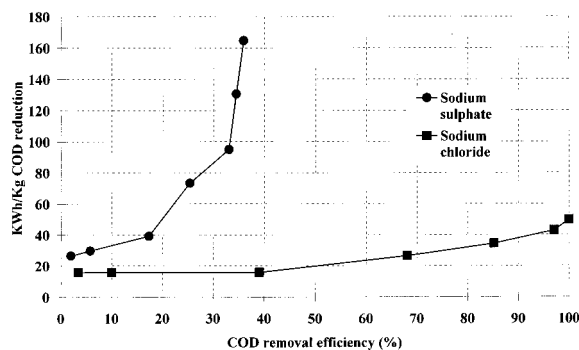
Pilot-plant simulation was carried out using the "backflow cell model".<sup>4</sup> Figure 9 shows the adopted scheme and respective balance equations of the reference substance for each reactor zone. Table 2 lists the working conditions of an example of application. Fluidodynamic parameters were quantified in a previous work by the same authors on the same reactor.<sup>11</sup>

Figure 10 shows simulation results as a function of the COD reduction which can be obtained in the pilot plant by varying the feed rate. These results are extremely encouraging, considering that this was a

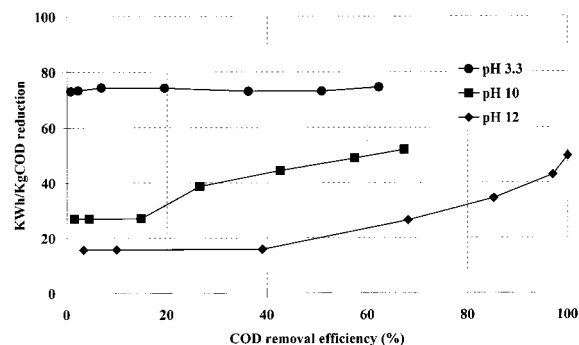




**Figure 10.** Backflow cell model: predicted COD removal efficiency against feed rate.



**Figure 11.** Effect of the type of supporting electrolyte on the specific mean energy consumption. Experimental conditions as in Figure 4.



**Figure 12.** Effect of pH on the specific mean energy consumption. Experimental conditions as in Figure 5.

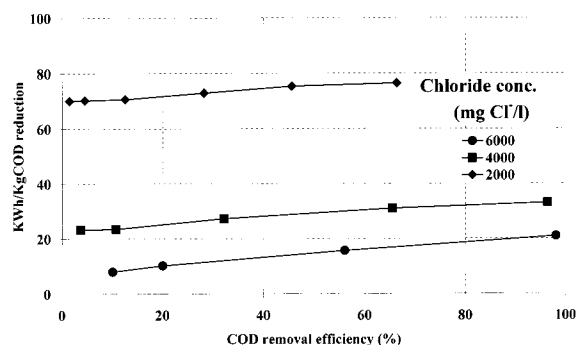
preliminary study on a pilot plant not yet optimized in regards to electrode type and geometry.

Because the application of electrochemical processes to wastewater treatment on an industrial scale is often limited by running costs, some evaluations of energy consumption were carried out. These values do not take into account electrical yields and are used in the form of "specific mean energy consumption", defined as the ratio between the quantity of energy consumed from the beginning of electrolysis for each value of the yield reached and the amount of COD removed.

To consider the effect of the type of supporting electrolyte used, comparative tests were carried out using sodium chloride versus sodium sulfate. Test results in actual alkaline conditions (pH = 12) were considered, because sodium sulfate did not cause any removal of COD at lower pH values.

Figure 11 shows that not only does the presence of chlorides in solution produce greater yields (application time being equal) but also energy consumption is lower (yields being equal).

Figure 12 shows the effect of pH in tests carried out using sodium chloride as the support electrolyte.



**Figure 13.** Effect of the chloride concentration on the specific mean energy consumption. Experimental conditions as in Figure 6.

Clearly, with increasing pH, not only are yields higher but also, degree of removal being equal, energy consumption is greatly lowered.

Figure 13 shows how, if the concentration of sodium chloride in solution is varied, the high salinity improves yields and lowers energy consumption (application time being equal). If the concentration of chloride in solution is increased by 3 times, energy consumption falls by about 4 times (yields being equal).

The considerable effect exerted by supporting electrolyte concentration on tannin reduction is especially favorable for applying this treatment to tannery wastewater which, as already mentioned, contains sodium chloride at concentrations which are much higher than those considered here.

This study on applying electrochemical processes to removal of tannins from wastewater was concluded by preliminary experiments carried out by combining oxidation and electrocoagulation processes.

First, the effect of chemical coagulation alone was tested, using tannin acid solutions (2 g/L) with added  $\text{FeCl}_3$  (120 mg/L) and NaOH up to a pH value favorable for the coagulation process (pH = 10).<sup>12</sup> The solution turned violet because of the formation of metal-organic complexes, and no slurry formed. In the same conditions, a series of tests was then carried out using an electrochemical cell with AISI 316L steel electrodes (agitation level = 100 rpm), applying a potential (1.1 V) ensuring stainless steel transpassivation but not chloride oxidation. Iron ions were found in solution, but no appreciable flocculation or removal of tannins occurred.

Last, a conclusive series of tests was carried out increasing the potential applied to 1.8 V, to obtain contemporary oxidation of both chlorides and water. In this case, a slurry did form, brought to the surface by nascent gases. After about 45 min of electrolysis, the solution showed no appreciable UV-vis absorption. COD values fell by more than 90%.

A comparison between the above tests indicated that when the tannin is, even partially, electrochemically oxidized, significant COD removal efficiency may be obtained by a coagulation process.

## Concluding Remarks

Aimed at removal of tannins from tannery wastewater, various experimental analyses examined phenomena occurring during the electrochemical processes of direct oxidation, indirect oxidation, and electrocoagulation. Results revealed aspects which, after further

study, will allow practical application of the treatment to industrial wastewater.

Analyses carried out using laboratory equipment showed that (i) only at actually alkaline pH can direct oxidation of tannins be achieved, but yields, expressed in terms of COD, are not appreciable in the working conditions considered; (ii) the effect of indirect oxidation by "hydroxyl radicals" is significant in very basic solutions (pH = 12), reaching yields of 40% in only a few hours; (iii) indirect oxidation by "chloride radicals" is significant, in both acid and basic solutions; (iv) the effect of pH during indirect oxidation by "chloride radicals" is considerable, allowing yields ranging from 60% to about 100%, application times being equal; (v) the effect of the concentration of chlorides in solution is strong: at values varying from 2000 to 6000 mg/L (application times being equal), yields of about 4 times higher may be obtained; (vi) in favorable although not optimal working conditions, energy consumption is competitive with that of alternative but less efficient chemicophysical processes; (vii) simulations carried out using experimentally determined parameters showed that the pilot plant considered in this work can remove tannins up to the legal thresholds for discharge; and (viii) electrocoagulation can lead to considerably lower application times and energy costs. Of fundamental importance here is how working conditions are defined: single phenomena are ineffectual, while the combination of direct oxidation, indirect oxidation, and electrocoagulation allows the complete removal of COD.

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