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Removal of vegetal tannins from wastewater by electroprecipitation combined with electrogenerated Fenton oxidation

B. BOYE[1], G. FARNIA[1,*], G. SANDONÀ[1], A. BUSO[2] and M. GIOMO[2]
[1]*Dipartimento di Scienze Chimiche, Università di Padova, Via Marzolo 1, 35131, Padova, Italy*
[2]*Dipartimento di Principi e Impianti di Ingegneria Chimica "I. Sorgato", Università di Padova, Via Marzolo 9, 35131, Padova, Italy*
*(*author for correspondence, e-mail: G.Farnia@chfi.unipd.it; fax: +39-049-827-5135)*

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Abstract

Synthetic solutions containing up to 2000 ppm of gallotannic acid and real wastewater from vegetal tanning processes with values of chemical oxygen demand (COD) exceeding 100 000 ppm were decontaminated by electrolysis using a sacrificial iron anode coupled to either a titanium-platinised or an O_2-diffusion cathode. Experiments were performed in the presence of oxidants and oxidation promoters such as air, oxygen and hydrogen peroxide, the latter being directly added to the solution or electrogenerated by the O_2-diffusion cathode. COD and UV-visible absorbance evolution showed that tannins are removed from electrolysed solutions down to relatively low values, permitting more than 94% elimination. Partial oxidation of the mother compound generates short-chain by-products (mostly carboxylic acids) responsible for the remaining low COD values. Contaminants (tannins and non-tannins) contained in industrial wastewater were removed by combining electroprecipitation with a Fenton-assisted process; a final oxidation step, carried out on a boron-doped diamond electrode, was performed in order to decrease the COD to very low final values.

1. Introduction

Natural and synthetic tannins are widely used in vegetal tanning processes and further expansion of their use in mixed tanning processes involving chromium is expected. Traditional biological methods of wastewater treatment are inefficient in destroying biorefractory tannins, whereas more sophisticated methods, including electrochemical ones, are not advantageous, due to their high cost and low efficiency, as observed during mineralisation by indirect electrochemical oxidation. Complete removal of contaminants from wastewater constitutes a great challenge.

The scarcity of water resources and their contamination are becoming a concern. Existing regulations and norms covering wastewater [1] cannot completely avoid pollution of surface and ground water.

Many methods are currently applied in treating wastewater from tanning processes. For instance, $K_2Cr_2O_7$-based chemical oxidation gives tri-nuclear complexes of Cr(III) containing OH- and O_2-bridge and pyruvate ion ligand [2]. Chemical methods, while offering complete oxidation, have the inconvenience of generating by-products even more toxic than the mother ones. Results obtained with high-temperature (supercritical) oxidation in sea-water [3] or the removal of sulphides (wet-air oxidation) [4] from tanning effluents have given COD and TOC removal values lower than 90%, although sulphides or other inorganic contaminants are eliminated to a high degree. Physico-chemical methods based on processes like adsorption on bentonites, zeolites, or other gel adsorbents and polyelectrolytes [5–9], sedimentation, coagulation, flocculation and flotation with alum and lime seem to be mainly used for removing tannins or other contaminants like lead or chromium from industrial tannery wastewater [10–13]. Ozone, hydrogen peroxide and UV light are also used as oxidising agents of tanning wastewater [14–18]. When used together, their combination is more efficient than single oxidation methods [19]. Pulse radiolysis has also recently been used in the process of tannin oxidation, although it was principally aimed at proving the antioxidant characteristics of gallic acid (a component of gallotannic acid), which reacts with the adducts generated from its attack by OH radicals, to give quite stable phenoxy radicals [20].

Electrochemical methods have been reported to perform appreciably in treating tanning wastewater, but their application depends to a great extent on the energy cost of the proposed method. Independently of this non-insurmountable barrier, works have been reported concerning removals of up to 99% COD by short-time electrolysis [21–25]. Peroxicoagulation using iron as sacrificial anode coupled with an O_2-diffusion cathode has shown good efficiency in removing herbicides from aqueous solutions [26–28]. The same iron used as cathode allows the total elimination of ammonia, with appreciable COD reduction [25].

We recently reported the complete elimination of gallotannic acid from solutions containing chlorine ions, by means of indirect electrolysis with a titanium-platinised electrode [29].

The present work deals with electrochemical removal, by means of iron sacrificial anodes, of gallotannic acid from aqueous solutions containing chloride ions, simulating the behaviour of industrial effluents. Furthermore, experiments were performed on real wastewater containing both tannins and non-tannins as pollutants, in order to investigate the combination of the precipitating capacity of iron ions with respect to tanning compounds with the degradation power of electrogenerated Fenton reagent, since this should result in the efficient and complete removal of all pollutants present in treated solutions.

2. Experimental

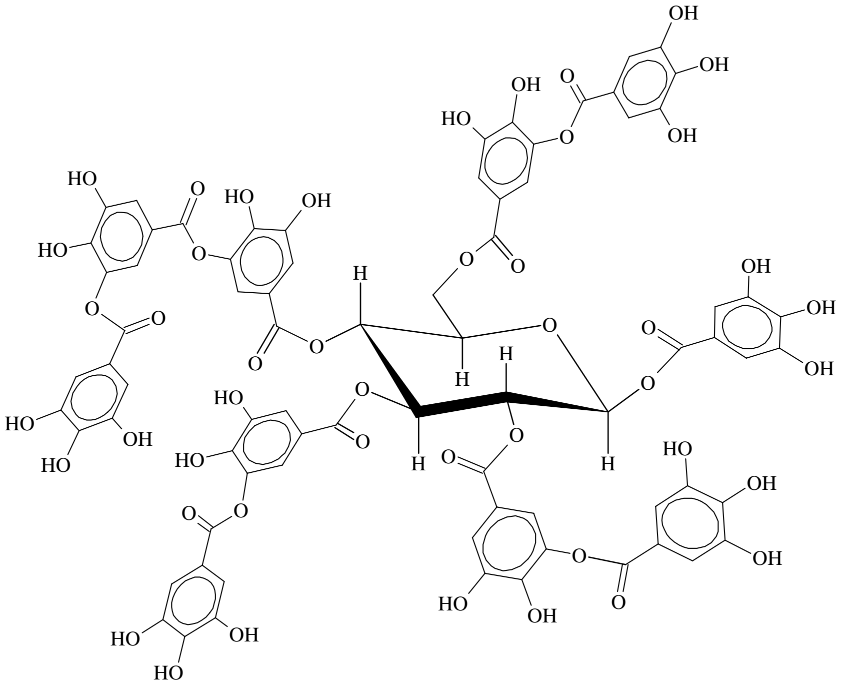
2.1. *Chemicals*

Gallotannic acid, hydrogen peroxide, Fe(II) sulphate and electrolyte reagents such as KCl and H_2SO_4 were purchased from Fluka at purity higher than 98%. Normal paper filters were used for sample filtration to determine absorbance, COD or TOC evolution during electrolysis. Double-distilled water was used in all cases. Industrial wastewater was obtained from a local vegetal tanning enterprise, and presented the following characteristics: COD ca. 100 000 ppm, TOC ca. 32 000 ppm, tannins ca. 2.0%, non-tannins (mainly proteins) ca. 5.0%, material in suspension ca. 0.1%, in a darkish-brown solution.

2.2. *Apparatus and equipment*

Experimental measurements were performed, at room temperature, in an undivided laboratory cell batch with solution volumes of 200 and 400 ml, at current intensities of 80 and 1500 mA respectively for synthetic and real wastewater. Gallotannic acid (0.5 to 2.0 g l^{-1}) solutions containing 2.0 g l^{-1} of Cl^- ions (as KCl) were used as synthetic wastewater. There was no need to add a supporting electrolyte to treat the industrial effluents, since they had a sufficient specific conductivity (ca. 12 mS cm^{-1} at 20 °C). A 3 cm^2 area iron wire and a 10 cm^2 area iron sheet (Steel C40) were used as anodes for synthetic and real wastewater, respectively. A 50 cm^2 area boron-doped diamond (BDD) electrode from CSEM-Neufchâtel (Switzerland) was also used as anode with real wastewater in the final experimental stage. Titanium-platinised (Ti–Pt) grids or O_2-diffusion electrodes (ca. 2.5 cm^2 area) [30, 31] were used as cathodes.

Electrochemical experiments were performed using a Princeton Applied Research (PAR) Model 173



Structure of Gallotannic acid

Scheme 1.

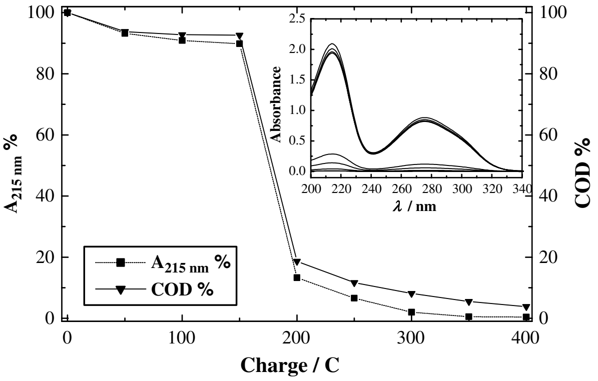


Fig. 1. Removal of gallotannic acid by electroprecipitation during air-exposed electrolysis with Fe anode and Ti–Pt cathode: percentile decrease of UV-vis absorbance at 215 nm and of COD values. Volume of solution 200 ml; initial concentration of gallotannic acid 2 g l^{-1}; $i_{Fe} \cong 30$ mA cm^{-2}; initial pH 3.3; final pH 7.4. Inset: progressive decrease of absorption spectra of solution during electrolysis, after charges indicated by experimental points, from 0 to 350 C.

potentiostat-galvanostat, equipped with a PAR Model 179 digital coulometer and a PAR Model 175 Universal programmer.

UV-visible spectra were recorded on a Perkin–Elmer lambda 20 spectrophotometer driven by UV Winlab software.

COD was measured on a HACH Water Analysis System. Total organic carbon (TOC) was measured on a Shimadzu 5050 TOC analyser.

2.3. *Methods of analysis*

UV-visible spectrophotometric measurements were performed on initial and electrolysed solutions, after filtration, appropriate dilution and pH adjustment to 2.0. COD values of filtered and suitably diluted solutions were determined during electrolysis after digestion of 2 ml-samples for 2 h at 150 °C. TOC values were determined, in some cases, for the initial and final wastewater and for the obtained precipitates.

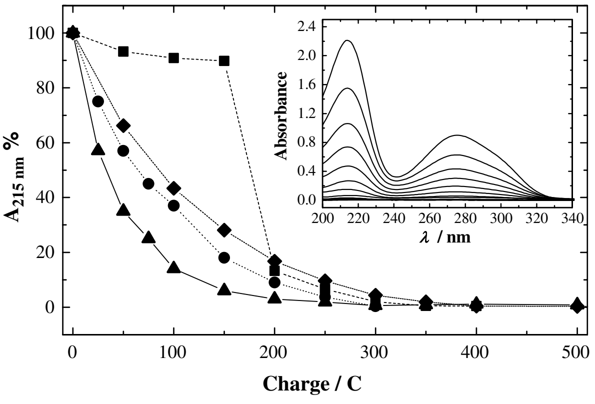


Fig. 2. Decay of percentile absorbance at 215 nm of gallotannic acid solutions during electrolyses with Fe anode and Ti–Pt or O_2-diffusion cathode, carried out in air (■), under oxygen bubbling (●), or in presence of added (◆) or electrogenerated (▲) H_2O_2. Volume of solution 200 ml; $i_{Fe} \cong 30$ mA cm^{-2}; initial concentration of gallotannic acid 2 g l^{-1}; $i = 80$ mA; initial pH 3.3, final pH varying between 2.2 and 7.5. Inset: progressive decrease of absorption spectra during electrolysis in presence of added H_2O_2, after charges indicated by experimental points, from 0 to 500 C.

3. Results and discussion

3.1. *Synthetic wastewater*

Preliminary voltammetric and coulometric measurements carried out in chloride-containing solutions, in both the presence and absence of gallotannic acid, showed that, at the current density experimentally applied during electrolyses, the anodic dissolution process of iron in de-aerated solutions quantitatively generates Fe(II) ions, as expected. Macroscale electrolyses of gallotannic acid de-aerated solutions, performed with an Fe anode and a Ti–Pt cathode, at pH range 3–7, gave a pale greenish-blue colour which, after exposure to free air, changed to intense blue, with the later formation of a dark precipitate composed of complexes of gallotannic acid and Fe(III). Similar electrolyses were performed, at initial pH 3.3, operating in different oxidation conditions of electrogenerated Fe(II): (a) in exposure to air; (b) with bubbled oxygen; in the presence of (c) added or (d) electrogenerated hydrogen peroxide. In all cases, a blue colour was immediately observed, becoming more intense as electrolysis continued, and was then followed by the formation of a black precipitate.

Figure 1 illustrates the progressive percentile decrease of both COD and absorbance corresponding to the maximum of the highest absorption peak of gallotannic acid (215 nm), during air-exposed electrolysis. It is noteworthy that quick breakdown occurs at a Fe(III)/tannin molar ratio between 4 and 5. The insert in Figure 1 shows the evolution of the absorbance of filtered solutions with electrolysis time.

When electrolyses were carried out in the presence of bubbled oxygen or H_2O_2, quicker decreases in both absorbance (see Figure 2) and COD percentile values

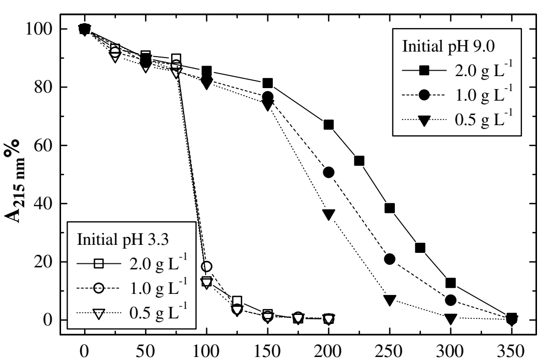


Fig. 3. Removal of gallotannic acid during air-exposed electrolyses with Fe anode and Ti–Pt cathode, at different initial gallotannic acid concentrations and pH values (see insert). Volume of solution 200 ml; $i_{Fe} \cong 30$ mA cm^{-2}.

were observed. Hydrogen peroxide was added step by step in amounts corresponding to those that might have been electrochemically generated if the O_2-diffusion cathode had been used. Absorbance decrease was quicker when hydrogen peroxide was progressively generated *in situ* by the diffusion electrode (Figure 2). This behaviour may be due to slight degradation of H_2O_2 when electrochemically generated, as a result of the greater homogeneity of its concentration in the bulk of the solution during electrolysis.

In each probe, the absorbance and COD percentile decrease substantially showed the same behaviour (see, e.g., Figure 1), although a relatively low but significant COD value (3–6% of the initial value, depending on the case) was found in the analysed solutions at the end of electrolysis, whereas the spectrophotometric results excluded the presence of either gallotannic acid or other species susceptible to significant absorption in the UV-visible region.

The data indicate that: (*i*) the principal process is composed of the precipitation of complexes of gallotannic acid and Fe(III), the latter generated *via* chemical oxidation of electrogenerated Fe(II) by oxygen or hydrogen peroxide; (*ii*) the low COD values observed at the end of the experiments are due to the fact that oxidation of Fe(II) by both H_2O_2 and O_2 generates radical species (such as $OH^\bullet$ and $O_2H^\bullet$) which react with contaminants, yielding organic products that are not detectable by UV-visible spectrophotometry; (*iii*) the total charge necessary for complete removal of gallotannic acid by electroprecipitation is, in the worse case (air-exposed experiments), less than 6% of that theoretically required for complete mineralisation (*i.e.*, transformation to CO_2 and H_2O) of the starting substrate by electrochemical oxidation, which implies the consumption of ca. 15 000 C g^{-1} of gallotannic acid; (*iv*) the quick breakdown of absorbance and COD observed when experiments were performed under air exposure (see Figure 2) is presumably due to the fact that slow dissolution of oxygen implies the more gradual growth of the solid particles of insoluble complexes, which reach almost contemporarily the appropriate dimensions for separation by filtration, in both acidic and basic conditions (see Figure 3); (*v*) the required charge is approximately proportional to the initial tannin concentration in both acidic and basic conditions, as may be noted, for instance, in Figure 3 for the experiment performed at air exposure; (*vi*) a higher charge, and hence a higher amount of dissolved Fe, is required in basic solutions to eliminate gallotannic acid (see, e.g., Figure 3), due to the competitive formation of Fe hydroxides; (*vii*) partial oxidation of the mother compound at the electrode or, in solution, by Fe(III) and/or radicals forming during the reaction between iron ions and H_2O_2 or O_2, can generate short-chain carboxylic by-products (mostly oxalic acid), responsible for the remaining low COD values.

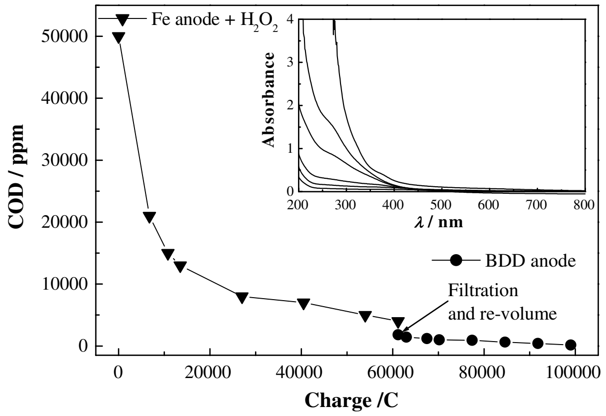


Fig. 4. Decay of COD of real wastewater solutions diluted at 50%, during electrolysis with Fe anode and Ti–Pt cathode in presence of H_2O_2 (▼), followed by anodic oxidation on BDD (●). Experimental conditions: volume of solution 400 ml, initial pH 3.0; final pH ca. 4; $i_{\mathrm{Fe}} = 150$ mA cm^{-2}; $i_{\mathrm{BDD}} = 30$ mA cm^{-2}; $[H_2O_2]_{\mathrm{initial}} = 2.0$ M. Inset: progressive decrease of absorption spectra during electrolysis with Fe anode, after charges at 0, 13 500, 27 000, 40 500, 54 000 and 61 200 C.

3.2. *Real wastewater*

Preliminary experiments were carried out on real wastewater with a COD value of at least 100 000 ppm, using Fe anodes and Ti–Pt cathodes, under air exposure. A decrease of about 40% of the starting COD values was observed after the consumption of about 54 000 C l^{-1}, corresponding to ca. 800 C g^{-1} of tannins and non-tannins. The residual solution obtained after the filtration of a black precipitate was even darker. This indicates that the electroprecipitation process alone can significantly reduce the COD of wastewater, but both obtained precipitate and final solutions need further treatment for complete removal of pollutants.

Consequently, similar experiments were performed on wastewater in the presence of hydrogen peroxide. Since preliminary tests had indicated that the O_2-diffusion cathode used here produced H_2O_2 in amounts smaller than those necessary to eliminate organic pollutants completely from real wastewater, all further experiments were performed in the presence of added hydrogen peroxide, introduced in a single dose, in order to achieve an initial concentration of 2.0 M. The results are illustrated in Figure 4 for industrial wastewater after 50% dilution.

In the earlier steps of the experiment, the electrochemical process was accompanied by a rapid increase in temperature, from ambient to near 80 °C, and a considerable evolution of gas. Both effects are attributed to the highly exothermic mineralisation process (2), which involves the reaction between organic substrates and OH radicals generated by reaction (1).

$$\mathrm{Fe(II)} + H_2O_2 \xrightarrow{H^+} \mathrm{Fe(III)} + OH^\bullet + H_2O \qquad (1)$$

$$\text{organic substrates} \xrightarrow{OH^\bullet,\,H^+} \ldots \xrightarrow{OH^\bullet,\,H^+} CO_2 + H_2O \qquad (2)$$

The occurrence of this highly exothermic reaction (2) (formally a combustion process) was indicated by the low amount of carbon contained in the both final solution and precipitate (see below) and by the detection (*via* absorption on a barium hydroxide solution) of CO_2 evolution during electrolysis. However, a competitive exothermic disproportion reaction of H_2O_2 ($\Delta H = -98$ kJ mol^{-1}) cannot be excluded. This process generates H_2O and O_2 (the latter also being an oxidising agent) and is partially responsible for the increase in temperature (together with the Joule effect) and gas evolution.

Figure 4 shows COD decay during electrolysis of industrial wastewater diluted to 50% (COD ca. 50 000 ppm, TOC ca. 16 000 ppm) and the evolution of the corresponding UV-visible absorption spectra of the electrolysed solution (after filtration and 1:100 dilution of the sample). Aromatic compounds, which are detectable by their absorption capacity in the UV-visible zone, were not found in the bulk electrolytic medium after a specific charge of ca. 30 000 C l^{-1}. The removal of 80% of the initial COD required a specific charge of ca. 40 000 C l^{-1}. After application of a specific charge of ca. 150 000 C l^{-1}, COD abatement was slightly more than 95%.

To reduce the remaining COD, direct oxidation of the obtained filtered solution (yellow) was then attempted on a BDD anode (see Figure 4). The almost complete removal of COD (final value ca. 150 ppm) and organic carbon (TOC = 36 ppm) required the consumption of a specific charge of 100 000 C l^{-1}, the final solution being colourless, with a pH close to neutral.

HPLC and spectrophotometric analysis of the electrolysed solution principally showed the formation of oxalic acid as main intermediate, especially after the first 5 h of electrolysis. Oxalic acid is in fact a substrate generally detected during the degradation of organic substrates *via* the electro-Fenton process [26–28].

The red precipitate obtained after electrocoagulation with the iron anode (80 g l^{-1} of wastewater) contained about 50% of Fe and only 0.65% of organic carbon, and was composed of Fe(III) oxides, mainly in their goethite form and, in some instances, of ferro-oxalate complexes [26–28]. This means that the organic part of the Fe-tannin precipitates obtained in the first steps of the electrolyses is oxidised *via* the Fenton process.

Analogous experiments, performed on real wastewater without initial dilution (COD ca. 100 000, TOC ca. 32 000) after the consumption of 270 000 C l^{-1}, (190 000 C l^{-1} with Fe anode and 80 000 C l^{-1} on BDD) showed similar behaviour. The final solution was colourless and had COD and TOC values around 200 ppm and 50 ppm respectively. The red precipitate (125 g l^{-1} of wastewater) contained about 50% Fe and about 1.0% organic carbon.

4. Conclusions

It has been shown that complete removal of gallotannic acid from synthetic wastewater solutions over a large range of pH can be successfully achieved by electroprecipitation using Fe anodes, with the consumption of a relatively low charge. It is noteworthy that this process is even more efficient both when oxygen is bubbled into the solution, contributing to the increase of the liquid-gas surface contact, and when H_2O_2 is added or electrogenerated.

With real effluent, electroprecipitation alone is not efficient, whereas its combination with the Fenton process (peroxicoagulation) ensures practically complete removal of both tannins and non-tannins, with a relatively low specific charge.

Final abatement of COD and TOC up to 99.8% of the initial value can be achieved with a BDD anode, but efficiency is very low, due to water discharge.

These results indicate that optimised electroprecipitation with added or electrogenerated H_2O_2 would be a suitable means of decontamination of concentrated effluents at the end of industrial tanning. The application of such an electroprecipitation method would allow re-circulation of usually treated technological water in shorter times compared with those resulting from biological or physico-chemical methods.

Further studies focusing on the formed precipitates would also allow them to be re-used in coagulant- and flocculant-manufacturing technology, which would make electroprecipitation an environmentally-friendly, waste-free technique for water and wastewater treatment.

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