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Tannery wastewater treatment by electro-oxidation coupled with a biological process

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Abstract

The paper is aimed at defining the best option of a combination of electrochemical and biological processes for tannery wastewater treatment. Kinetic data for the electrochemical process are derived from an extensive experimental study, while those relating to biological processes are taken from the authors' previously published studies or from the literature. Four different options based on a combination of electrochemical oxidation and biological treatment are defined and compared with the traditional tannery wastewater treatment with respect to the total required volume, energy need and the quantity of generated sludge.

1. Introduction

The majority of treatment plants for tannery wastewater are based on the biological activated sludge process. In Europe, where stringent limits for nitrogen have to be observed, a commonly applied treatment scheme for tannery wastewater is based on biological methods comprising nitrification–denitrification, sometimes preceded by chemical pre-treatment, generating huge quantities of sludge, particularly when high strength wastewater is treated [1]. Biological nitrification often suffers inhibition [2] as nitrifying bacteria are sensitive to many organic compounds and metal ions [3]. For this reason it is pertinent to investigate other, more reliable, methods to solve pollution problems associated with the tannery industry.

One of the possible alternatives to biological nitrification/denitrification is the use of electrochemical processes which are gaining popularity for industrial wastewater treatment. They have proved efficient in destroying a variety of pollutants found in tannery wastewater: ammonia [4], nitrites [5], benzoquinone [6], benzene [7], phenols [8, 9], chlorophenols [10], formaldehyde [11] and alcohols [12]. Studies on electrochemical oxidation of tannery wastewater [13–16] demonstrated the feasibility of this process to substitute biological nitrification, but data are presently insufficient to define a reliable alternative to biological processes. Among several anodes tested, Ti/Pt–Ir proved the most efficient for the removal of ammonia from tannery wastewater. While evaluating the feasibility of application of electrochemical oxidation for industrial wastewater it should be considered that the feed to the reactor will comprise a cocktail of several pollutants, for which the initial and target concentrations differ, which implies achieving different conversions for each contaminant. The individual values of the kinetic constants are insufficient to define the best treatment strategy and a thorough analysis of the whole process, including its layout and the running costs of single units, is necessary. To have a better insight on the issue of combination of electrolysis with a biological technology it is necessary to consider how, by inserting electrolysis in different process schemes, the total energy requirements can be modified (in biological units energy is needed to ensure sufficient mixing and/or an adequate aeration of a biomass), along with the global plant volume (considering both the biological and electrochemical sections) and the quantity of generated sludge. Since the kinetics of the electrochemical process are about 100-fold faster than biochemical oxidation, by using a combination of the two techniques a substantial saving in plant volume can be expected. It can also be foreseen that, as no solids are produced in electro-oxidation, adding this process to the treatment scheme would give the benefit of a decrease in the total quantity of sludge to be handled and disposed.

This paper addresses the analysis of several possible technological schemes to treat tannery wastewater, combining electrochemical and biological processes. In each of them the objective of the electrochemical process is to eliminate ammonia in excess to the requirements resulting from the mass balance for the biological treatment. Electrochemical incineration of organic pollutants of tannery wastewater is considered as a side-effect and is given less attention, since these pollutants are easily biodegradable. For each of the proposed layouts of a hypothetical plant treating wastewater of 1000 m^3 day^{-1} flow, volumes required by electrochemical and biological units are computed, along with their energy need and the quantity of generated sludge. Such an integrated approach of electrochemical and biological processes has not yet been proposed and is intended to give a contribution for implementation of electrochemical processes to solve industrial pollution problems.

2. Materials and methods

The wastewater used in the study was collected at the Common Effluent Treatment Plant of Ranipet (India), in which about 400 small tanneries, based on both chrome and vegetable tanning, discharge their raw effluent. Three types of samples of tannery wastewater, characterised by a different degree of pollutant removal, were subjected to electrolysis: raw tannery wastewater after equalisation and settling, wastewater after anaerobic treatment and wastewater after aerobic treatment, sampled from secondary clarifier.

A schematic view of the experimental set-up is depicted in Figure 1. The undivided electrochemical reactor (0.15 m × 0.06 m × 0.205 m, 1.4 l working volume) was made of glass and was equipped with a cathode and anode arranged in parallel. As cathode a 316 stainless steel plate was used. The anode consisted of a 0.1 × 0.1 m Ti/Pt–Ir plate. Among the electrode materials known for their electrocatalytic properties towards chlorine evolution (metallic Pt, graphite, Ti/Pt obtained by galvanic or thermal procedures, RuO_2 and TiO_2) the Pt + Ir coating, developed in 1975 by Atanasoski et al. [17] is the one that assures good performance over a wide range of pH values and combines durability of the metallic Pt and a high electrocatalytic activity of TiO_2. The IrO_2 oxide present in the coating is, after RuO_2, the more active electrocatalyst for chlorine evolution, and is superior to it regarding resistance under anodic polarisation, particularly under alkaline conditions. The composition: 70% Pt + 30% of Ir (molar percentage) was chosen as, for lower quantities of Ir, the electrocatalytic properties of the electrode diminish, while for higher quantities the mechanical properties (in particular adherence of the coating) get worse. The anode was obtained by brush painting (thirty layers) of a water–methanol solution of H_2PtCl_6 and $IrCl_4$, intermediate (every second layer) drying at 350 °C and final drying at 530 °C. A semi-quantitative X-ray analysis of the electrode surface revealed the presence of a bi-metallic mixture of Pt and Ir, along with IrO_2 and PtO_2 and some trace quantities of TiO_2, that indicates that the Ti plate used as a supporting surface was oxidised marginally. The final drying of the electrode under high temperature leads to sintering of the surface, that causes the coating to be more compact and resistant to erosion. A negative impact of high temperature is observed only on exceeding 600 °C, under which the TiO_2 layer thickness increases significantly and can become an isolator or, at higher temperatures, cause exfoliation.

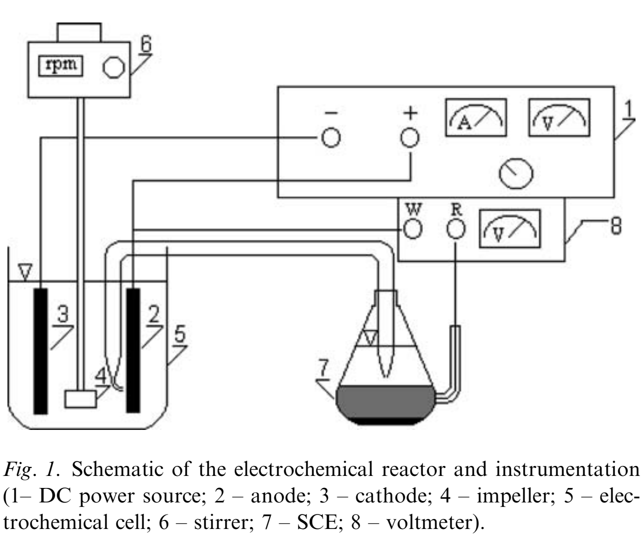

Fig. 1. Schematic of the electrochemical reactor and instrumentation (1– DC power source; 2 – anode; 3 – cathode; 4 – impeller; 5 – electrochemical cell; 6 – stirrer; 7 – SCE; 8 – voltmeter).

Experiments were carried out under galvanostatic conditions at two current densities (c.d.) of 200 and 400 A m^{-2}, using a DC stabilised power source (DD Associates, India), while the anode potential was measured against a home-made saturated calomel reference electrode (SCE) in a Luggin capillary probe, using a high impedance voltmeter (Keithley 169 Multimeter). Mixing was performed by a mechanical stirrer, using a glass paddle at 8 Hz.

Changes in COD, TOC, S^{2-}, Total Kjeldahl Nitrogen (N-TKN), $N\text{-}NH_3$, Cr, chlorides, pH and conductivity were regularly monitored with a frequency of sampling varying as a function of the applied current density and the initial concentration of pollutants. The concentration of N-TKN was obtained after distillation of the digested sample (performed by boiling under strongly acidic conditions for 30 min once all organic compounds were mineralised, a condition indicated by clarity and transparency of the sample), and an analysis of the ammonia content in the trap solution. The detection limit of this method is 1 mg N l^{-1}. Ammonia was determined via Nessler reaction using a Spectronic-21spectrophotometer; TOC was analysed using a Shimadzu TOC-5050A apparatus; pH was monitored by Beckman pH meter and conductivity by WTW conductivity meter (MERCK, Germany). COD, S^{2-} and Cl^- were estimated as per the Standard Methods [18]. Chromium was analysed both as Cr^{6+} and as total chromium, using atomic absorption (Varian AA model 250 plus).

Cyclic voltammetric measurements pertinent to the elucidation of the electrode processes involved in the removal of pollutants were performed using working electrodes of ca. 2 mm^2 surface area and the background electrolyte containing 5500 mg l^{-1} of NaCl.

Cyclic voltammetric tests were performed with and without raw tannery wastewater, using an EG & G PAR model 283A potentiostat–galvanostat, controlled with a PC via EG & G PAR 270 software.

In the second part of the paper, four schemes of combination of electrochemical oxidation conducted in a plug-flow reactor and biological processes are proposed and evaluated, calculating the volumes of single process units, energy requirements and quantities of generated sludge of a hypothetical plant treating wastewater of 1000 m^3 day^{-1} flow. Final concentrations of N-NH_3, COD and S^{2-} to be reached in the plant effluent were assumed equal to, respectively, 15, 160 and 1 mg L^{-1}, according to Italian discharge standards. Operational parameters and kinetic rate constants for the electrochemical reactor are derived from the experimental study described in the present paper. The values of kinetic coefficients for biological processes are taken from previous investigations performed by the authors on tannery wastewater [19–21] and from the literature [22]. The following options are compared: anaerobic treatment of raw wastewater followed by electrolysis, anaerobic pre-treatment followed by electro-oxidation and by an aerobic conventional process (the last aimed at removing any residual COD), electrolysis of raw wastewater followed by a conventional aerobic process and conventional aerobic process, directed towards the removal of COD, followed by electro-oxidation (the last designed to eliminate the remaining nitrogen). The salient characteristics of these schemes are compared with those of a biological single sludge process, which is commonly used at present to treat tannery wastewater.

3. Results and discussion

3.1. *Experimental study of the kinetics of electro-oxidation of tannery wastewater*

Figures 2 and 3 depict trends of normalised N-TKN values during electro-oxidation of the three types of tannery wastewater (whose initial characteristics are shown in Table 1), conducted at, respectively, 200 and 400 A m^{-2} c.d. Figures 4 and 5 show analogous data for COD. After 1 h of electrolysis at 400 A m^{-2} c.d. (passage of 14.4 kC) excellent efficiencies of elimination

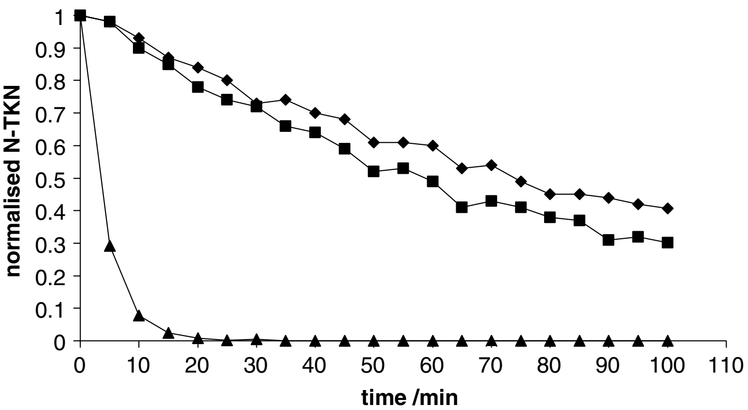

Fig. 2. Normalised N-TKN, c.d. 200 A m^{-2}; ◆ – raw wastewater; ■ – wastewater after anaerobic treatment; ▲ – wastewater after aerobic treatment.

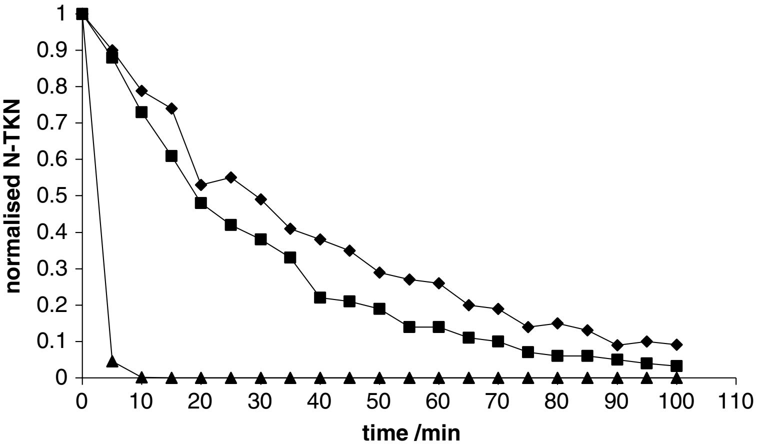

Fig. 3. Normalised N-TKN, c.d. 400 A m^{-2}; ◆ – raw wastewater; ■ – wastewater after anaerobic treatment; ▲ – wastewater after aerobic treatment.

Table 1. Mean characteristics of tannery wastewater undergoing electrolysis

Parameter considered	Mean values of examined parameters (mg l^{-1})*		
	Raw waste	After anaerobic lagoon	After aerobic process
N-NH_3	335	284	22
N-TKN	370	363	39
COD	2426	1250	351
TOC	462	319	84
S^{2-}	286	150	0
Cr_{tot}	29.3	13.0	6.3
Cl^-	5486	5383	4788
pH	7.7	7.7	7.7
Conductivity	18.4	16.7	15.4

*Exception being conductivity/mS cm^{-1} and pH.

of COD and N-TKN were achieved, 70% in the raw wastewater and about 85% in the pre-treated effluents. A particularly high rate of depletion of nitrogen was obtained for the wastewater pre-treated by a sequence of anaerobic–aerobic processes (95% elimination in 5 min). These results confirm previous observations [14, 15] in that the more extensively the wastewater had been pre-treated before electrolysis, the better the efficiency of electrochemical treatment.

Under the conditions of the present study, characterised by a high concentration of chloride ions, two mechanisms can be responsible for the removal of pollutants: direct anodic oxidation and oxidation in the bulk solution, mediated by oxidising species formed *in situ*. In order to obtain information on the electrochemical processes occurring at the anode, a series of cyclic voltammetric experiments were performed, using Ti/Pt–Ir as the working electrode. Figure 6 shows typical cyclic voltammograms obtained in the raw tannery wastewater and in an aqueous solution containing only NaCl as the supporting electrolyte. The potential range explored varied between −1.5 and 1.8 V, in order to include the hydrogen and oxygen evolution processes [23]. From these voltammograms it is evident that a shoulder, conceivably due to chlorine evolution [24], appears before oxygen evolution and no process attributable to direct oxidation is evident, or is not clearly visible due to

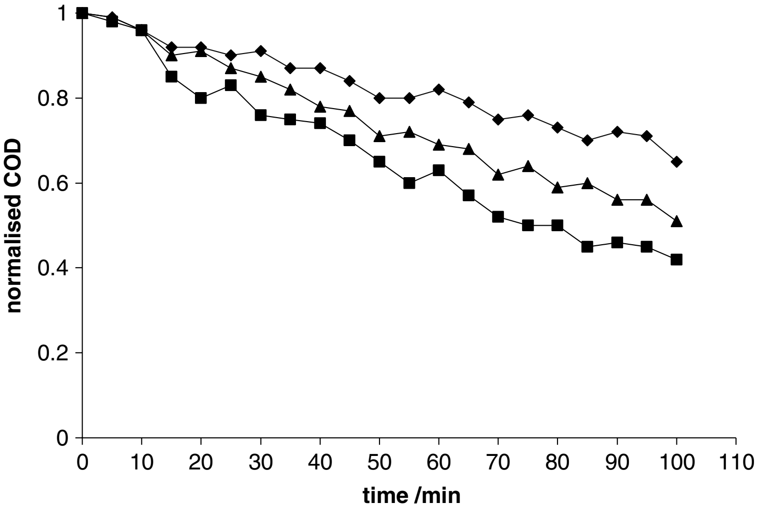

Fig. 4. Normalised COD, c.d. 200 A m^{-2}; ◆ – raw wastewater; ■ – wastewater after anaerobic treatment; ▲ – wastewater after aerobic treatment.

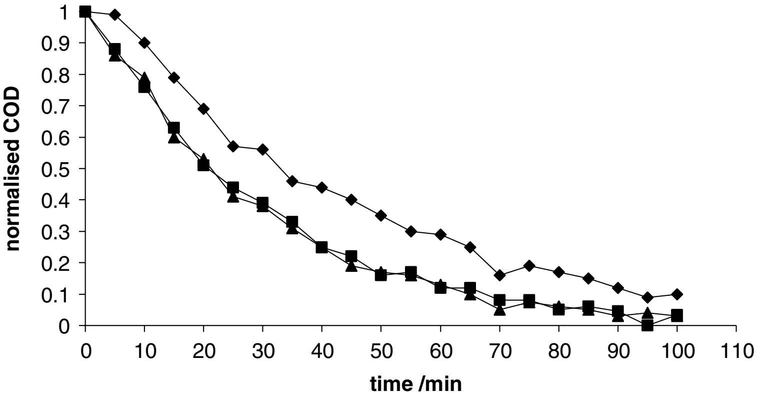

Fig. 5. Normalised COD, c.d. 400 A m^{-2}; ◆ – raw wastewater; ■ – wastewater after anaerobic treatment; ▲ – wastewater after aerobic treatment.

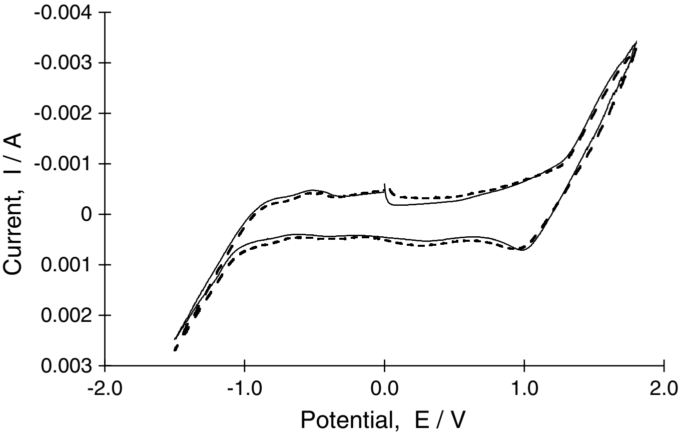

Fig. 6. Cyclic voltammograms recorded at the 4 mm^2 Ti/Pt–Ir electrode over the potential window from −1.5 to 1.8 V without the wastewater (dotted line), and with the addition of the wastewater (solid line).

low concentration of single contaminants. These results support the hypothesis about the involvement of indirect electro-oxidation as the main mechanism of destruction of the pollutants.

At the conditions applied during the experiments the anode potential was equal to 1.8 and 2.3 V, respectively for 200 and 400 A m^{-2} c.d., which is far above the normal potential of chlorine and oxygen evolution typical for solid electrode materials [23]. Thus the oxidation of chloride and water probably occurred, in which active chlorine and oxygen, respectively, are produced, giving surface mediators (e.g. $Cl_{ads}^{\bullet}$ or $OH_{ads}^{\bullet}$), which participate in indirect electrochemical oxidation of pollutants. A direct link between the mechanism of the chlorine evolution reaction and the oxygen evolution reaction has been postulated by Bonfanti et al. [25]. As the result of this interaction a decrease in anode potential takes place, due to the potentiostatic buffering by the chlorine evolution reaction.

To explain the removal of the pollutants it was hypothesised that various forms of chlorine were the predominating oxidising species. This assumption is particularly pertinent regarding the elimination of ammonia, the mechanism of which would be similar to the "break-point" chlorination, as discussed in [14]. In fact, direct oxidation of ammonia proceeds at observable rates only under very alkaline conditions, when free N-NH_3 is present [4] and cannot be expected under the conditions of the present study, in which the bulk solution pH was neutral. The production of chlorine occurs subsequent to the surface reaction of electrochemical oxidation of chloride ions at the anode:

$$2Cl^- \leftrightarrows Cl_2(el) + 2e^- \tag{1}$$

$$Cl_2(el) \rightarrow Cl_2(sol) \tag{2}$$

Chlorine formed at the electrode (Cl_2(el)) can undergo a dismutation reaction in the bulk solution (Cl_2(sol)) to form hypochlorous acid and hypochlorite ion, depending on whether pH is low or high, respectively:

$$Cl_2(sol) + H_2O \leftrightarrows HClO + H^+ + Cl^- \tag{3}$$

$$HClO \leftrightarrows H^+ + OCl^- \tag{4}$$

The following parasitic reactions of chlorate and perchlorate production, leading to the depletion of hypochlorite concentration, may also occur at the anode [26]:

$$\begin{aligned} 6HClO + 3H_2O \rightarrow{} & 2ClO_3^- + 4Cl^- \\ & + 12H^+ + 3/2O_2 + 6e^- \end{aligned} \tag{5}$$

$$ClO_3^- + H_2O \rightarrow ClO_4^- + 2H^+ + 2e^- \tag{6}$$

Other loss reactions may occur in the bulk solution and at the cathode [26]. Under the conditions of the present study the occurrence of the loss reactions is very probable as the reactor was an undivided cell. The possible cathode loss reaction is:

$$ClO^- + H_2O + 2e^- \rightarrow Cl^- + 2OH^- \tag{7}$$

which occurs simultaneously with the cathode primary reaction of hydrogen evolution.
The bulk solution loss reactions are:

$$2ClO^- \rightarrow O_2 + 2Cl^- \tag{8}$$

$$2HClO + ClO^- \rightarrow ClO_3^- + 2Cl^- + 2H^+ \tag{9}$$

Chlorine, hypochlorous acid and hypochlorite ions are strong oxidizing species and are often collectively referred to as "active chlorine". Several radical species can also be formed in solutions containing active chlorine compounds, e.g. $ClO^{\bullet}$, $Cl^{\bullet}$, $OH^{\bullet}$ and $H^{\bullet}$ [27]. Active chlorine present in the solution undergoes homogeneous phase reactions with pollutants, in which it is being reduced. This leads to the "recovery" of chloride ions which are, in turn, continuously oxidised at the anode to form chlorine/hypochlorite again. It follows that in solutions containing chloride ions, the pollutant removal rate due to electrochemical oxidation is a function of the pollutant concentration ([c], mg l^{-1}) and also of the active chlorine concentration ([Cl_2], mg l^{-1}), since the indirect oxidation is mediated by chlorine/hypochlorite. The mass transport limited current density of chlorine evolution can be estimated from:

$$j_{\mathrm{L}} = nFk_{\mathrm{m}}[\mathrm{Cl}^-] \tag{10}$$

where j_{L} – mass transport limited c.d. (A m^{-2}), n – number of electrons involved (n = 1), F – Faraday constant (F = 96500 C mol^{-1}), A – surface of the anode (m^2), (k_{m} – mass transport rate coefficient (m s^{-1}), [Cl^-] – concentration of chloride ions in the solution (mol m^{-3}). Assuming k_{m} equal approximately to 10^{-5} m s^{-1} and considering that [Cl^-] was equal to 160 mol m^{-3}, the mass transport anodic c.d. can be roughly estimated to be 160 A m^{-2}. Even if chlorine evolution could explain most of the total current under the conditions of the lower c.d., a contribution of other reactions was of considerable importance when the c.d. was equal to 400 A m^{-2}. In particular, the reactions in which other mediators such as hydroxyl radicals or ozone are generated, could occur. The normal potential of ozone evolution is 2.07 V and is lower than the anode potentials determined at the out-set of electrolysis conducted at the higher c.d. with the tested anode. It follows that even if "active chlorine" can be considered the main oxidising species responsible for the destruction of pollutants when the process was conducted at 200 A m^{-2}, at a higher c.d. other mediators have probably contributed to the overall treatment.

Regarding reactions of pollutants with "active chlorine" two different reaction regions can be distinguished: the hydrodynamic boundary layer where, due to the reactions of water discharge and to the loss reactions (5) and (6) the pH is low and the bulk solution, where the pH is neutral. Consequently it is likely that under the 200 A m^{-2} c.d., when the predominant mediator was "active chlorine", removal of pollutants having instantaneous or fast reaction kinetics with chlorine could have been mediated mostly by hypochlorous acid, while other pollutants were eliminated by reaction with hypochloric ions. The redox potentials of both mediators are different, thus the pH effect in the two regions is reflected by still lower reaction rates occurring in the bulk.

Assuming active chlorine mediation as a predominant process leading to pollutant depletion during electrolysis of chloride-containing wastewater, in accordance with the results of Comninellis and Nerini [28] and Bonfanti et al. [29], under the conditions of the present study the following equation should apply:

$$-\frac{\mathrm{d}[c]}{\mathrm{d}t} = k[c][\mathrm{Cl}_2] \tag{11}$$

Assuming steady state conditions under which there is no accumulation of chlorine in the solution and the rate of its production (which is proportional to the applied current) and the rate of consumption are equal, the concentration of active chlorine during electrolysis can be assumed to be constant and the observed constant k_{obs} can be measured experimentally. Under this hypothesis Equation (11) can be approximated by pseudo-first order kinetics:

$$-\frac{\mathrm{d}[c]}{\mathrm{d}t} = k_{\mathrm{obs}}[c] \tag{12}$$

The first order analytical model for the evaluation of indirect electrochemical reaction rate provided a reasonable framework for process design [30] and was also applied in the present study. Using an integrated form of equation (12):

$$\ln\frac{c_t}{c_0} = -k_{\mathrm{obs}}t \tag{13}$$

and plotting the logarithms of normalised concentration of parameters monitored during the exhaustive electrolysis vs time, values of the apparent pseudo-first order kinetic constant k_{obs} were obtained. The constants relative to the removal of COD, N-TKN and sulphides are reported in Table 2. It has to be underlined that k_{obs} is a lumped parameter and includes the effect of any other mediator, apart from "active chlorine", that contributes to the removal of pollutants.

The time needed to eliminate pollutants by electro-oxidation, from their initial concentration [c_1] to the final concentration [c_2], indicated for each of analysed schemes in Section 3.2, is:

$$t = \frac{\frac{\ln[c_1]}{[c_2]}}{k_{\mathrm{obs}}} \tag{14}$$

The specific electrical energy consumption (SEC), the dominant component of the running costs of most electrochemical processes, was calculated according to:

$$\mathrm{SEC} = iEt \tag{15}$$

where SEC – energy consumption (kWh m^{-3}); t – time needed for the removal of a given pollutant (h); i– total current applied (A); E – overall cell voltage (V) (values shown in Table 3).

Table 2. Values of the pseudo-first order rate constant for removal of pollutants from tannery wastewater by electro-oxidation

Wastewater type	Parameter	Value of the rate constant (min^{-1})	
		Current density I = 200 A m^{-2}	Current density I = 400 A m^{-2}
Raw wastewater	N-TKN	0.0090	0.0239
	COD	0.0037	0.0237
	S^{2-}	0.0267	0.2521
After anaerobic lagoon	N-TKN	0.0120	0.0343
	COD	0.0087	0.0336
	S^{2-}	0.0904	0.3115
After aerobic process	N-TKN	0.2496	0.6166
	COD	0.0060	0.0346

Table 3. Variation of operational parameters during wastewater electrolysis

Wastewater type	Variation of cell potential (V)		pH variation	
	I = 200 A m^{-2}	I = 400 A m^{-2}	I = 200 A m^{-2}	I = 400 A m^{-2}
Raw waste water	6.9–6.8	8.3	7.8–7.5	7.4–7.6
After anaerobic lagoon	6.9–7.3	8.6	7.5–8.3	7.5–8.3
After aerobic sludge process	7.0	8.6	7.2–8.6	7.3–8.3

3.2. *Evaluation of various schemes of combining electrochemical and biological processes*

Initial values of parameters of the feed to the hypothetical treatment plant were assumed equal to the characteristics of raw (settled) tannery wastewater reported in Table 1.

Evaluation of the treatment time and the volumes of biological processes comprised in the indicated options was done assuming Monod based kinetics for both the aerobic and anaerobic removal of the organic load (COD) [31]. In particular the following expressions describe:

– the bacterial growth:

$$\frac{dX}{dt} = Y\frac{d[c]}{dt} - k_d X \tag{16}$$

where X – mixed liquor volatile solids (g m^{-3}), $[c]$ – substrate concentration (g m^{-3}), Y – biomass yield (kg VSS kg COD^{-1}), k_d – decay coefficient (day^{-1}).

– The specific substrate utilisation rate (U):

$$U = \frac{d[c]}{dt}X = \frac{\mu_{max}[c]X}{Y(K_s + [c])} \tag{17}$$

where K_s–half velocity saturation constant (g m^{-3}); μ_{max} – maximum specific growth rate (day^{-1}).

The reactor volume required to lower the substrate concentration from $[c_0]$ to $[c]$ was calculated from:

$$V = \frac{YQ([c_0] - [c])}{X[\frac{1}{Q_c} + k_d]} \tag{18}$$

where Q – wastewater flow (m^3 day^{-1}); Q_c – sludge age (day^{-1}); other symbols have the meaning as above. The values of biokinetic parameters used for an evaluation of biological processes are listed in Table 4. The MLVSS (Mixed Liquor Volatile Suspended Solids) concentration in the mixed liquor was assumed to be 3 kg m^{-3}, unless otherwise stated.

Table 4. Values of biokinetic parameters used for an evaluation of aerobic (heterotrophic) and anaerobic processes

Process	Parameter					Literature source
	K_s (m^{-3})	Y	K_d (dy^{-1})	a	b (day^{-1})	
Aerobic	1200	0.300	0.084	0.4	0.14	[22]
Anaerobic	100	0.050	0.032	–	–	[20]

The volume required by the single-sludge nitrification/denitrification unit was evaluated assuming nitrification and denitrification rates of 0.087 kg N-NH_3 kg^{-1} MLVSS day^{-1} and 0.13 kg N–NO_3 kg^{-1} MLVSS day^{-1}, respectively [32].

The energy requirement for the biological section operating under aerobic conditions was calculated considering that energy is used by the aeration equipment to deliver oxygen necessary for the growth and the metabolic activity of heterotrophic bacteria (removal of COD) and that of authotrophic bacteria (removal of N-NH_3 by nitrification). It was assumed that oxygen is supplied by means of surface low-speed aerators for which the oxygen transfer capability is 1 kg O_2 hp^{-1} h^{-1} [31]. The oxygen requirement (O_2) for the removal of COD from the initial $[c_0]$ to the final $[c_e]$ concentration is:

$$O_2 = Qa([c_0] - [c_e]) - bXV \tag{19}$$

where a – oxygen utilisation rate, b – endogenous respiration rate (day^{-1}), V – reactor volume (m^3). Oxygen requirements for nitrification were calculated applying the stoichiometric factor 4.57, as follows from the overall reaction:

$$2NH_4^+ + 3O_2 \rightarrow 2NO_2^- + 2H_2O + 4H^+ \tag{20}$$

The total oxygen demand was calculated as a sum of the quantity necessary for oxidation of COD and N-NH_3. The quantity of nitrogen to be removed by nitrification/denitrification was established on the basis of the nitrogen balance. Since during the growth of heterotrophic micro-organisms nitrogen is used for the biomass synthesis, this element is removed with the wasted sludge in a proportion of about 12.5%, considering that the nitrogen content of microbial cells can be assumed to comprise $C_5H_7O_2N$ [31].

The following gives information on the details of the computation procedure for each of the technological options. Figure 7 depicts the main characteristics of the options considered, and the results of computation are shown in Table 5.

(a) *Biological single sludge nitrification/denitrification*

Considering the allowable ammonium concentration in the final effluent of 15 mg l^{-1}, the calculated quantity of nitrogen removed by the biomass synthesis was 54 mg l^{-1} and the quantity of nitrogen to be removed by nitrification/denitrification was 301 mg l^{-1}. In computing the oxygen demand, the depletion of COD in the anoxic section (the process of denitrification) was computed and

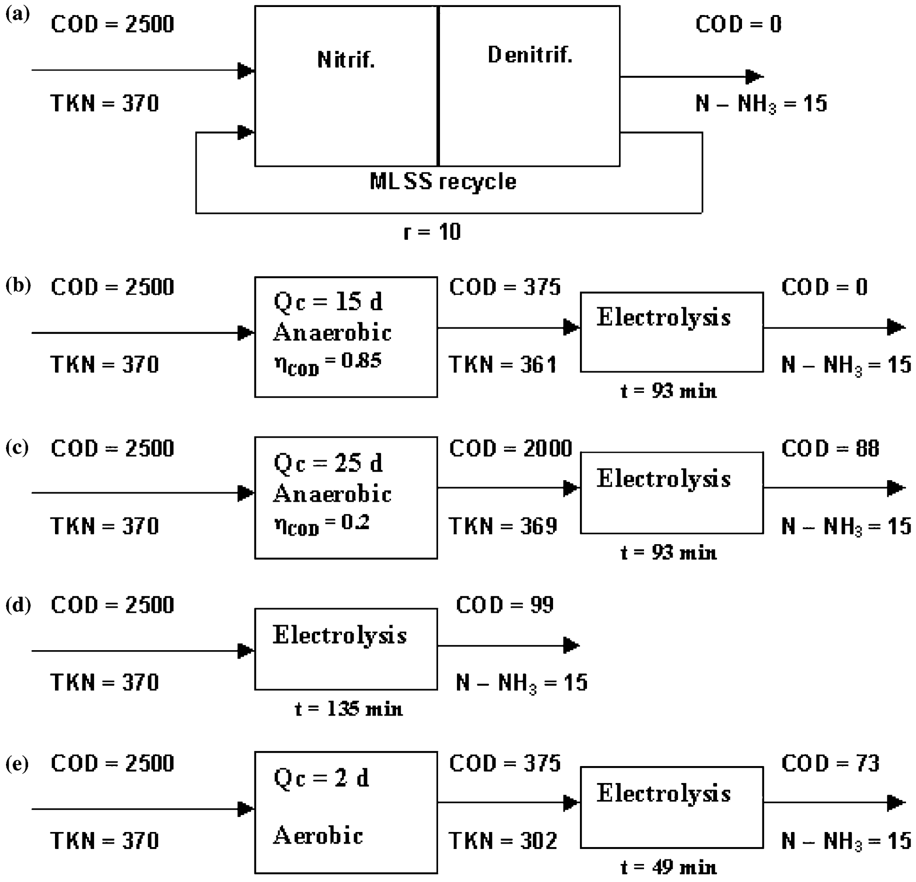

Fig. 7. Main details of the schemes of possible combinations of electrochemical and biological processes.

Table 5. Volumes, energy requirements and sludge production for different combinations of electrochemical and biological processes (concentrations in mg l^{-1})

No.	Option		Energy consumption (kWh m^{-3})		Required volume (m^3)		Sludge produced (kg day^{-1})
			For each unit	Totally for the option	For each unit	Totally for an option	
(a)	Single sludge	Nitrification	3.02	8.47	1153	1925	431
		Denitrification	0.55		772		
		Pumping	4.90		–		
(b)	Anaerobic		47.2×10^{-3}	53.31	1736	1800.5	72
	Electrolysis		53.30		64.5		
(c)	Anaerobic conditioning		5.22×10^{-3}	53.31	174	238.5	17
	Electrolysis		53.30		64.5		
	Aerobic		–		–		
(d)	Electrolysis		74.70	74.70	93.75	93.75	0
	Aerobic		–		–		
(e)	Aerobic		1.10	29.00	364	398	546
	Electrolysis		27.90		34.0		

subtracted from the oxygen balance. The energy need for denitrification was calculated for unit mixing power requirements of 30 W m^{-3} [19] and the wastewater and sludge recycle ratios equal to 10 and 1, respectively [32]. The efficiency, η, of the pump was assumed to be 0.75 and the pumping head 3 m. The power P (kW) necessary for wastewater and sludge recycling was calculated from [33]:

$$P = \frac{Qrhg}{86.400\eta} \tag{21}$$

where r – total recycling rate (–); h – pumping head *(m)*; g – acceleration due to gravity (m^2 s^{-1}).

It was assumed that sludge produced in this option was mainly due to the heterotrophic growth.

(b) *Anaerobic treatment of raw wastewater followed by electrolysis*

In this case, the anaerobic process was designed in such a way as to recover the energy by biogas production. Assuming an efficiency of COD removal of 85% [34] and a methane yield of 0.30 m^3 of CH_4 per 1 kg of removed COD [20], the quantity of 0.64 m^3 of methane is produced from each m^3 of the raw wastewater, enabling recovery of about 4.9×10^{-3} kWh.

The volume of the anaerobic unit calculated using Equation (18) and assuming a sludge concentration of 2 kg m^{-3} was 1736 m^3 and requires 52.1 kWh for mixing. Subtracting the energy recovered from the biogas, 47.2×10^{-3} kWh will be required per 1 m^3 of incoming wastewater. By applying Equation (16), 72 kg of sludge will be produced daily. The effluent from anaerobic process contains a COD of 375 mg l^{-1} and a TKN of about 361 mg l^{-1}.

The subsequent electrolysis will require 93 min to reduce the nitrogen concentration to 15 mg l^{-1}. The electrochemical reactor volume will be 64.5 m^3. The energy needed to treat 1 m^3 of wastewater by electrolysis is 53.3 kWh. There will be no COD or sulphides in the final effluent from this option, as the time of electrolysis necessary to lower the nitrogen content will be sufficient to eliminate them completely.

(c) *Anaerobic conditioning followed by electro-oxidation and by an aerobic conventional process aimed at removal of the residual COD*

This sequence will result in a reduced electrolysis time by comparison to option (b), the necessary conversion for nitrogen being lower, as the wastewater is further subjected to an aerobic sludge process, in which the proportion between the removed nitrogen and COD is higher then in anaerobic treatment. Placing the anaerobic conditioning as the first stage of the sequence results in the rupture, in an anaerobic process, of big organic molecules. This leads to an increase, by comparison to the option (b), of the kinetics of electrolysis, as shown in Section 3.1

To reduce the plant costs, the anaerobic process will be operated with the aim to pre-condition the wastewater and will be designed to remove about 20% of COD only. As shown by data relative to option (b), the energy, which can be recovered from the anaerobic process is very low and does not justify application of energy recovery, particularly when the quantity of the produced biogas is low. Thus no energy recovery from the anaerobic process is foreseen in this option. Under the above assumptions, the calculated volume of the anaerobic section will be 174 m^3, 5.22 kW day^{-1} of energy will be required for mixing purposes and the sludge production will be 17 kg day^{-1}. Ammonia removal, associated with sludge growth, will contribute only marginally to lowering the N-TKN, and its concentration in the outflow from anaerobic pre-treatment will be 369 mg l^{-1}.

The effluent from the anaerobic pre-treatment (COD and TKN equal to, respectively, 2000 and 369 mg l^{-1}) will be subjected to electrolysis. The time calculated for lowering the nitrogen concentration to 15 mg l^{-1} was 93 min, which is exactly the same as in option (b). Also the energy consumption will be analogous to that required by the scheme presented in option (b). In the present option, since the values of the rate constants for COD and nitrogen removal by electrolysis are very close, these two parameters will be depleted simultaneously, and the effluent from the electrochemical reactor will not have such characteristics as to enable the aerobic process to be used as a final polishing step. Due to the removal of COD, occurring in the electrochemical process simultaneously to nitrogen removal, the value of this parameter in the outlet will be 88 mg l^{-1}.

(d) *Electrolysis of raw wastewater followed by a conventional aerobic process*

In this option electrolysis is to be implemented to remove nitrogen in excess to the quantity needed for biomass production in the biological section. However, being in the course of electrolysis the removal of nitrogen accompanied by the destruction of COD, the elimination of the latter parameter cannot be avoided, and some organic compounds contributing to COD will also be destroyed. Thus it will be necessary to remove, by a biological process, only that part of COD, which remains after electrolysis.

For the characteristics of raw wastewater indicated in Table 1 it can be calculated that the conversions necessary to respect the discharge standards would be 0.96 and 0.94, respectively for nitrogen and COD. For the experimental values of the reaction rate constants during electrolysis, the removal of nitrogen in the electrochemical reactor will require 135 min. The final value of COD reached after this time will be 99 mg l^{-1}, which is lower than the discharge standard for this parameter. Since the rate constants for COD and nitrogen removal are very close and the N/COD ratio is high (always above 0.14) it is not possible to selectively remove nitrogen and leave COD to be subsequently eliminated by a conventional aerobic process. Electrolysis of raw wastewater leads to complete removal of all target pollutants at the same time, thus it cannot be applied as a pre-treatment of raw tannery wastewater. The energy requirement for the complete removal of pollutants would be 74.7 kWh m^{-3}.

(e) *Aerobic pre-treatment followed by electrolysis*

By virtue of higher biokinetic constants, the aerobic process generally generates more sludge, in comparison to the anaerobic one, and removes more nitrogen. Consequently its implementation as a pre-treatment step could allow a subsequent electrochemical unit with lower nitrogen content in the inflow, as compared to options (b) and (c) and lower time/energy will be needed. In this option the aerobic pre-treatment would be aimed at removing most of the COD and that part of the nitrogen, which is necessary for biomass synthesis, without allowing nitrification to occur (otherwise the lack of denitrification would result in exceeding the standard for nitrate). Under such conditions the sludge age should be chosen low enough as not to favour nitrification and, in this option, it was taken equal to 2 days. The aerobic unit will yield an effluent with low COD (375 mg l^{-1}) and high nitrogen (TKN = 302 mg l^{-1}).

An advantage of this option is that the effluent from the aerobic process can be treated by electrolysis at high reaction rates. Thus the nitrogen removal by electrolysis will require only 49 min, which results in a reactor volume of 34 m^3 and an energy requirement of 27.9 kWh per m^3 of the wastewater.

4. Conclusions

Applying any of the four proposed alternatives of electro-oxidation coupled with a biological process reduces the total plant volume and avoids implementation of biological nitrification, a process that can be easily inhibited and which, as such, cannot be considered as totally reliable. If cheap energy is available (this is often possible by operating the plant at night), electro-oxidation can be proposed as a unique treatment process, reducing the plant size by about 95%. Placing the electrochemical reactor as a final polishing stage after the conventional biological aerobic sludge process (designed for the removal of COD) allows 80% reduction of the total volume of the plant. In this case the energy requirement, of 29 kWh per m^3 of treated wastewater, is much higher than the 8.47 kWh theoretically needed in a single-sludge biological plant. However, as in practice even 20 kWh were reported to be used in a common treatment plant treating tannery wastewater, this solution can still be considered competitive, as it offers the advantage of high reliability and low plant volume.

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