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Electrochemical oxidation process in application to raw and biologically pre-treated tannery wastewater

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ABSTRACT

This study on tannery wastewater treatment showed that indirect electrooxidation by chlorine generated at a Ti/SnO_2/PdO_2/RuO_2 (SPR) anode led to full ammonia removal and a decrease in chemical oxygen demand (COD) up to 58.9%. Summarized current efficiency of ammonia removal and apparent current efficiency of COD removal was very high and (up to 127.2%). Individual compounds present in raw and electrochemically treated wastewater and in synthetic tannin solutions were identified by GC-MS method. Dibutyl phthalate was determined in all samples of raw and/or wastewaters treated by electrooxidation and also in tannin solutions. For the wastewater sample *D*, current density of 1.0 A/dm^2 values of adsorbable organically bound halogens were: 15.7, 19.8 and 12.9 mg/L after 15, 30 and 46 min, respectively. Additionally, a cost evaluation of this process was established. At a current density of 1.5 A/dm^2, the energy consumption was in range from 78.2 to 171 kWh/kg of N–NH_4^+.

Keywords: Chemical oxidation; Electrochemical oxidation; Tannery wastewater; AOX; GC-MS

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1. Introduction

Tannery wastewaters are characterized by high concentrations of organic and inorganic pollutants and a wide variety of compositions due to variations of production processes. Most pollutants are soluble, though some occur as suspensions or colloids [1]. Chlorides and ammonia are the primary inorganic impurities; chloride concentrations range from several hundred to >10,000 mg/L Cl$^-$, while ammonia concentrations range from tens to several hundred mg/L. Additionally, the content of organic pollutants is high; it is predominantly composed of proteins (collagen) and amino acids (from the skin) as well as fatty aldehydes and quinones (tannins used in skin treatment) [2]. High concentrations of pollutants of low biodegradability make biological tannery wastewater treatment insufficient in most cases. A more effective electrooxidation process has recently been extensively investigated. Results from published studies [3–15] show that electrooxidation can occur both directly and indirectly; the effectiveness of the process strongly depended upon the electrode material, operational conditions (pH, current density, temperature) and the characteristics of the wastewater. In the case of tannery wastewaters, ammonia is an important impurity so the effectiveness of chlorine generation on the anode surface is crucial. In our own research [3], the Ti/SnO_2/PdO_2/RuO_2 (SPR) anode was the most effective one of all six anodes investigated.

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There are three main parameters which affect the purification method effectiveness: ammonia, chlorides and organics concentration (COD). The effectiveness increases with increased COD and ammonia concentrations [4,7]. Most researchers carried out the electrooxidation of wastewaters during a predefined time, with no attempt to optimize the process duration. The process is often terminated when ammonia is still present in wastewaters in high quantities. Ammonia is one of the primary impurities in tannery wastewater and is readily removed by chlorine; so the proper time for ending anodic oxidation of tannery wastewaters is when the concentration of ammonia disappears. A few studies [4,6,7] addressed this issue. Szpyrkowicz et al. [6], examined four anodes for removing ammonia and COD. They obtained the best results for biologically pretreated (anaerobically) wastewater. In the case of a Ti/Pt-Ir anode, ammonia was removed by 66% after 90 min (200 A/m^2); in the case of the Ti/PbO-Co_3O_4 anode, 82.2%. Analogical results obtained for raw wastewater were as follows: 55.5% and 46.3%. Under the same conditions, COD was removed from pretreated wastewater by 53.5% using a Ti/Pt-Ir anode and by 72% using a Ti/PbO-Co_3O_4 anode. Continuation of electrooxidation after complete removal of ammonia resulted in further COD removal, but with low efficiency. Additionally, it caused a significant increase in chlorine concentration, which increases the toxicity of wastewater.

There are few studies (including our own publications [16]) devoted to chlorination products as a result of anodic oxidation of tannery wastewaters. Rao et al. [17] compared the effectiveness of three anodes: Ti/Pt, Ti/PbO_2 and Ti/MnO_2; the best results were obtained using the Ti/Pt anode. GC-MS results showed that phenol, naphthalene and steroids were totally removed during the process, while concentration of other chemical compounds were also reduced. On the other hand, some new substituted phenolic compounds formed. Among the chloroorganic compounds, only tetrachloroethane was detected. Results from GC-MS analysis of raw tannery wastewaters were also reported by Vijayalakshmi et al. [18] and indicated that phthalates (and other esters), hydrocarbons, nitro compounds, acrylamide and benzoquinone were all present.

Conclusions drawn from a tannery wastewater treatment literature review provided the foundation for the goals of this study, which significantly expand the knowledge of chemical tannery wastewater treatment.

The main goals of presented studies were as follows:

- assessment of the effectiveness of ammonia, organic compounds (COD), total Kjeldahl nitrogen (TKN) removal by electrooxidation;
- assessment of the effects of current density, chloride concentration and process time on the effectiveness of electrooxidation;
- calculation of the current efficiency of ammonia removal and apparent current efficiency (ACE) of COD removal for all wastewater samples and current densities;
- identification of organic compounds in raw and treated wastewaters and in synthetic tannin solutions (GC-MS).

2. Experimental and methods

Tannery wastewater samples were collected from tanneries located in Poland. They were refrigerated before analysis, but not for longer than 72 h.

Four tannery wastewater samples were subjected to electrooxidation:

- Samples A and B – raw tannery wastewater;
- Samples C and D – tannery wastewater biologically pretreated in the tannery;

The characteristics of the wastewater samples are shown in Table 1. All samples were characterized by different COD values – from 2,288 (sample C) to 4,982 (sample B) mg/L O_2. However, significantly higher concentrations of ammonia were observed in cases of biologically pretreated wastewater (samples C and D); three samples (A, C and D) had similar TKN to ammonia ratios of approximately 1.2; sample B had a

Table 1
Characteristic of wastewater subjected to electrooxidation

	A	B	C	D
pH	6.7	6.6	8.2	7.7
Conductivity µS/cm	24,800	23,600	21,700	10,800
Total suspended solids mg/L	70	30	27	26
Chlorides mg/L Cl	6,738	6,735	4,821	3,600
Sulfates mg/L SO_4	3,200	5,000	4,200	4,200
Ammonia mg/L N–NH_4^+	346	340	745	608
Nitrites mg/L N–NO_2^-	0.04	0.12	0.18	0.02
Nitrates mg/L N–NO_3^-	1.0	1.3	0.4	10.4
Total Kjeldahl nitrogen mg/L N	426	501	905	724
Orthophosphates mg/L PO_4^{3-}	2.0	4.2	2.7	1.6
COD mg/L O_2	2,417	4,982	2,288	3,017
Sulfides mg/L S^{2-}	27.2	210	100	84
Anionic surfactants mg/L	21.2	400	24	12.0

higher ratio (~1.5). Differences discussed above are due to the different tanning processes applied in that tannery. Different skin types required different chemical treatments during the tanning process. Ammonia present in wastewater primarily comes from ammonium salts used as chemicals. Ammonia is also the product of deamination process which occurs under anaerobic conditions in an expansion tank after biological treatment. On the other hand, the TKN contains amino acids and proteins leached from skins. However, wastewater samples C and D were biologically treated in the tannery, their characteristics indicate that biological treatment at the plant worked incorrectly (what was also reported by tannery workers). On the other hand, the concentrations of chlorides in samples C and D were almost two times lower than samples A and B. Chlorides primarily come from the added salts during the tanning process, though small amounts also come from the skin.

Other parameters were similar in all wastewater samples. The concentration of Cr in wastewater was <5 mg/L (Table 1).

Additionally, synthetic solutions of tannin used in that tannery were subjected to electrooxidation. The tannin was added (in two concentrations: 300 and 500 mg/L) to chloride and ammonia solutions in concentrations from 3,510 to 22,000 and 190 to 1,176 mg/L, respectively, as well as to the same solutions without ammonia containing the same concentration of chloride ions. The aim of that part of the study was to determine the influence of ammonia on indirect electrooxidation of the tannin and identification of tannin electrooxidation products.

The studies on electrooxidation were conducted in a rectangular, Plexiglas electrolyzer (200 (height) × 120 × 70 mm) in which five electrodes were placed in parallel and alternately – two SPR anodes and three steel cathode (100 × 100 × 2 mm); the gap between the electrodes was 12 mm and distance from the bottom of electrolyzer was 3 cm. The SPR anode $Ti/RuO_2/SnO_2/PdO_2$ 40%/30%/30% was prepared according to the Comminelis and Vercessi [19]. The volume of tested wastewater was 1,030 mL. During electrolysis, wastewater was magnetically stirred. Wastewater samples, 10–20 mL, were taken from the reactor at pre-selected time intervals for analysis (after 5, 15 and then after every 15 min of the process). When the concentration of ammonia became below 15 mg/L its concentration was determined every 1 min in order to get the point in which it was removed totally. The process was conducted until the removal of ammonia was complete. The current was kept constant while the voltage and temperature were controlled continuously. The current density used in the process varied from 0.5 to 2 A/dm^2.

The efficiency of tannery wastewater electrooxidation was evaluated based on the following parameters: temperature, pH, COD, ammonia, chlorides, as well as free and total chlorine concentration. Additionally, for the selected experiments, TKN was determined. For wastewater sample D, the AOX was determined at a current density of 1 A/dm^2 and electrolysis times of 15, 30 and 46 min. In case of tannin solutions, the effectiveness of the process was evaluated by changes in COD and tannin concentrations. All determinations were conducted in accordance to European Standards The test values are presented as the average of the three measurements, and the standard deviations of measured data were below 5%.

Additionally, the current efficiency of ammonia and ACE of COD removal was calculated for each wastewater sample and current densities. Calculation assumptions (from Faraday's Law) for the removal of 8 mg O_2 (in case of COD) or 14/3 mg of N (in case of ammonia) required an electrical charge of 96.5°C. Current efficiency calculations for ammonia removal assumed that ammonia reacts with chlorine generated at the electrode surface according to reaction 1:

$$6\,Cl^- + 2NH_3 - 6e^- \rightarrow 3N_2 + 6HCl \tag{1}$$

In our paper, the term ACE used in case of COD is equal to the electrochemical oxidation index (EOI) introduced by Comninellis and Plattner [20], and used by other researchers. EOI is defined as a mean value of instantaneous current efficiency calculated during the entire process. However, in calculations of ACE of COD removal, it was assumed that organic compounds were oxidized by chlorine generated at the electrode surface; it is highly probable that some additional oxidation reactions took place, which "apparently increased" the current efficiency of COD removal. ACE COD removal was calculated according to the following formula:

$$\text{ICE} = \frac{(\text{COD}_0 - \text{COD}_t)}{8 \times I \times \Delta t} F \times V \tag{2}$$

where COD_0 and COD_t – COD at times 0 and t respectively; V – the volume of electrolyte; I – current; F – Faraday's constant

For samples A and D, chromatographic analyses (GC-MS) were performed using a Hewlett Packard 5890II /5971 HP-1 capillary column chromatography (24 m, 0.2 mm, 0.33 µm). The following temperature conditions were used: the initial temperature was 35°C, heated at a rate of 5°C/min until it reached 310°C and held there from 15 min. The mass detector worked in SCAN mode, from 20 to 570 u (250°C). Samples were extracted twice with 200 mL with dichloromethane (15 + 10 mL) at pH 8 and 2. As an internal standard, 1.0 mL of pure (2,6,10,16-tetramethylpentadecane) in dichloromethane (0.1 mg/mL) was added.

3. Results and discussion

3.1. Electrooxidation of wastewater

Table 2 shows the summary of wastewater electrooxidation results; Fig. 1 shows the ammonia concentration changes during the electrolysis of wastewater and Fig. 2 shows analogous changes in COD values.

The COD values decreased by 48.6%–58.9% in time required for total ammonia removal for all wastewater samples. Those values strongly depended on the current density and for higher values they were lower.

Those results were just slightly worse than those obtained in our previously published results [16]. In that studies, the coagulation of four raw wastewater samples resulted in a COD decrease of 56.5%–74.1%, while electrooxidation gave a decrease of 55.9%–73.1%. These differences in COD reduction were probably due to differences in the quantity and quality of the organics in the studied samples. However, those results, together with results published earlier [21,22]

Table 2
Summary of research results on electrochemical treatment of tanning effluents and values of energy consumption, current yields and final concentrations of total chlorine

Wastewater	Current density (A/dm^2)	pH final	Electrolysis time (min)	Final concentration Cl$^-$ (mg/L)	COD removal (%)	N–NH$_4$ current efficiency (%)	COD current efficiency (%)	Total current efficiency (%)	Energy consumed (kWh/m^3)	Energy consumed (kWh/kg N–NH$_4$)	Voltage (V)
A	1.5	6.1	60	6,050	48.8	33.5	65.9	89.4	28.1	82.6	5.4
	2.0	6.0	46	6,060	48.6	32.8	64.2	97.0	32.4	95.3	6.4
B	1.0	5.0	139	6,130	58.9	21.1	106.1	127.2	43.6	127	4.7
	1.5	4.9	92	6,100	53.8	21.2	97.6	118.8	51.0	149	5.5
	2.0	4.7	70	5,970	51.8	20.9	92.7	113.6	58.6	171	6.3
C	1.5	5.0	106	4,000	55.0	40.4	39.7	80.1	58.3	78.2	5.5
	2.0	4.9	80	4,040	54.5	40.1	39.2	79.3	64.0	85.9	6.0
D	1.0	6.0	156	3,200	58.0	33.6	56.4	90.0	49.9	82.1	4.8
	1.5	5.9	102	3,170	56.6	34.2	55.3	89.5	57.1	93.9	5.6
	2.0	5.8	78	3,180	56.7	33.6	55.1	88.7	67.6	111.2	6.5

enable a comparison of the effectiveness of the coagulation and electrooxidation processes with respect to COD removal from tannery wastewater. However, these results show that the effect of both processes was similar; the main advantage of the electrooxidation process is a total removal of ammonia, which in addition to organics is the main impurity in tannery wastewaters. Additionally, results published earlier [16] enabled the comparison of the effectiveness of the decrease in COD by electrooxidation with that achieved by AOPs. In case of wastewater sample C-k, the Fenton process gave a 54.0% decrease in COD, the H_2O_2/UV process gave a 77.6% decrease in COD, and electrooxidation gave a 39.6% decrease in COD. In the case of wastewater sample D-k, the H_2O_2/UV process gave a 70.4% decrease in COD, and the electrooxidation process gave a 46.0% decrease. However, electrooxidation resulted in the total removal of ammonia, which can be considered as a definite advantage of this method.

Values of ACE of COD removal and current efficiency of ammonia removal are shown in Table 2. The ACE of COD removal for wastewater B was higher than that for other wastewaters and ranged from 92.7% to 106.1%. For wastewater samples A and D, they were similar and ranged from 55.1% to 67.9% but was significantly lower for wastewater sample C (39.2%–39.7%). The ACE of COD removal depended strongly on the concentration of chlorides and organics – higher values of both increased the efficiency.

The current efficiency of ammonia removal was the highest at a current density of 1.5 A/dm^2 and depended on the concentration of other oxidized impurities. For wastewater samples with lower organic concentrations, especially the biologically pretreated wastewater sample D (the lowest COD, high ammonia concentration), the efficiencies at 1.0 and 2.0 A/dm^2 were similar (33.6%) and was slightly lower than the efficiency obtained at 1.5 A/dm^2 (34.2%). For sample B (high COD), current efficiency at densities of 1.0 and 1.5 A/dm^2 was similar (21.1% and 21.2%) and slightly higher than at 2.0 A/dm^2 (20.9%).

Results presented in Table 2, together with results published elsewhere [16], allow for the conclusion that ammonia removal efficiency and ACE of COD removal generally decreases at higher current densities. In the case of samples B and D, the highest current efficiency of ammonia removal was at current density of 1.5 A/dm^2 and for COD removal, it was at 1.0 A/dm^2. In case of samples A and C, the current efficiency of ammonia and ACE of COD removal was higher at 1.5 than it was at 2.0 A/dm^2. The influence of current density on ammonia and COD removal might be explained by the kinetics of chlorine reaction with impurities. Chlorine reactions with ammonia, hydrogen sulfide, amino acids and proteins occur rapidly. Tannery wastewater contains many other organic pollutants which react with chlorine at a much lower rate; the current density decrease results in slower chlorine generation and prolongation of ammonia removal and formation of chloramines. The prolongation of the electrooxidation process favors the slower reaction of chlorine with organics. It results in an increase in the COD removal ratio to the removal of ammonia.

Temperature may influence the difference in the degree of ammonia and COD removal, which was increased during the process. At the end of the process, it ranged from 30°C

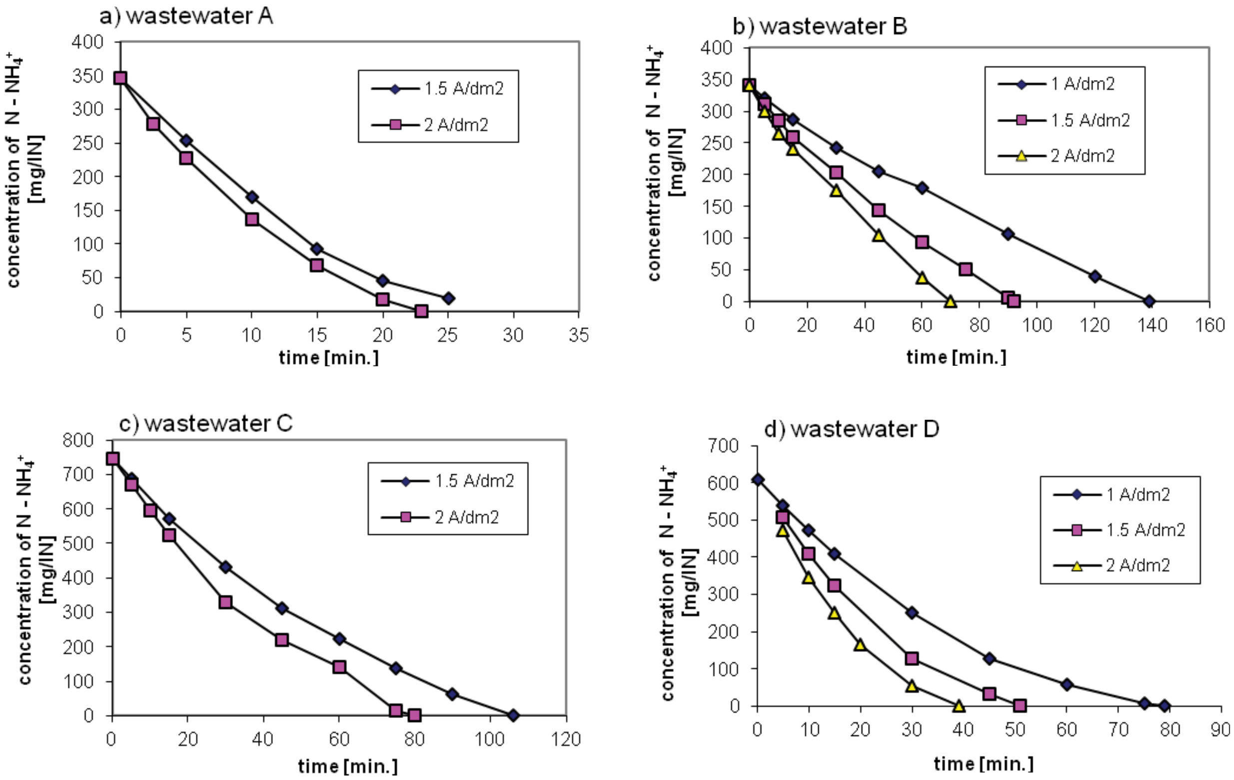

Fig. 1. Changes in ammonium nitrogen concentration during tannery wastewater electrolysis.

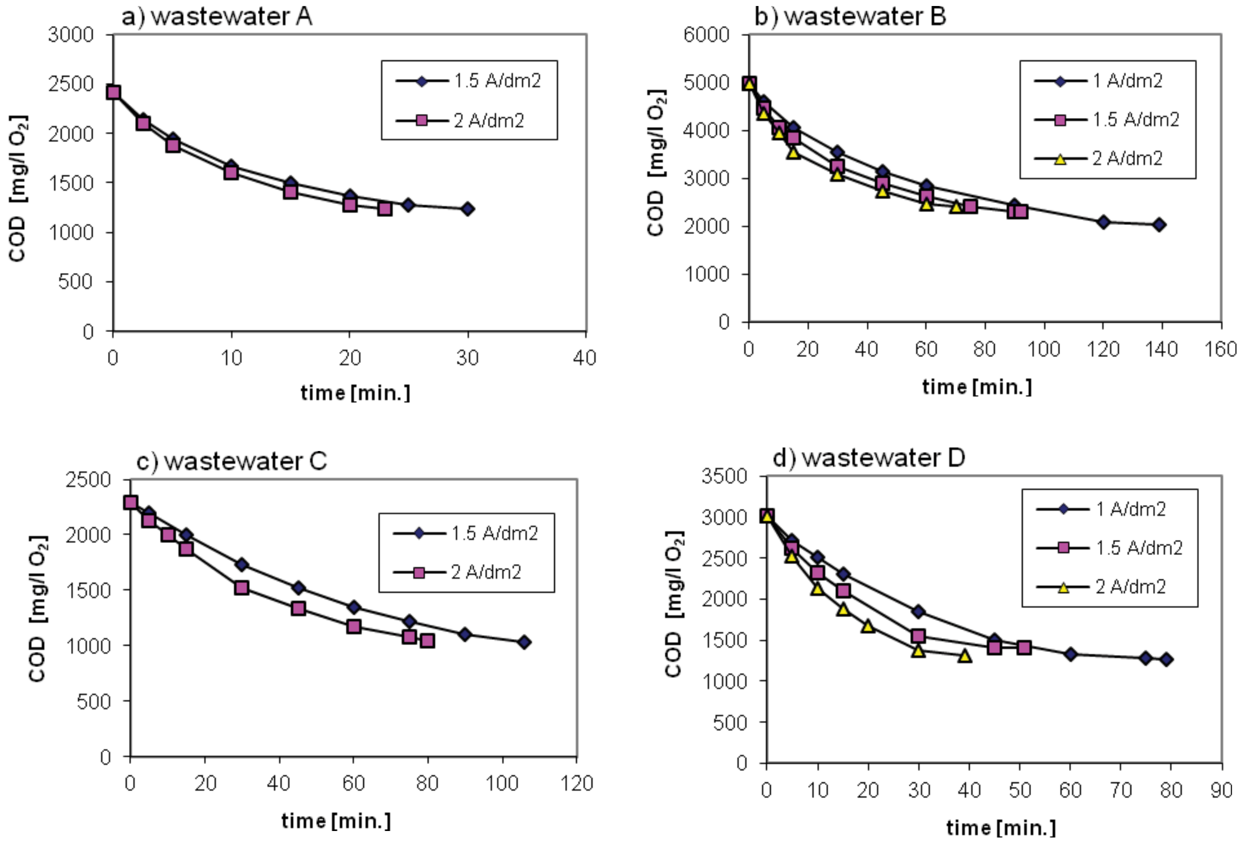

Fig. 2. Changes in COD values during tannery wastewater electrolysis.

to 46°C and increased as the current density increased (the initial temperature was always 19°C–20°C). Higher temperature accelerates slower processes, such as chlorine reactions with some organic impurities. It also accelerates the reaction of chlorine with ammonia. The reactions of chlorine with hydrogen sulfide and organic compounds compete with chlorine/ammonia reactions. This explains the significant decrease in the current efficiency of ammonia removal when organic compounds are present in the solution.

During electrolysis some changes in pH value were observed and for all investigated samples the character of those changes was similar. At the beginning of the process, pH value increased slightly than after about 15 min decreased to values between 3.5 and 4.5 (depending on the sample) for current density 2A and rose again up to final value presented in Table 2. Discussed changes in pH value were effect of different reactions ongoing in bulk solution during electrolysis. It is well known that form of chlorine depends strongly on the pH value of the solution, and below pH 2.0 it is present only as Cl_2, in pH in range from 2.0 to 5.5 dominates HClO and ClO^- is in low concentration. In case of presented studies pH value of the solution was up to 6.0 during the whole electrolysis time, which allow to conclude that the dominant oxidizing factor was HClO. HClO is considered as weaker oxidant than ClO^- that is why substitution of Cl in organic compound molecules took place rather than destruction. Additionally with the time of the process, pH value of solution rose and chlorine started to be present also as ClO^- which is stronger oxidant and cause destruction of big organic compounds without substitution of Cl atom. That thesis was reflected in AOX and GC-MS results which are discussed later in this paper.

In addition to chlorine generation on the anode surface, the oxidation of water occurs which results in the generation of hydroxyl radicals (reaction 2):

$$H_2O + e^- \rightarrow H^+ + OH^{\bullet} \quad (3)$$

Hydroxyl radicals produced in that way and adsorbed on the anode surface are also involved in the oxidation of organics. As previously reported [23], hydroxyl radicals, in the absence of chlorides, are the main factors responsible for the degradation of organic compounds.

The generation of hydroxyl radicals on the Boron-doped diamond anode is quite high in comparison with the DSA type anodes [24]. On the other hand, on the DSA anodes, the generation of chlorine is very effective. In solutions with high chloride content, the production of chlorine on DSA anodes significantly exceeds the production of hydroxyl radicals [22]. The efficiency of chlorine generation on the anode surface increases with the concentration of chlorides [3]. The oxidation of ammonia with hydroxyl radicals does not occur [23]. However, in the present study, hydroxyl radicals measurements were not conducted. Radical scavengers (e.g., HCO_3^- [3]), which reduce the concentration of hydroxyl radicals in the oxidation of organic compounds, are produced during the tannery process.

For samples with higher chloride and organic compound concentrations (sample B), the total current efficiency was higher than 100%. Such high current efficiencies have a few possible explanations. It could be due the presence of additional oxidants in treated wastewater, such as oxygen from the atmosphere (the solution was mixed on magnetic stirrer during the entire process). In the reaction of $OH^{\bullet}$ and $Cl^{\bullet}$ with organic compounds, some organic radicals are created which react with oxygen. These reactions are likely responsible for the >100% efficiency of the oxidant in AOPs as well [25].

Another possible reason could be due to secondary oxidation reactions of some impurities by chloramines. The reactions of chloramines, especially monochloramine, with organic compounds and sulfides cause a rapid loss of chloramine content.

Removal of organic nitrogen concentration was higher than that of COD removal, but never reached 100% during the time needed to total removal of ammonia. In wastewater sample B, this value reached 79% after 60 min and 80% for wastewater sample C after 80 min of electrolysis (current density of 2.0 A/dm^2). Prolongation of the electrolysis to 120 min increased this value only to 87.5%. Total removal of nitrites occurred within 5 min for each process.

The reaction of chlorine and chloramines with organics in wastewater led to the formation of chlorinated organic compounds. The total content of chlorinated compounds was measured as AOX. For wastewater sample D, at a current density of 1.0 A/dm^2, the AOX values were: 15.7, 19.8 and 12.9 mg/L after 15, 30 and 46 min, respectively. These results, together with the results published elsewhere [3], indicated that the content of the halogenated derivatives during electrolysis initially increased then decreased. Similar phenomena were observed by Chiang et al. [26] during electrolysis of coking wastewater and by Rebhun et al. [27] during chlorination of household wastewater. The initial increase in the AOX value could be explained by the fact discussed in case of pH – initially dominates in solution HClO. The subsequent drop in AOX values could be explained by further degradation of chlorinated derivatives. The rate of this degradation after electrolysis exceeds the rate of new chloroorganics formation.

Substances identified by GC-MS in raw wastewaters represented less than 1% of all organic impurities present in tannery wastewaters (determined as COD). This is due to the fact that the organic substances that enter the wastewater from different technological processes have high molecular weight and high polarity; therefore, they are not identified by GC-MS. The wastewater samples differed in the composition of pollutants due to different technological processes and different preparations used during those processes. The results obtained for wastewater samples A and D are presented in Table 3 (together with results for electooxidized wastewaters A-e and D-e).

The total concentration of identified substances in wastewater sample A was 2.01 mg/L. The decomposition of nonionic surfactants (e.g., Rokafenol) could explain the origin of 4-nonylphenol and 4-dodecylphenol. The amount of identified carboxylic acids was small. Approximately 70% of electrooxidation products constituted non-chlorinated compounds, among which dihydro-4-methyl-2 (3H)-furanone was the primary species present (178 μg/L).

On the other hand, the amount of substances identified by GC-MS in biologically treated wastewater (*D*) was very small. Their total concentration was approximately 669 μg/L

Table 3
Results of GC-MS research of raw wastewater A. after electrolysis (A-e). and wastewater D and D after different electrolysis times (D-e). Current density – 1.0 A/dm^2

	A (µg/L)	A-e (µg/L)		D (µg/L)	D-e 15 min (µg/L)	D-e 30 min (µg/L)	D-e 78 min (µg/L)
P-Cresol	283		Dibutyl phthalate	615	585	542	510
Phenol	237		Cyclopropane-1-caproic acid butyl ester	30	8		
Dibutyl phthalate	158	144	N-Dodecane	14	10		
Pyridine	149		Trimethyltetradecane	8			
Lenthionine	139		Butoxyethanol		82	44	
2-Bis (1,1-dimethylethyl) phenol	135		3,5-Diphenyl-1,2,4-trioxolane		39	16	4
Cholesterol	116		2-Methylpropyl acetate		28	12	
Indole	112		Isovaleric acid		25	10	
4-Nonylphenol	96		Pelargonium acid		24	8	
4-Dodecylphenol	94		Lauric acid		12	13	6
4-(1,1,3,3-Tetramethylbutyl)phenol	91		Tetradecanecarboxylic acid		12	7	5
Cyclohexene-3-methanol	85	7	Caprylic acid		11	12	10
4-(2,2,3,3-Tetramethylbutyl) phenol	75		Palmitic acid		8	3	
2-Ethylbenzofuran	58		Margarine			4	10
2-Methylpyridine	54		Capronium			2	6
3,5-Dimethylpyridine	52		1-H-isoindole-1,3(2H)–dione			2	12
Aniline	38		1,3-Dichloro-propanol-2		42	161	106
3-Methylpyridine	30		Ethyl chloroacetate		30	40	84
2,6-Dimethylpyridine	13		1,3-Dichloropropan-2-one		29	48	65
Dihydro-4-methyl-2 (3H)-furanone		178	2-Bromo-1,2-dichloropropane		16	46	20
3-Methoxybutanol-1		103	2,2,2-Trichloroacetamide		10	14	
1-Phenylpropandione-1,2		98	1,2,3-Trichloropropene			75	18
1-Methoxybutane		97	1,1,1,2-Tetrachloroethane			50	6
Butyric acid		62	Dichloroacetonitrile			15	
Tetrahydro-2H-pyran-2-one		52	1,3-Dichloropropene			13	30
Valeric acid		29	1,1,2-Trichloropropane			11	48
3-Hydroxybutanone-2		23	3-Chlorobutanol-2				
Dihydro-5-ethyl-2 (3H)-furanone		7	1,2,3-Trichloropropane			6	
Bis(2-ethylhexyl) phthalate		6	1,2-Dichloroethane			4	30
Benzyl alcohol		6	2-Chloro-N,N-diethylacetamide				6
1,1-Dimethoxybutene-1		6					
Propyl 3-methylbutyrate		5					
1-Chloro-2-nitropropane		78					
1,1,1,3,3-pentachloropropane		50					
2-Chloroethylbenzene		33					
1,3-dichloropropanon-2-ol		32					
Ethyl 2-chloropropionate		22					

and main compound was dibutyl phthalate (615 µg/L). Such a small amount of identified impurities is probably due to the fact that the products of biological processes are compounds with higher polarity and/or higher molecular weight which are not detectable by GC-MS. Products of electrooxidation of wastewater samples A (A-e) and D (D-e) determined by GC-MS are listed in Table 3. Mono- and dicarboxylic acids dominated the identified non-chlorinated products of tannery wastewaters. Some substances present in raw wastewater (such as furan and pyran derivatives in wastewater sample A) were not identified in wastewaters after electrooxidation (A-e).

During electrooxidation, the total concentration of chlorinated compounds initially increased but after some time decreased. Analogous phenomenon were observed for most of the identified chlorinated organic compounds. This demonstrates that destructive oxidation by chlorine (instead of chlorine substitution) controls the process after some time. In wastewaters after electrooxidation, the following chlorinated compounds were identified: lower aliphatic chlorohydrocarbons (including chloroform), chlorinated derivatives of acetone and other ketones (including 1,3-dichloropropanol-2), chlorinated nitrile derivatives, lower carboxylic acids, aldehydes and alcohols. These chlorinated compounds were normally identified among the products of chlorine reaction with amino acids, humic compounds and lignin.

Based on the identified products of tannery wastewater electrooxidation, it is not possible to determine the mechanism of the process. On the other hand, the mechanisms of chlorination of some substances present in tannery wastewater are well known. This knowledge allows to draw some conclusions based on the origin of some electrooxidation products. Chlorination of phenols results in the formation of chlorophenols, which are readily oxidized to quinones and dicarboxylic acids. The absence of these compounds in the GC-MS results, especially in case of wastewaters A-e, is likely due to the total oxidation of chlorophenols within 15 min of the process or the polymerization of the phenols [28].

Some of the identified electrooxidation products are probably chlorination products of proteins and amino acids. In particular, dichloro acetonitrile is a product of chlorination of alanine present in collagen. Other possible chlorination products of amino acids are: 2-chloropropanenitrile, 2-chloro-N,N-diethylacetamide, chloroaldehydes and benzaldehyde. The absence of other amino acid chlorination products present in collagen was probably caused by their very low concentrations or/and further chlorination.

Some of the identified electrooxidation products–derivatives of furan and furanone, probably originated from tannin. Furanone derivatives are reported as products of lignin oxidation [29–32], which are similar in structure to tannins. However, chlorinated dibenzidioxins, dibenzofurans, highly mutagenic – MX and 2-chloropropanol are also known as products of chlorination of lignin; they were not identified among electrooxidation products of tannery wastewater. On the other hand, in wastewater sample A-e, mutagenic 1,3-dichloropropan-2-ol was detected and it was also present among the electrooxidation products of tannin. Other chlorinated products identified in both samples of wastewaters and in synthetic solutions of tannin were: 1,1,1,3,3-pentachloropropanone, 1,3-dichloropropan-2-one, ethyl chloroacetate, 1,3-dichloropropanol-2 and 1,3-dichloropropene-1,1,2,2-trichloropropane. It can be assumed that other compounds with similar chemical structures such as: aliphatic and aromatics, mono- and dicarboxylic acids derived from tannins would be present in tannery wastewaters. Some of these compounds may also be the products of electrooxidation of amino acids [33–42] and humic compounds [43–51] with similar functional groups to those in tannins. In conclusion, electrooxidation products were the primary products detected from tannery wastewater electrooxidation.

3.2. Cost evaluation

From cost effectiveness point of view, the most important parameter of electrooxidation is energy consumption, equal to the multiplication of the voltage, intensity and time of electrolysis. These values for all wastewater samples and current densities are given in Table 2. Additionally, the voltage and COD load removed with 1 kg of ammonia nitrogen. Energy consumption decreased as the current density decreased and related to the lower voltage required to achieve a lower current.

The energy consumed to purify a defined volume of wastewater is, as expected, low when the load of removed impurities is also low. The energy consumed to remove a particular load of pollutant is lower when this load is higher, due to the higher current efficiency.

At a current density of 1.5 A/dm^2, the lowest energy consumption required to remove 1 kg of ammonia was 78.2 kWh/kg of N–NH$_4^+$ for wastewater sample C; the concentration of this compound was high – 745 mg/L N–NH$_4^+$. On the other hand, the highest energy consumption was observed for wastewater sample B; from 127 to 171 kWh/kg of N–NH$_4^+$ (ammonia concentration was 340 mg/L).

Another parameter which affects the energy consumption is the distance between electrodes. When that distance is large (a low value of the electrode surface area to the solution volume), the resistance of the solution is high which requires a higher voltage. For that reason, in industrial electrolysis, the distance between electrodes should be small (electrode surface area/wastewater volume should be high).

4. Conclusions

This study shows that indirect electrooxidation by chlorine allows for total removal of ammonia and significant reduction of COD (48.6%–58%) in tannery wastewaters. The efficiency of the process increased with increasing current density. The current efficiency increased together with increasing initial chlorides concentration and initial organics amount (in case of COD removal) and initial ammonia concentration (in case of ammonia removal). However, when concentration of ammonia was high, the current efficiency of COD removal was lower and analogously when COD was high the current efficiency of ammonia removal was lower which allows to state that ammonia and COD removal processes are competing with each other. The current efficiency of ammonia electrooxidation ranged from 20.9% to 40.4%. The summarized efficiencies of ammonia and

COD removal for sample B exceed 100% (113.6%–127.2%). In GC-MS studies of wastewater, many organic compounds were identified; however, the identified compounds were a negligible part of all substances present in the wastewater. Furthermore, the number of identified compounds in biologically pretreated wastewater samples C and D was lower than for samples A and B. This was due to the fact that more polar compounds were produced in electrooxidation processes from biologically pretreated wastewaters. Among the identified compounds: dibutyl phthalate, pyridine, indole, phenols, mono- and dicarboxylic acids predominated.

Electrooxidation of wastewaters led to the formation of many new organic compounds. Despite a significant drop in COD value, the number of identified substances in the wastewaters after electrooxidation was significantly higher than the number of substances identified in the raw wastewater. This suggests that during electrooxidation, the decomposition of macromolecular compounds occurs along with the formation of lower molecular weight compounds (and less polar products), determined by GC-MS. The products of electrooxidation were both chlorinated and non-chlorinated compounds. The number of identified chlorinated organics was relatively small (<5%) relative to the total chlorinated organics concentration, (12.9–19.8 mg/L Cl). Several electrooxidation products: derivatives of furan and furanone (probably originated from tannin) – 1,3-dichloropropan-2-ol (mutagenic), 1,1,1,3,3-pentachloropropanone, 1,3-dichloropropan-2-one, ethyl chloroacetate, 1,3-dichloropropanol-2, 1,3-dichloropropene-1,1,2,2-trichloropropane.

The substance determined in all samples of raw and electrooxidation treated wastewater as well as in tannin solutions was dibutyl phthalate. This compound was probably a product of tannin decomposition.

Additionally, a cost evaluation of the process was conducted. At a current density of 1.5 A/dm^2, the energy consumption was in range from 78.2 to 171 kWh/kg of N–NH$_4^+$.

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