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ELECTROCOAGULATION, ELECTROFLOTATION AND OXIDATION PROCESSES WITH ALUMINIUM ANODE IN THE TRETMENT OF WASTEWATERS

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ABSTRACT
Our previous studies have shown purification of leather industry wastewater by different compounds, including chlorides. Special focus was given to electrocoagulation, electroflotation and electrooxidation. Electrocoagulation has been in use for water production or wastewater treatment. Advanced oxidation processes were shown as effective against recalcitrant biological and chemical contaminants. After 5 minutes of electrolysis at 0.5, 1, 2 and 3 A/dm^2 with aluminium electrodes, the changes were observed on the GCMS and UV/VIS spectrophotometer results comparing to the ones before the treteament. With this technology, metal cations are produced on the electrodes through electrolysis and these cations form various hydroxides in the water depending on the water pH.
Keywords: Electrolysis, Electrocoagulation, Electroflotation, Leather industry wastewaters.

1. INTRODUCTION
Electrochemical treatment is a powerful tool for the purification of many kinds of wastewater. The technique has been successfully used for treatment of domestic sewage, wastewaters from tanneries, the metal plating industry, dye production, wastewater containing cyanides, phenols and EDTA and landfill leachate. [1]
The leader industry wastewater used in this research contained high concentrations of chlorides. The effect of the main parameters – initial pH, current density and electrolysis cell construction – on chloride removal were investigated. The electrochemical treatment of wastewaters containing chlorides is a relatively new technique. Generally, during electrochemical treatment, pollutants can be destroyed by direct anodic oxidation or an indirect oxidation process. Both processes play an important role in the electrochemical treatment of wastewater containing chlorides.
Aluminium and iron metal salts are used in raw water and wastewater treatment. Both metals can form multivalent ions, Al^{3+}, Fe^{2+} and Fe^{3+}, and various hydrolysis products. [2] Metal cations go through a series of hydrolytic reactions depending on the pH of the solution and mononuclear (Fig. 1 and Eq. 1) and polynuclear hydroxides form in the solution. [3]

$$Me^{3+}(aq) + nH_2O \leftrightarrow Me(OH)_n^{3-n} + nH^+(aq) \quad (1)$$

Neutral amorphous metal hydroxide, $Al(OH)_3$ is poorly soluble species. Electrodes which produce coagulants into water are made from either iron or aluminium. In addition, there can be inert electrodes, typically cathodes, which are sometimes used as counter-electrodes in the system.

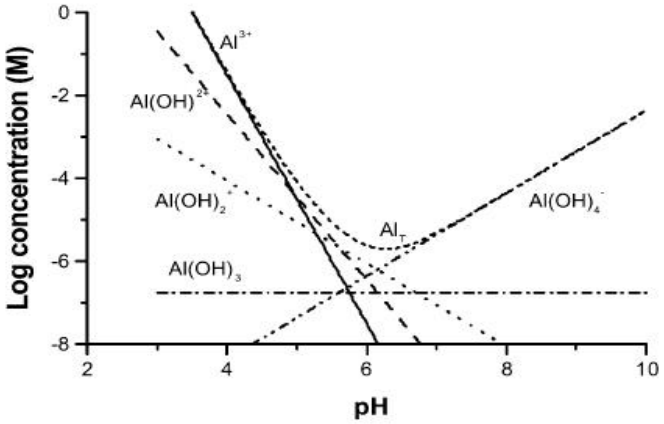

Figure 1. Concentrations of soluble monomeric hydrolysis products of Al(III) in equilibrium with the amorphous hydroxides at zero ionic strength and 25 °C [2]

Main reactions of electrocoagulation by aluminium anode are:

$$Al \rightarrow Al^{3+} + 3e^- \quad (2)$$

in an alkaline medium:

$$Al^{3+} + 3OH^- \rightarrow Al(OH)_3 \quad (3)$$

in an acidic medium

$$Al^{3+} + 3H_2O \rightarrow Al(OH)_3 + 3H^+ \quad (4)$$

2. EXPERIMENTAL

The wastewaters were sampled from a tank containing a mixture of treated water at a leather factory producing 1097 m^3 of wastewater per day. Aluminum electrodes and laboratory glassware were used for the experiment process which is described in detail elsewhere. [3] It consisted of a glass cell inside which cathode-anode was arranged in the middle. The working area of anode and cathode was 0.42 dm^2 each, and the gap between them 5 mm. We have chosen aluminium anode and cathode (high-purity aluminum) because of research [3].

All the experiments described here were carried out under batch conditions in order to ensure a sample aliquot sufficient for analytical determinations. The sample volume for all tests was 500 ml. For aluminium electrodes the current density was 0.5; 1; 2 and 3 A/dm^2. The electrochemical treatment of chlorides containing wastewater was carried out for the time interval of 5 min, after which pH, adsorptivity at 200-240 nm were determined. For selected time interval of electrolysis, total chlorine was also determined and UV/VIS and GC-MS studies were made. pH was determined by PHYWE pH meter.

The UV/VIS spectra in the range 190-900 nm were made by a Perkin-Elmer Lambda 25 Spectrophotometer. The GC-MS identification of the products of electrochemical treatment of the wastewater containing chlorides was made after extraction with dichloromethane (200 ml sample, 10 ml CH_2CI_2). QP2010S Gas-Mass Spectrophotometer with 2B-5 W/Guardian column (30 m length, 0.25 mm i.d., 0.25 μm film thickness) was used. Chromatographic separation involved an isothermal run of 1 min at 50°C, followed by a temperature increase at the rate 5°C/min up to 310°C, and finally by a 15 min isothermal run. The mass detector (MSD) worked in the SCAN mode, at 280°C, in the range of molecular weight of 40-570.

3. RESULTS AND DISCUSSION

The UV/VIS spectrum of raw leather industry wastewater (Fig. 2) contained medium absorption band with maximum at 205, 214: 225, 235 nm, a high absorption band with maximum at 210, 216, 227, 233 and 237 nm, a very high intensity with maximum 194, 212 and 218 nm, a wide and very high absorption with maximum in range 221-222 nm and 229-230 nm.

Table 1. Absorption of benzene derivates in water. [4]

Substituent X	λ_{max}, nm	Solvent	Signal reduction [%]		
			0.5 A	1 A	2 A
-OH	210	H_2O	64.98	69.46	66.93
$-NH_2$	230	H_2O	77.77	75.19	66.91
$-NO_2$	266	H_2O	49.23	63.27	68.53
$-SO_2NH_2$	217,5	H_2O	63.40	57.96	65.49
-	194	hexane	94.20	95.86	97.16
-	205	ethanol	48.60	35.77	49.53

The intensity of absorption between 190 and 237 nm gradually decreased during the electrochemical treatment (Tab. 1). This can easily be explained by the destruction of other chromophoric groups: nitro- and above all the azo-groups. These absorption bands correspond to many chromophores, so interpretation of the spectrum is difficult. In the course of electrochemical treatment the adsorption disappeared very quickly. The comparison of the UV absorption spectra of leather industry wastewaters after treatment with the Al anode-cathode on 0.5, 1 and 2 A/dm^2 with respective spectra before treatment confirms the conclusion that 2 A/dm^2 is the most effective current density for electrochemical treatment for leather industry wastewaters (Tab. 1 and Fig. 2).

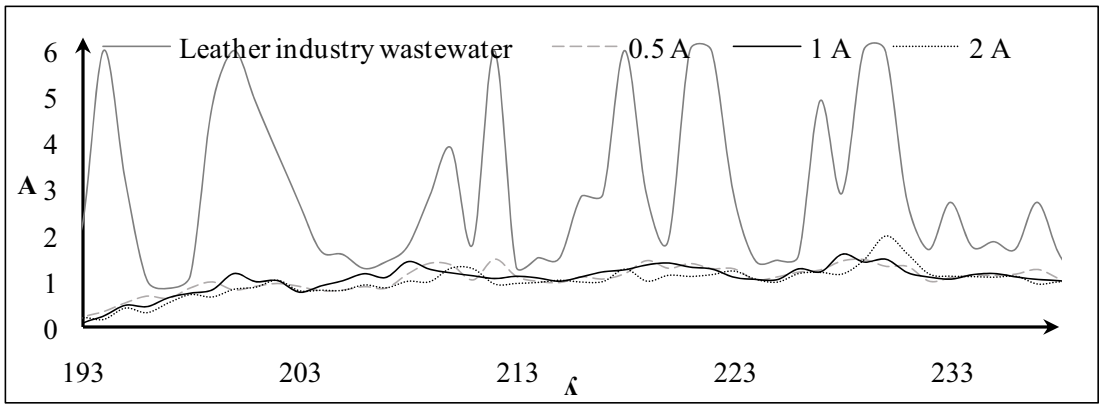

Figure 2. UV spectra of raw and electrochemically treated (Al anode-cathode) wastewater.

Overall results of the experiment are shown in Table 1. A GC-MS investigation showed that the gas chromatogram of raw wastewater (Fig. 3) contained lot of detected compounds. Fig. 4: A; B; C; D shows a decrease in the intensity of the largest peaks.

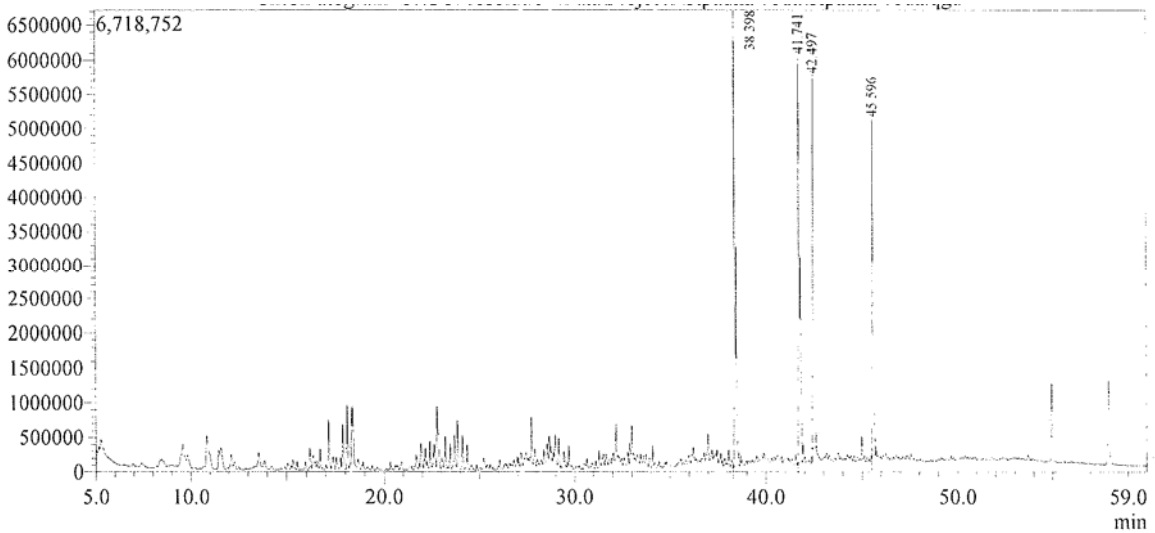

Figure 3: Gas chromatogram of a CH_2C1_2 extract of raw wastewaters

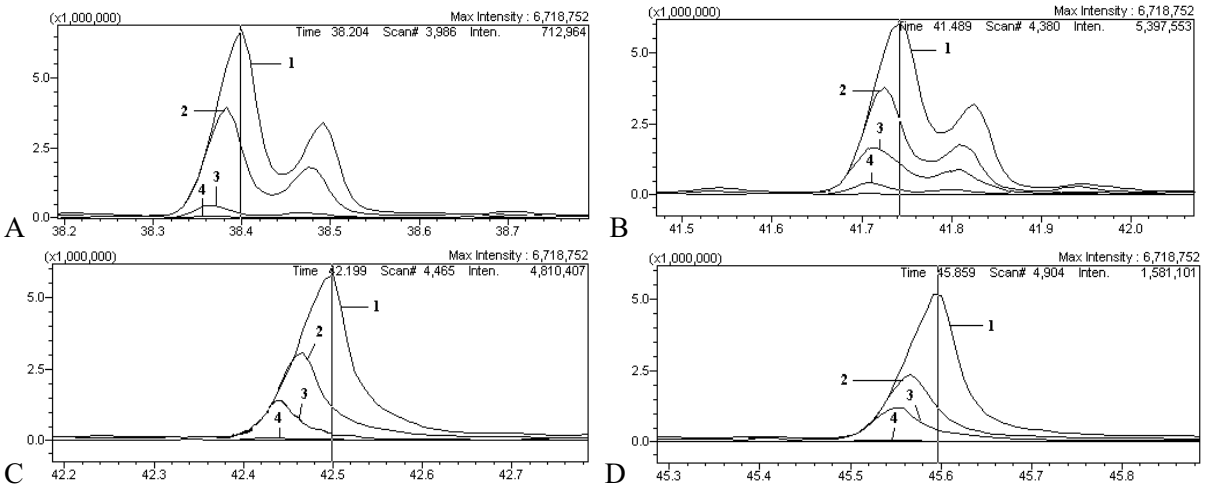

Figure 4. Intensity of the largest peaks, 1- raw wastewater; 2-0.5 A; 3-1 A; 4-2 A and the line for 3A is in the bottom of all graphs(see Fig. 5); (R. Time: A-38.39; B-41.74; C-42.49; D-45.59)

Table 2 presents reduction of the largest peak areas identified in the selected samples of wastewater after electrochemical treatment (Fig. 4).

Table 2. Reduction of largest peak areas.

R.Time	A/dm^2	0.5	1	2	3
38.39	%	46.73	73.04	94.53	99.99
41.74		42.88	72.71	94.23	99.56
42.49		53.58	78.77	98.48	100.00
45.59		55.11	83.79	98.46	99.98

pH of raw wastewater was 8, and after treatment on 0.5; 1; 2; 3 A/dm^2 were 7.88, 7.9, 7.95 and 7.98 correspondently. Hence, main reaction of electrocoagulation by aluminium anode is reaction 3.

4. CONCLUSIONS

The data from Table 2 and the UV spectra prove that the mechanism of electrochemical destruction of compounds present in wastewater is slightly different for the four current density.

Main reaction of electrocoagulation by aluminium anode in experiment with leather industry wastewater is $Al^{3+} + 3OH^- \rightarrow Al(OH)_3$.

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