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## Electrochemical oxidation of a textile dye wastewater using a Pt/Ti electrode

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### Abstract

Textile dye wastewater (TDW) from a reactive azo dyeing process was treated by an electrochemical oxidation method using Ti/Pt as anode and stainless steel 304 as cathode. Due to the strong oxidizing potential of the chemicals produced (chlorine, oxygen, hydroxyl radicals and other oxidants) when the wastewater was passed through the electrolytic cell the organic pollutants were oxidized to carbon dioxide and water. A number of experiments were run in a batch, laboratory-scale, pilot-plant, and the results are reported here according to residence time and initial addition of HCl in raw wastewater. When of 2 ml of HCl 36% were added and after 18 min of electrolysis at 0.89 A/cm<sup>2</sup>, chemical oxygen demand (COD) was reduced by 86%, biochemical oxygen demand (BOD<sub>5</sub>) was reduced by 71%, ADMI color units were reduced by 100%, and TKN was reduced by 35%. The biodegradability of the wastewater was improved because the COD/BOD ratio decreased from 2.16 to 1.52. At the same time the efficiency of the electrode was about 170 g h<sup>-1</sup> A<sup>-1</sup> m<sup>-2</sup>. and the mean energy consumption was 21 kW h/kg of COD. These results indicate that this electrolytic method could be used for effective TDW oxidation or as a feasible detoxification and color removal pretreatment stage for biological post treatment. © 1999 Elsevier Science B.V. All rights reserved.

*Keywords:* Azo dye; Textile; Color removal; Wastewater; Electrolysis treatment; Ti/Pt electrode

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## 1. Introduction

Textile dye processes are among the major industrial water users; in many areas, this industry has the wastes most difficult to treat satisfactorily. Textile dye wastewater is well known to contain strong color, high pH, temperature and COD and low biodegradability especially the effluent from the dyeing stages of the dyeing and finishing process [1]. The removal of dyes (color) is therefore a challenge to both the textile industry and the wastewater-treatment facilities that must treat it.

Dyeing wastewater is usually treated by conventional methods such as biological oxidation [2] and adsorption [3]. Because of the large variability of the composition of textile wastewaters, most of these traditional methods are becoming inadequate. Ozonation has been proposed as a potential alternative [4–6]. It has been shown to be quite effective in decolorizing textile wastewater; however, the cost of ozonation for such purposes needs to be further ascertained to insure the competitiveness of this method [7].

In recent years there has been increasing interest in the use of electrochemical methods for the treatment of wastewaters [8–10]. The organic and toxic pollutants present in treated wastewaters such as dyes and phenols are usually destroyed by a direct anodic process or by an indirect anodic oxidation via the production of oxidants such as hydroxyl radicals, ozone, etc. Electrochemical methods have been successfully applied in the purification of several industrial wastewaters [11,12] as well as landfill leachate [13].

This study deals with the treatment of TDW by an electrochemical method using a Ti/Pt anode.

## 2. Theoretical approach

The time of oxidation depends upon the stability and concentration of compounds, concentration of NaCl used, temperature, pH of the solution, time of recirculation, size of the anode and current and voltage applied.

The electrochemical reactions which take place during the electrolysis of a brine solution are complicated and not entirely known. For the time being only assumptions can be made, based on the products that can be determined ( $\text{Cl}_2$ ,  $\text{ClO}_2$ ,  $\text{O}_3$ ,  $\text{OH}^\cdot$ ,  $\text{O}^\cdot$ ,  $\text{ClOH}^\cdot$ ,  $\text{H}_2\text{O}_2$ ,  $\text{O}_2$ ,  $\text{H}_2$ ,  $\text{CO}_2$ ). The radicals  $\text{OH}^\cdot$ ,  $\text{O}^\cdot$  and  $\text{ClOH}^\cdot$  have a very short life owing to their high oxidation potential and they are either decomposed to other oxidants ( $\text{Cl}_2$ ,  $\text{O}_2$ ,  $\text{ClO}_2$ ,  $\text{O}_3$ , and  $\text{H}_2\text{O}_2$ ) or they oxidise organic compounds (direct oxidation). The primary ( $\text{Cl}_2$ ,  $\text{O}_2$ ) and secondary ( $\text{ClO}_2$ ,  $\text{O}_3$ , and  $\text{H}_2\text{O}_2$ ) oxidants that are produced from the destruction of radicals have quite a long life and are diffused into the area away from the electrodes continuing the oxidation process (indirect oxidation).

The direct electro-oxidation rate of organic pollutants is dependent on the catalytic activity of the anode, on the diffusion rates of organic compounds in the active points of the anode and the applied current density. The indirect electro-oxidation rate is dependent on the diffusion rate of secondary oxidants into the solution, temperature and the pH. An effective pollutant degradation is based on the direct electrochemical process

because the secondary oxidants are not able to completely convert all organics into water and carbon dioxide. From previous investigations [14] in acid solutions, oxygen, free chlorine and maybe some amounts of ozone and chlorine oxides are the main secondary oxidants as by-products of the direct oxidation process. In moderate alkaline solutions a cycle of chloride–chlorine–hypochlorite–chloride takes place, which produces  $\text{OCl}^-$ , oxygen and some amounts of hydrogen peroxide and maybe ozone. In strong alkaline solutions the cycle of chloride–chlorine–chloride is reduced owing to the production of  $\text{ClO}_3^-$  that is a stable chlorate anion. Therefore, in low pH the chlorides are reduced during the electrolysis process producing free chlorine, while at high pH the chlorides are reduced producing chlorates. Only in moderate alkaline to neutral conditions, the initial concentrations of chlorides remain stable the continuous production of free hydroxyl radicals [15,16].

### 3. Methods

#### 3.1. The laboratory pilot plant

The experimental plant (Fig. 1) consisted of the electrolytic cell, the recirculation reactor, the wastewater feed system, and the cooling system for the wastewater.

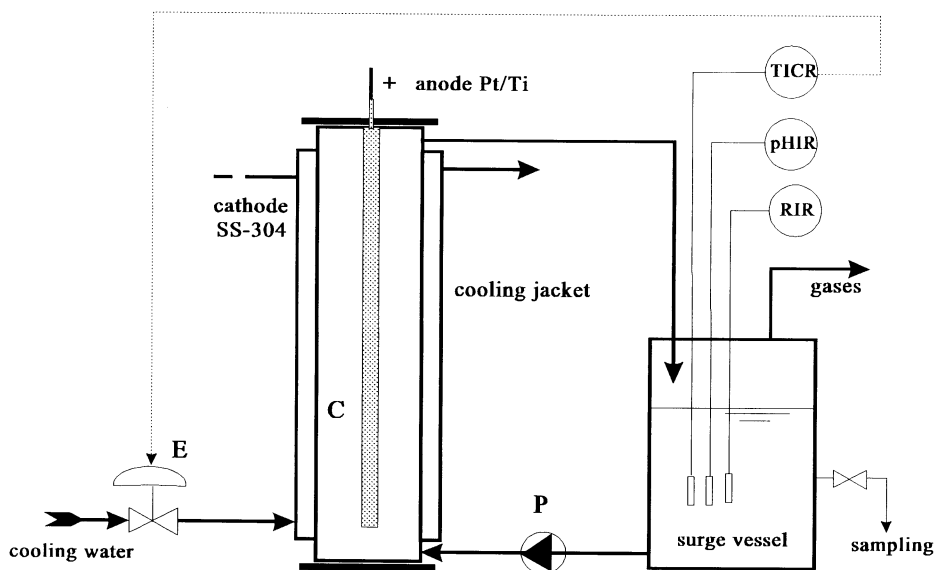


Fig. 1. Experimental laboratory pilot-plant. C = electrolytic cell; E = electromagnetic valve; P = recirculating pump; TICR = temperature indicator controller, recorder; pHIR = pH indicator recorder; RIR = redox indicator recorder.

### 3.1.1. Electrolytic cell

The electrolytic cell consisted of the cathode, which was a stainless steel 304 cylinder of 5 cm diameter, and the anode, which was located in the centre of the cylinder and which was made of titanium alloy, measuring 18 cm long and 1 cm diameter, covered by platinum alloy foil approximately 0.25 mm thick. The electrodes were operated at 20 volts dc and 50 A.

### 3.1.2. Recirculation reactor

The recirculation reactor (V) included a vessel of 5 l, which contained the wastewater to be treated, and a peristaltic pump (P) of 10 l/min flow rate, which continuously recirculated the reactor content into the electrolytic cell.

### 3.1.3. Cooling system

The cooling system included a temperature indicator controller (TIC), an electric valve for the water and a cooling water jacket, which was located in the reactor. The cylinder wall and the cooling jacket constituted the cathode. When the temperature of the water increased above 45°C cooling water circulated in the jacket until the temperature returned to the desired value.

The change of redox potential and pH in the reactor was continuously recorded by the RIR and pHIR respectively. The samples for analysis were drawn from the recirculation reactor.

## 3.2. Materials

The composition of the TDW used in all experiments is shown in Table 1.

## 3.3. Methodology

The efficiency of the electrolytic cell was studied when HCl 36% was added in amounts 0, 1, 2, 3, and 4 ml per liter of raw wastewater. The temperature remained stable at 42°C during all experiments. Four experiments under the same conditions were run and the results that are presented in this work are the average of the four separate

Table 1  
Characteristics of wastewater used

Character	Value
Total suspended solids (TSS, mg/l)	34
Total organic carbon (TOC, mg/l)	1810
BOD <sub>5</sub> (mg/l)	1540
COD (mg/l)	3325
pH	11.82
Color (ADMI units)	41 530
Clorides (mg/l)	24 200
Total Kjeldahl nitrogen (TKN, mg/l)	314

measurements. Each experiment was of batch operation and its duration was 18 min. Every 2 min samples were taken from the reactor and chemical oxygen demand (COD), biochemical oxygen demand (BOD<sub>5</sub>), ADMI color units, total Kjeldahl nitrogen (TKN), redox, pH were measured.

### 3.4. Methods of analysis

COD, BOD<sub>5</sub> and TKN were carried out according to the Standard Methods for Examination of Water and Wastewater [17]. The pH and redox were measured using a Cosort ion-analyser (Model P 603). The color was measured using the ADMI tristimulus filter (Tentative) method, section 2120 D of Standard Methods. A Hitachi 2000 spectrophotometer with 1-cm path length was used to measure transmittance of samples.

## 4. Results and discussion

### 4.1. Chemical oxygen demand (COD)

As shown in Fig. 2, the more the initial feed is increased in HCl 36% the higher the rate of COD reduction. Thus for 0, 1, 2, 3, and 4 ml HCl 36% addition per liter of TDW the rate of COD reduction was 146, 202, 300, 342, and 349 mg/l per minute respectively as well as the COD reduction after 18 min of electrolysis was from 3325

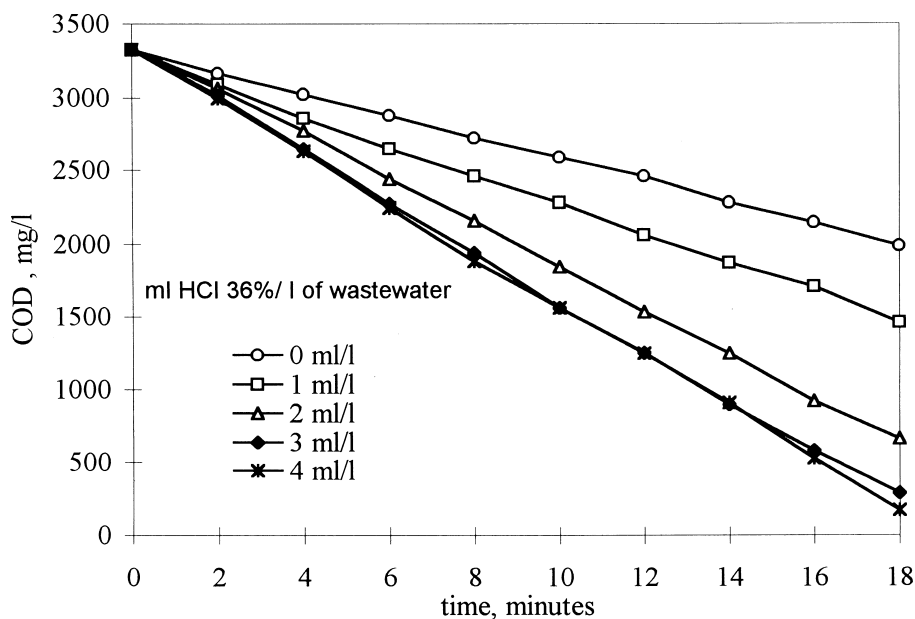


Fig. 2. Chemical oxygen demand (COD) reduction during electrolysis treatment.

mg/l to 2115, 1553, 533, 275, and 148 mg/l respectively. The increase in the rate of COD reduction is not significant for over 2 ml HCl 36% addition per liter of TDW.

#### 4.2. Biochemical oxygen demand ( $BOD_5$ )

$BOD_5$  reduction follows a similar trend with COD (Fig. 3). Thus for 0, 1, 2, 3, and 4 ml HCl 36% addition per liter of TDW the rate of  $BOD_5$  reduction was 30, 72, 117, 146, and 154 mg/l per minute respectively as well as the  $BOD_5$  reduction after 18 min of electrolysis was from 1540 mg/l to 1260, 910, 440, 207, and 155 mg/l respectively. The increase in  $BOD_5$  reduction rate was not significant for over 3 ml HCl 36% addition per liter of TDW.

#### 4.3. COD/ $BOD_5$ ratio

COD/ $BOD_5$  ratio is an indicator for the biodegradability of a wastewater. The COD/ $BOD_5$  ratio for TDW is about 2.16, which indicates that TDW is not much amenable for biological treatment. Fig. 4 shows that during electrolysis the COD/ $BOD_5$  ratio is reduced. Thus for 0, 1, 2, 3, and 4 ml HCl 36% addition per liter of TDW the rate of COD/ $BOD_5$  ratio reduction was 0.042, 0.0557, 0.0764, 0.0657, and 0.0316 per minute respectively as well as the COD/ $BOD_5$  ratio reduction after 18 min of electrolysis was from 2.16 to 1.78, 1.67, 1.48, 1.52, and 1.87 respectively. The rate of COD/ $BOD_5$  ratio increases up to 2 ml HCl 36% addition per liter of TDW and from then on it starts to increase. Therefore, using electrolytic oxidation as a pretreatment and decolorization method of TDW, followed by a biological treatment, the addition up to 2

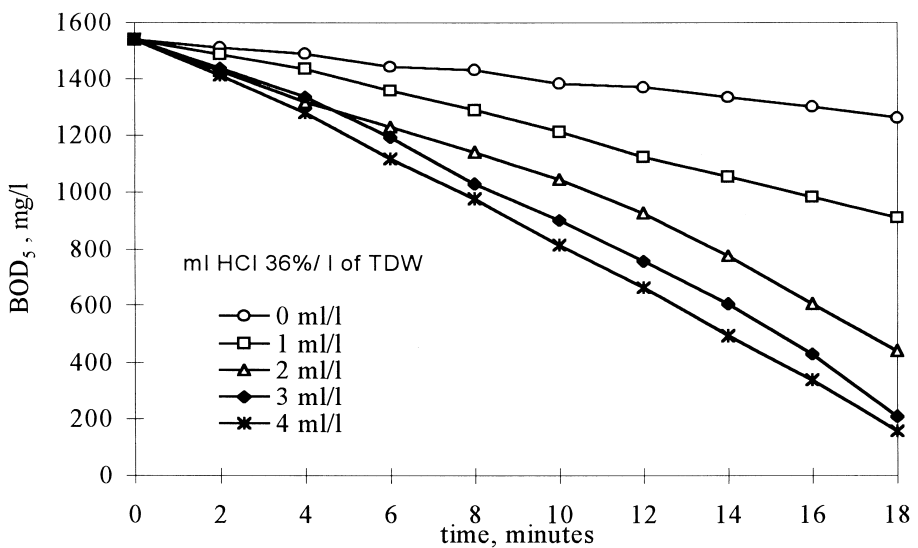


Fig. 3. Biochemical oxygen demand ( $BOD_5$ ) reduction during electrolysis treatment.

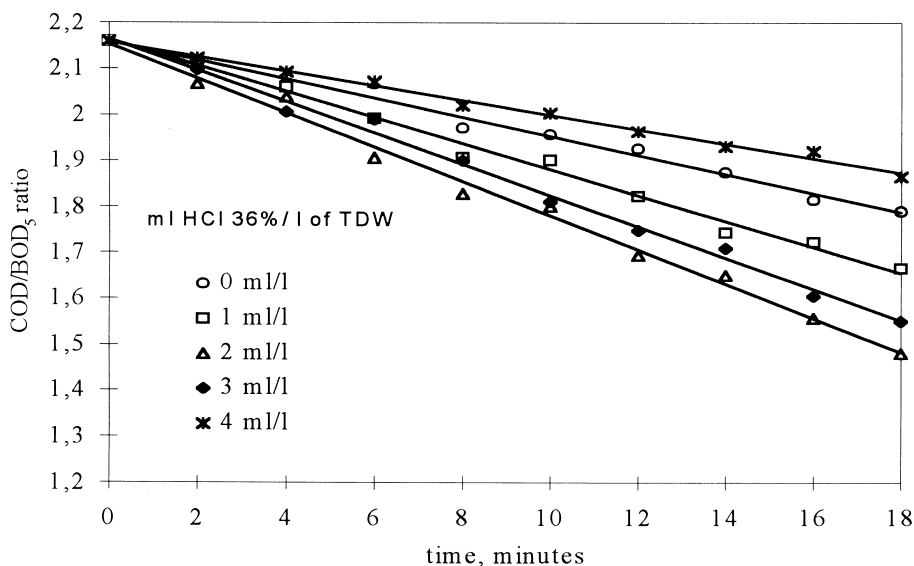


Fig. 4. COD/BOD<sub>5</sub> ratio reduction during the electrolysis treatment.

ml HCl 36% addition per liter of TDW continuously improves the biodegradability of the TDW.

#### 4.4. Total Kjeldahl nitrogen (TKN)

The TKN drop follows a similar trend with COD (Fig. 5). Thus for 0, 1, 2, 3, and 4 ml HCl 36% addition per liter of TDW the rate of TKN reduction was 8.5, 11.9, 19.4,

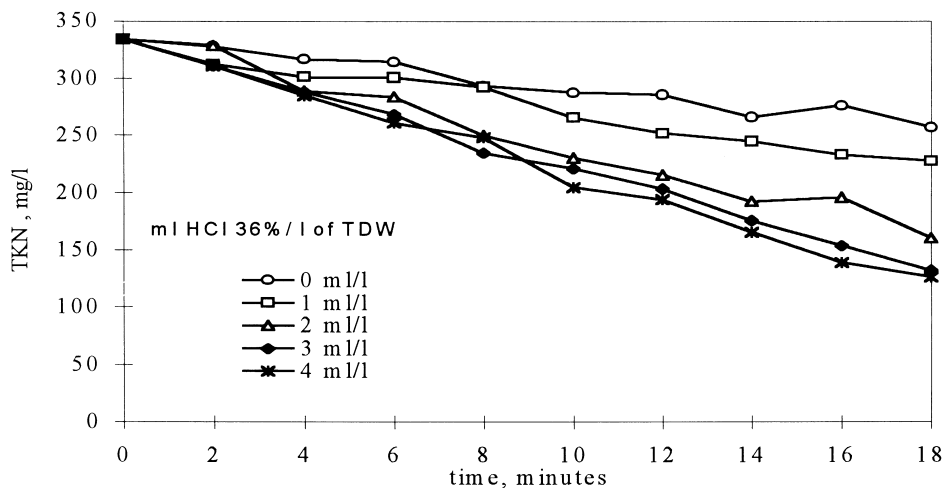


Fig. 5. TKN reduction during electrolysis treatment.

22.35, and 23.7 mg/l per minute respectively and the TKN reduction after 18 min of electrolysis was from 334 mg/l to 261, 218, 164, 141, and 125 mg/l respectively. The increase of TKN reduction rate was not significant for over 2 ml HCl 36% addition per liter of TDW.

#### 4.5. Colour

The colour removal is of the greatest interest because colour is considered the most important polluting parameter of TDW. Fig. 6 shows the reduction of ADMI colour units of TDW under various experimental conditions. With the addition of HCl, the colour from 41 500 ADMI color units is reduced to zero in almost 4, 6, 8, and 18 min for 1, 2, 3, and 4 ml HCl 36% addition per liter of TDW respectively while with no HCl addition the colour units are reduced asymptotically at 15 000 ADMI colour units. This strongly suggests that the presence of  $H^+$  is necessary for the oxidation of colour-bonds of the organic compounds.

#### 4.6. pH

The changes in pH are shown in Fig. 7. The starting pH values for 0, 1, 2, 3, and 4 ml HCl 36% addition per liter of TDW were 11.82, 10.19, 8.57, 6.2, and 3.86 respectively while the end values of pH after 18 min of electrolysis were 11.22, 10.43, 9.65, 9.5 and 9.35 respectively. This can be explained from Table 1 where it is evident that  $H^+$  production is smaller than  $HO^-$  resulting in a shift of pH to the alkaline region.

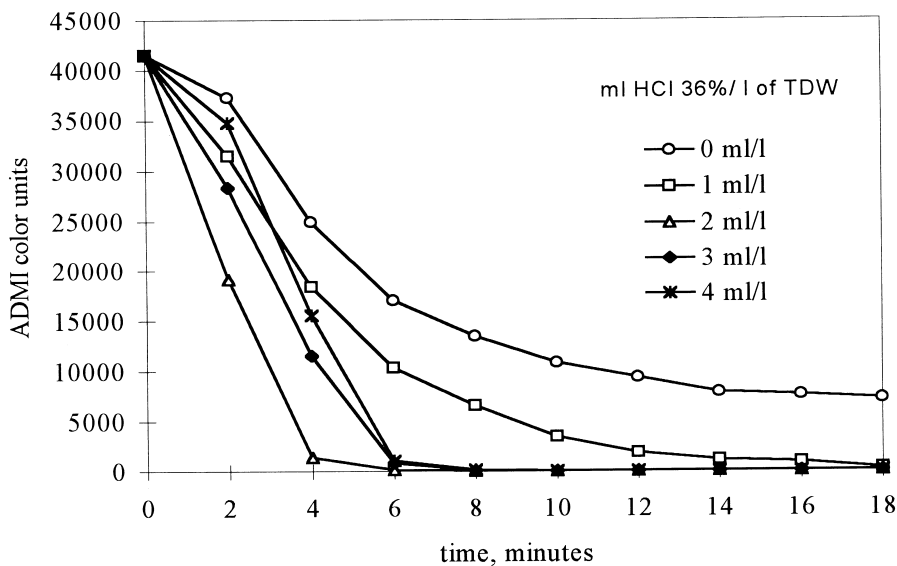


Fig. 6. Colour reduction during electrolysis treatment.



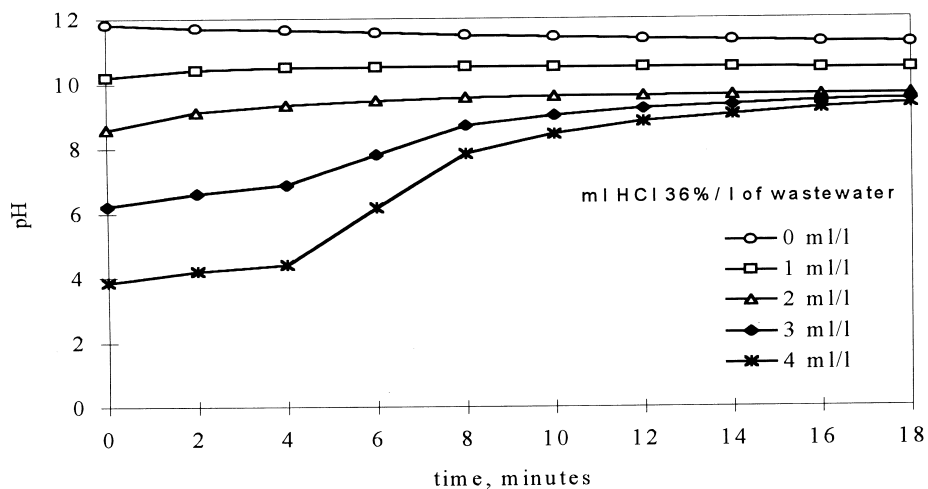
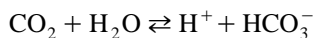


Fig. 7. pH changes during the electrolysis treatment.

However the pH was stabilised around 9.5 due to the buffer formed from the carbon dioxide production according to the reaction:



#### 4.7. Oxidation potential (redox)

The changes of redox values during the electrolysis are shown in Fig. 8. After 6–8 min the redox is stabilized. Thus for 0, 1, 2, 3, and 4 ml HCl 36% addition per liter of

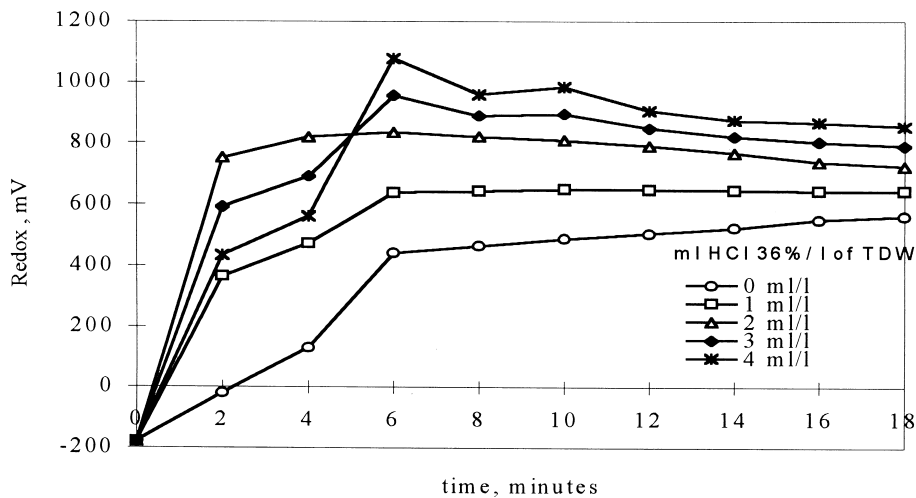


Fig. 8. Redox changes during the electrolysis treatment.

TDW, the redox values were stabilized at 563, 642, 722, 788, and 854 mV respectively. It can be concluded that the higher the pH, the lower the redox. This is in agreement with [16], according to which during the electrolysis of alkaline solutions hydroxyl radicals are formed which are capable of oxidizing to a great extent the organic matter and for this reason they have a very short life, thus reducing the total oxidation potential of the solution.

#### 4.8. Energy consumption

Fig. 9 shows the energy consumption during the electrochemical oxidation. The energy demand measured in kilowatt hours per kilogram of COD reduced ( $COD_r$ ) during 18 min of electrolytic oxidation is stabilized during the first 4 min of electrolysis for every case of HCl addition. Thus for 0, 1, 2, 3, and 4 ml HCl 36% addition per liter of TDW the energy consumption was measured 49.9, 32.8, 21.2, 19.9, and 19.55 kWh/kg  $COD_r$  respectively. These values indicate that the presence of  $H^+$  improves the efficiency of electrolysis concerning the COD reduction. Also with addition of more than 2 ml of HCl 36% per liter of TDW the energy consumption was about the same.

#### 4.9. Anode efficiency

The efficiency of the anode of the electrode is shown in Fig. 10. It has been calculated in grams of COD removed ( $COD_r$ ) per hour per ampere and per square meter. The anode efficiency during the 18 min of electrolytic oxidation is stabilized in the first 4 min of electrolysis for every case of HCl addition. Thus for 0, 1, 2, 3, and 4 ml HCl 36% addition per liter of TDW the anode efficiency was measured 70, 107, 166, 177,

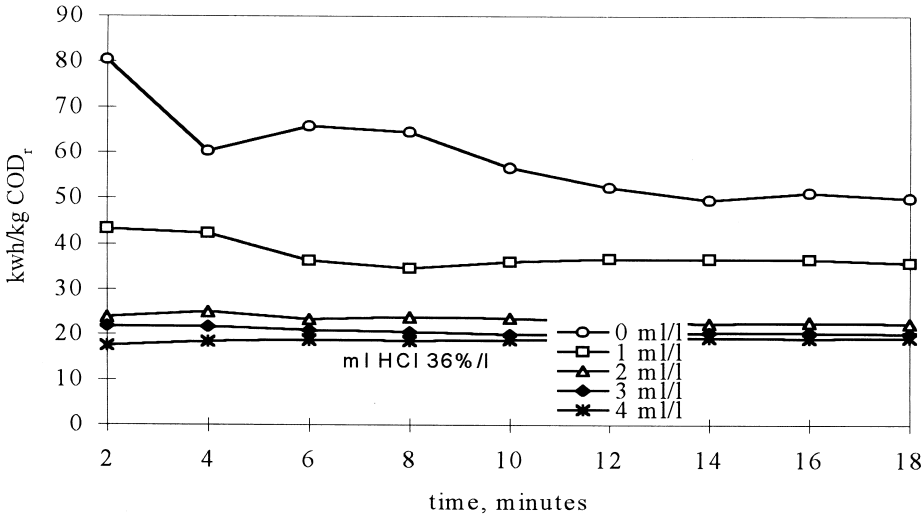


Fig. 9. Energy consumption during the electrolysis treatment.

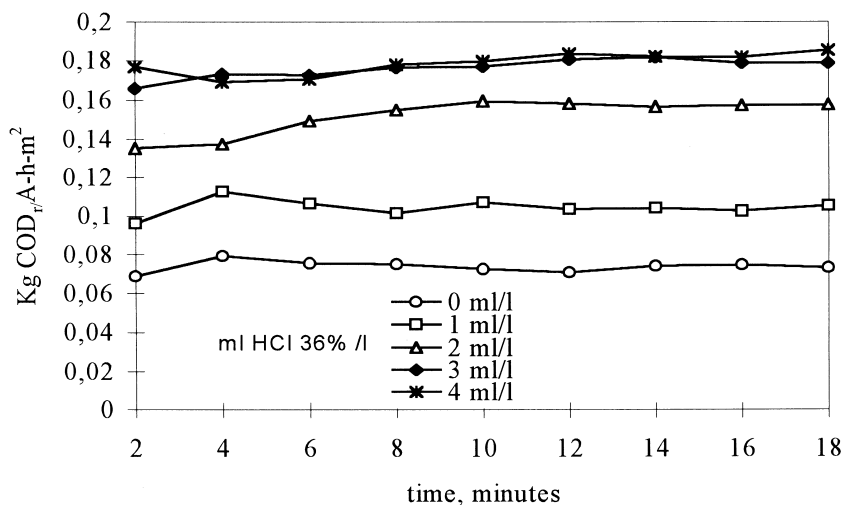


Fig. 10. Anode efficiency during the electrolysis treatment.

and  $180 \text{ g h}^{-1} \text{ A}^{-1} \text{ m}^{-2}$  respectively. These values indicate that the presence of  $\text{H}^+$  improves the anode efficiency. Also, above 2 ml of HCl 36% addition per liter of TDW, the anode efficiency was about the same.

## 5. Conclusions

For the experiments run in laboratory pilot-scale plant, using Ti/Pt electrode as anode, it can be concluded that the electrolytic oxidation of TDW stream containing about 4% (w/v) concentration of NaCl and 40 000 ADMI colour units is effective. For addition of 2 ml of HCl 36% and after 18 min of electrolysis at  $0.89 \text{ A/cm}^2$ , COD was reduced by 86%,  $\text{BOD}_5$  by 71%, ADMI colour units by 100%, and TKN by 35%. The biodegradability of the wastewater was improved because the COD/BOD ratio decreased from 2.16 to 1.52. At the same time the efficiency of the electrode was about  $170 \text{ g h}^{-1} \text{ A}^{-1} \text{ m}^{-2}$  and the mean energy consumption was  $21 \text{ kW h/kg}$  of COD.

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