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Electrochemical oxidation of wastewater generated from a dyeing and stamping process of a textile factory in chloride-containing aqueous media

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ABSTRACT

Electro-oxidation of wastewater from a textile factory was studied in chloride media using dimensionally stable type anodes (i.e., DSA-type), specifically Ti/PtPb(1%)Ox or Ti/PtPd(10%)Ox. The study variables were electrode composition, cell voltage, electrolyte concentration (NaCl), pH, and electrolysis time. Removal of color and organic matter from the wastewater was evaluated by measuring its UV-Vis absorbance and chemical oxygen demand (COD). These measurements revealed the generation of hypochlorite ions during the electro-oxidation of the wastewater. The ability of the electrode to generate active chlorine species (Cl_2, HClO, and ClO^-) was dependent on the chemical composition of the anode and pH conditions. The Ti/PtPd(10%)Ox anode favored the formation of active chlorine species, but these species were not generated when using the Ti/PtPb(1%)Ox anode. The Ti/PtPd(10%)Ox anode eliminated the color in short periods of time and removed 97% of the COD with 45 min of electrolysis ($4 \leq pH \leq 8$). In contrast, the Ti/PtPb(1%)Ox anode required longer electrolysis times to eliminate the color, and only removed 25% of the COD at 65 min. Therefore, the Ti/PtPd(10%)Ox anode was concluded to function through an indirect mechanism involving active chlorine species. The relative amount of ClO^- generated, determined by the relative absorbance at $\lambda = 290$ nm, was directly associated with the cell voltage applied, concentration of chloride ions, and electrolysis time.

Keywords: Electrochemical oxidation; DSA-type anodes; Textile wastewater; Color and COD removal; Chloride; Hypochlorite

1. Introduction

The textile industry consumes a lot of water and produces polluting wastewater containing various chemical reagents. The textile dyeing stage produces the greatest contamination due to the use of dyes and dyeing auxiliary chemical reagents [1,2]. Textile dyes consist of complex chemical structures with various substituents. There are many structural varieties of textile dyes, for example, acidic, basic, dispersed, azo, diazo, anthraquinone-based, and metal complex dyes [2]. The examples of dyeing auxiliary reagents include gums, salts, humectants, fats, thickeners, adhesives, peroxides, chlorine, silicates, alkalis, acids, phosphates, starch, mordants, conditioners, defoamers, waxes, dyes, and pigments [2]. Conventional methods of treating effluents from the textile industry include biological treatment, adsorption, or coagulation [1,3]. While these treatments reduce the load of organic matter, effluents containing recalcitrant nonbiodegradable compounds remain polluting. Therefore,

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the wastewater from the textile industry requires effective purification treatments.

Robinson et al. [2] and Wang et al. [4], published review papers on the remediation of dyes in textile effluent, they reviewed a set of investigations involving various treatment methods (chemical, physical, and biological). Among the advanced oxidation processes used to treat wastewaters, electrochemical oxidation has been receiving increasing levels of attention [5–7]. Here, the organic pollutants present in wastewaters are usually destroyed by a direct anodic process or by an indirect anodic oxidation via the production of oxidants such as hydroxyl radicals, ozone, and hypochlorite ions [5,6,8]. The effectiveness of electrochemical oxidation applied to organic matter depends critically on the electrocatalytic activity of the electrode material that constitutes the anode; therefore, the appropriate selection of the anode can increase the efficiency of the removal of organic matter [9]. The complete mineralization of organics can be realized using high oxygen overpotential anodes such as SnO_2 [10,11], PbO_2 [12], and boron-doped diamond [13]. Also, chloride ions in the electrolysis process have been demonstrated to increase the efficiency of pollutant removal through the participation of electrogenerated intermediates, in particular chlorine, hypochlorous acid and hypochlorite ions, which are denoted as active chlorine species [5,6,8,14–22]. This oxidation of organic matter mediated by active chlorine has been indicated to occur by way of an indirect oxidation mechanism, where the oxidant intermediates (active chlorine) are electrogenerated in situ [5,6,8,14–22].

Despite the improved understanding of the indirect oxidation mechanism, there is still controversy over the influence of the variables in the process [16]. In the work, we used dimensionally stable anode (DSA)-type anodes, specifically Ti/PtPb(1%)Ox and Ti/PtPd(10%)Ox, to investigate the effects of the electrode material, cell voltage, electrolyte concentration (NaCl), and pH on the effectiveness of electro-oxidation of the effluent from a dyeing and printing process used in the textile industry.

2. Materials and methods

2.1. Physicochemical characterization of wastewater from a textile factory

The wastewater used in this study was obtained from the dyeing and stamping process of a textile factory located in the city of Puebla, Mexico. The wastewater was stored at 4°C and then was characterized for pH, conductivity, total dissolved solids (TDS), chemical oxygen demand (COD), color, and turbidity.

2.2. Reagents

Sodium chloride (Merck AR) was used as the support electrolyte. The Spectroquant® COD Cell Test (a mixture of potassium dichromate, mercury sulfate, silver sulfate, and sulfuric acid; Merck, Germany) with different sensitivity ranges were used to determine the COD.

2.3. Electrodes

PtPb(1%)Ox-coated titanium (Ti/PtPb(1%)Ox) and PtPd(10%)Ox-coated titanium (Ti/PtPd(10%)Ox) were used as the anodes, and RuO_2-coated titanium (Ti/RuO_2) was used as the cathode in all cases. These electrodes were prepared in our laboratory and the anodes were DSA-type. A titanium mesh (American Society for Testing and Materials (ASTM) grade 2) was used to support the oxide layers. The mesh was prepared by thermally decomposing the precursors in an alcoholic solution and was applied by brushing onto the metallic support. The solvent was evaporated at a low temperature (100°C) and each electrode was annealed for 1 h at 450°C to form the metallic oxide phase. The relative amount of each metal in the film corresponded to the nominal molar percent of the metal in the precursor solution. The area of each electrode was 41.25 cm^2 (7.5 cm × 5.5 cm).

2.4. Electrochemical methodology

The electrochemical oxidation process was performed in an electrochemical cell with a capacity of 150 mL and a sample volume of 100 mL. The parallel electrodes (anode and cathode) were placed vertically and 3 mm apart. Raw wastewater samples (100 mL) were subjected to electrolysis. The cell voltage was applied from an external power source (DS-304M, Zurich), and the current and voltage were measured using a conventional multimeter. The effects of the electrode material, cell voltage, electrolyte concentration (NaCl), and pH on the electrochemical oxidation of wastewater from the textile factory were analyzed.

2.5. Analytical control

The effects of the electrochemical treatment were analyzed by determining the COD, and acquiring UV-Vis absorption spectra of the samples using a PerkinElmer Lambda 20 spectrometer. Also, pH measurements were made using a Conductronic PC 18 pH meter. The COD and color were monitored using a spectrophotometer (SQ118, Merck). COD was evaluated using COD vials (Merck, Germany) with different sensitivity ranges. The COD expressed the amount of oxygen originating from potassium dichromate that reacted with the oxidizable substances contained in 1 L of water under the working conditions of the specified procedure. Sample digestion was performed in a TR 300 thermoreactor (Merck) for a period of 2 h at 148°C; subsequently, the COD was determined by means of absorbance measurements.

3. Results and discussion

3.1. Physicochemical characterization of wastewater resulting from a dyeing and stamping process used in a textile factory

The physicochemical parameters of wastewater from the investigated textile factory are shown in Table 1. The wastewater was observed to be translucent yellow and slightly acidic, and to have a low conductivity value and moderately low values of COD, SDT, color, and turbidity.

A UV-Vis absorption spectrum of wastewater from the investigated textile factory (see Fig. 2) showed a well-defined local maximum (I) at a wavelength of 429 nm, associated with electronic transitions of dyes that promote the yellow coloration of wastewater. At wavelengths below 350 nm, an intense band was observed to be accompanied by a shoulder (II) at about 236 nm, which may have resulted from

Table 1
Physicochemical parameters of wastewater from the textile factory

Parameters	Magnitude
Turbidity (NTU)	54
Color (m^{-1})	24.9
COD (mg/L)	245
TDS (mg/L)	250
Conductivity (mS/cm)	0.42
pH	6.7

electronic pi transitions of the aromatic compounds present in the wastewater.

3.2. Electrochemical oxidation of textile industry wastewater

3.2.1. Influence of the anode composition

The textile factory wastewater in the presence of NaCl (2.5 g/L) was subjected to electrolysis for various durations at 7 V, using the Ti/PtPb(1%)Ox and Ti/PtPd(10%)Ox anodes. The relative absorbance at a wavelength of 429 nm (A_{429}) (peak I, Fig. 2) and percent removal of the COD of the wastewater as a function of electrolysis time for each of the anodes is shown in Figs. 1(a) and (b), respectively.

Both anodes were observed to reduce the relative absorbance and COD of the wastewater to a practically constant value. Using the Ti/PtPd(10%)Ox anode, the relative absorbance reached its lowest observed value, of about 0.095, after 15 min of electrolysis, whereas with the Ti/PtPb(1%)Ox anode, the lowest relative absorbance value (0.135) was obtained only at 45 min of electrolysis. These results indicated that the removal of the compounds responsible for the coloration of the wastewater occurred more rapidly with the Ti/PtPd(10%)Ox anode than with the Ti/PtPb (1%)Ox anode. When using the Ti/PtPd(10%)Ox anode, the maximum percent of the COD removed was 97%, which occurred at 45 min of electrolysis. In contrast, with the Ti/PtPb(1%)Ox anode, the maximum percent of the COD removed was 25%, which occurred at 60 min of electrolysis (Fig. 1(b)). The difference between percent removals of the COD indicated that the Ti/PtPd(10%)Ox anode removed organic matter from the wastewater more effectively than did the Ti/PtPb(1%)Ox anode. These observations taken together showed that both anodes managed to remove the color of the wastewater relatively rapidly, but required a prolonged period to remove excess oxidizable organic matter.

We also acquired UV-Vis absorption spectra of the textile factory wastewater samples subjected to electrochemical oxidation treatment using the Ti/PtPb(1%)Ox (Fig. 2(a)) and Ti/PtPd(10%)Ox (Fig. 2(b)) anodes under the same electrolysis conditions. In general, the intensity of the absorption of UV-Vis light by wastewater decreases as the wastewater is subjected to increasing durations of electro-oxidation. And indeed, in our experiments, peak I and shoulder II of the UV-Vis spectra of the two samples (Figs. 2(a) and (b)) decreased in intensity and eventually disappeared as the electrolysis time was increased, implying that the oxidation process removed or transformed the species responsible for the coloration of the textile wastewater. However, electrolysis of the wastewater sample using the Ti/PtPd(10%)Ox anode for at least 30 min resulted in the formation of a new absorption peak, at a wavelength of 290 nm (peak III in Fig. 2(b)), and the intensity of this peak increased as the electrolysis time was further increased.

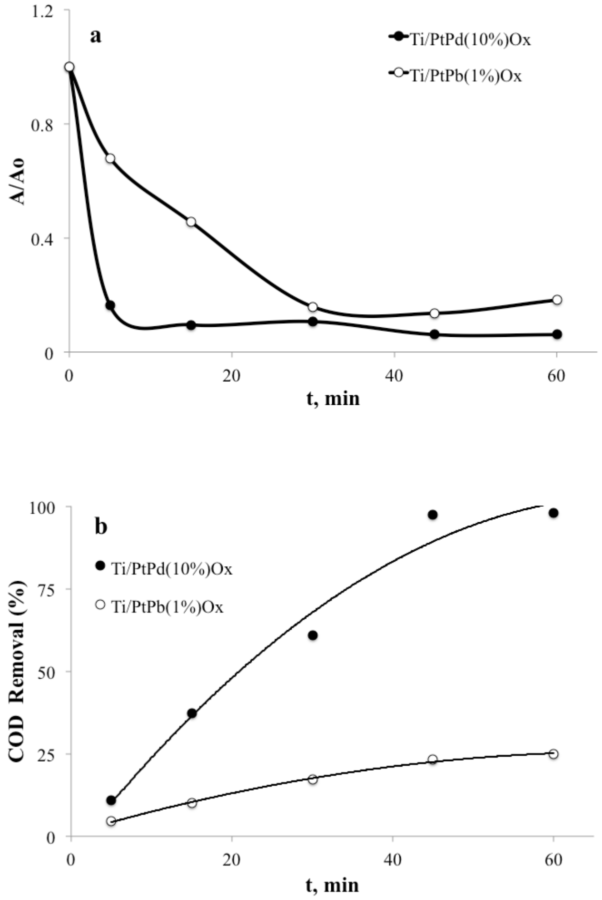

Fig. 1. (a) Relative absorbance (λ = 429 nm) and (b) percent removal of the COD of the investigated textile factory wastewater as a function of electrolysis time using the Ti/PtPb(1%)Ox and Ti/PtPd(10%)Ox anodes. Cell voltage: 7 V, NaCl concentration: 2.5 g/L, and pH 6.7.

The absorption peak at 290 nm was assigned to the hypochlorite ion [17], produced in situ from the oxidation of the chloride ions of the supporting electrolyte, according to the sequence of reactions [8,14,15,22,23].

$$2\,Cl^- \rightarrow Cl_2 + 2e \quad (1)$$

$$Cl_2 + H_2O \rightarrow HClO + H^+ + Cl^- \quad (2)$$

$$HClO \rightarrow H^+ + ClO^- \quad (3)$$

Molecular chlorine (Cl_2), hypochlorous acid (HClO), and hypochlorite ions (ClO^-) are all strongly oxidizing chlorine species and are collectively referred to as active chlorine [5,6,8,14–22]. These species are responsible for the indirect mechanism of oxidation of organic matter that occurs in the bulk solution [15]. Which of these active chorine species

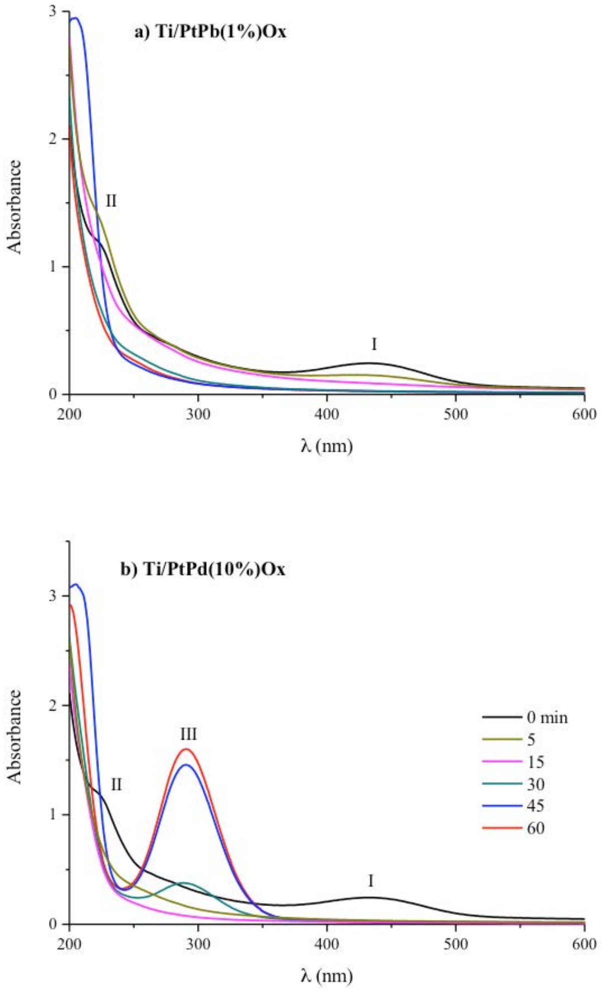

Fig. 2. UV-Vis absorption spectra of the textile wastewater before and after the electrochemical oxidation treatment as a function of electrolysis time using the (a) Ti/PtPb(1%)Ox and (b) Ti/PtPd(10%)Ox DSA-type anodes. Cell voltage: 7 V, NaCl concentration: 2.5 g/L, and pH 6.7 ($t = 0$ min, for raw wastewater).

predominate depends on the pH and temperature conditions [17]. However, some authors have pointed out that during the generation of chlorine, other radicals can be formed, such as $Cl^{\bullet}$, $ClO^{\bullet}$, and $Cl_2^{\bullet}$, which have higher oxidation potentials than does active chlorine [20,24,25]. Additionally, chlorate ions may be generated by side reactions of hypochlorite in solution and on the anode [20,24]. Based on this scheme, it has been proposed that the possible occurrence of these chlorine radicals on a DSA-type electrode, generated analogously to the way that hydroxyl radicals are generated during the electrocatalytic oxidation of chloride ions, might increase the oxidation strength of active chlorine for the indirect degradation of organic pollutants [18].

As described earlier, in our electrolysis experiments with the Ti/PtPd(10%)Ox anode, the intensity of UV-Vis absorption peak III increased with electrolysis time, indicating that increasing the duration of the electrolysis promoted oxidation of the chloride ion (Eq. (1)) and consequently production of the hypochlorite ion (Eq. (3)). And, in contrast, the electrochemical oxidation of wastewater with the Ti/PtPb(1%)Ox anode did not produce peak III in the UV-Vis spectrum (Fig. 2(a)), even with prolonged electrolysis times. This behavior indicated that the anode composition had a significant influence on the formation of active chlorine species, and this relationship is consistent with that observed by others [9,18,26]. The properties of the electrode material that favor the electrogeneration of active chlorine could be related to the overpotentials of the oxygen evolution reaction (OER) and/or the chlorine formation reaction [9]. Our observations indicated that the overpotential of the Ti/PtPd(10%)Ox anode for the chlorine evolution reaction must be lower than that of the Ti/PtPb(1%) Ox anode. The oxidation of organic matter with DSA-type anodes in the presence of chloride ions may involve, simultaneously, the direct and/or indirect mechanisms involving the presence of active chlorine and/or $OH^{\bullet}$ radicals electrogenerated by the discharge of water [27]. The removal of 97% of the COD from the wastewater with the Ti/PtPd(10%) Ox anode at 45 min of electrolysis suggested that the electrode material mostly operated using an indirect mechanism involving the hypochlorite ion, in accordance with Eq. (4).

$$R + ClO^- \rightarrow CO_2 + H_2O + Cl^- \tag{4}$$

where R corresponds to the oxidizable organic compounds.

For electrolysis times of ≤15 min, there was no evidence of absorption peak III in the UV-Vis spectrum (Fig. 2(b)), yet during that time interval the wastewater became colorless. These results suggested that the electrogenerated hypochlorite ion was consumed during the oxidation of the organic compounds (R) responsible for the color, in agreement with the indirect mechanism involving active chlorine. However, considering that the textile wastewater became colorless within a short period of time relative to the time required to remove the COD, the rapid decoloration of the wastewater observed in the chloride medium may have been due to the formation of chlorine radicals as was suggested by Costa and Olivi [19].

For electrolysis times of >15 min, absorption peak III was observed in the UV-Vis spectrum when using the Ti/PtPd(10%)Ox anode (Fig. 2(b)), and the removal of the COD therefore occurred simultaneously with the electrogeneration of active chlorine. In contrast, the absence of the hypochlorite ion during the electro-oxidation of the residual water with the Ti/PtPb(1%)Ox anode suggested that the oxidation of the organic matter in this case may have been mediated by the $OH^{\bullet}$ radicals from the discharge of H_2O [28]. Here, the absence of hypochlorite ions may have been responsible for the low removal of COD since only 25% of the COD was observed to be removed with 60 min of electrolysis. Another possibility was that ClO^- production with the Ti/PtPb(1%) Ox anode was much lower than that required to oxidize the organic matter (R), so that this anion was not detected in the UV-Vis spectra using this anode. The Ti/PtPd(10%)Ox anode favored the use of the hypochlorite ion, electrogenerated during the electrolysis, to oxidize the organic matter in the textile factory wastewater.

3.2.2. *Influence of cell voltage*

Samples from a mixture containing wastewater from the investigated textile factory with 2.5 g/L NaCl and a pH of 6.7 were subjected to electrolysis for various durations and applied cell voltages between 6 and 8 V using the Ti/PtPd(10%)Ox anode, and the products were characterized by obtaining their relative absorbance (λ = 429 nm) (Fig. 3(a)) and COD removal percentage values (Fig. 3(b)). Regardless of the cell voltage, the relative absorbance at λ = 429 nm decreased sharply as the electrolysis time was increased for short electrolysis times, and then remained constant as the electrolysis time was increased further. For an applied voltage of 7 V, the lowest relative absorbance value was 0.095, whereas for either 6 or 8 V, it was 0.165. Therefore, the vast majority of the color of the tested wastewater was removed within short electrolysis times, and this general behavior did not depend on the cell voltage.

For each of the different cell voltages applied, the COD removal percentage in our experiments generally increased with electrolysis time with no leveling off observed below a COD removal percentage of nearly 100% (Fig. 3(b)). The maximum percentage of the COD removed was 97%, which occurred when applying voltages of 7 and 8 V with electrolysis time of 60 min. For each of the electrolysis times tested, the lowest percentage of the COD removed occurred when a voltage of 6 V was applied; at this voltage, the maximum percent of the COD removed was 82%, which occurred for an electrolysis time of 60 min (note that the 60-min test was the longest duration treatment tested). Thus, whereas the wastewater color removal occurred with relatively short electrolysis times and was independent of cell voltage, a complete (nearly 100%) removal of the COD required longer electrolysis times and a cell voltage greater than 6 V.

UV-Vis absorption spectra of the textile factory wastewater as a function of the oxidation time for 6 and 8 V using the Ti/PtPd(10%)Ox anode are shown in Figs. 4(a) and (b), respectively. The absorption bands I and II corresponding to the residual water disappeared after 5 and 15 min of electrolysis when applying 8 and 6 V, respectively. As the electrolysis time was increased above 15 min, peak III appeared at a wavelength of 290 nm, and its intensity increased as the electrolysis time was further increased, due to the increase in the concentration of hypochlorite ions generated.

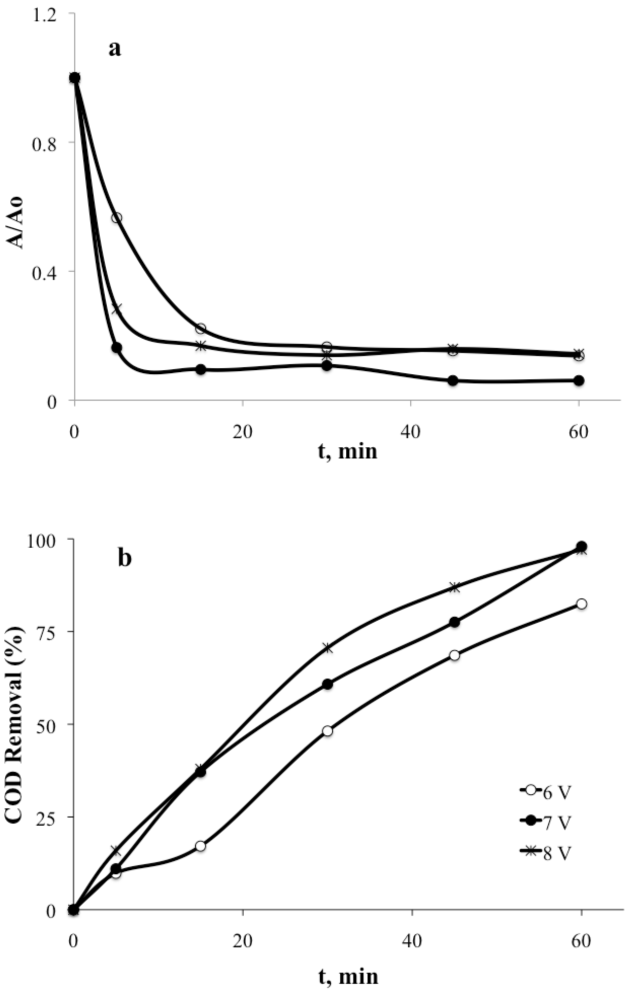

Fig. 3. (a) Relative absorbance (λ = 429 nm) and (b) percent removal of the COD of the textile factory wastewater as a function of the electrolysis time. Cell potential difference: 6–8 V, 2.5 g/L NaCl, and pH 6.7.

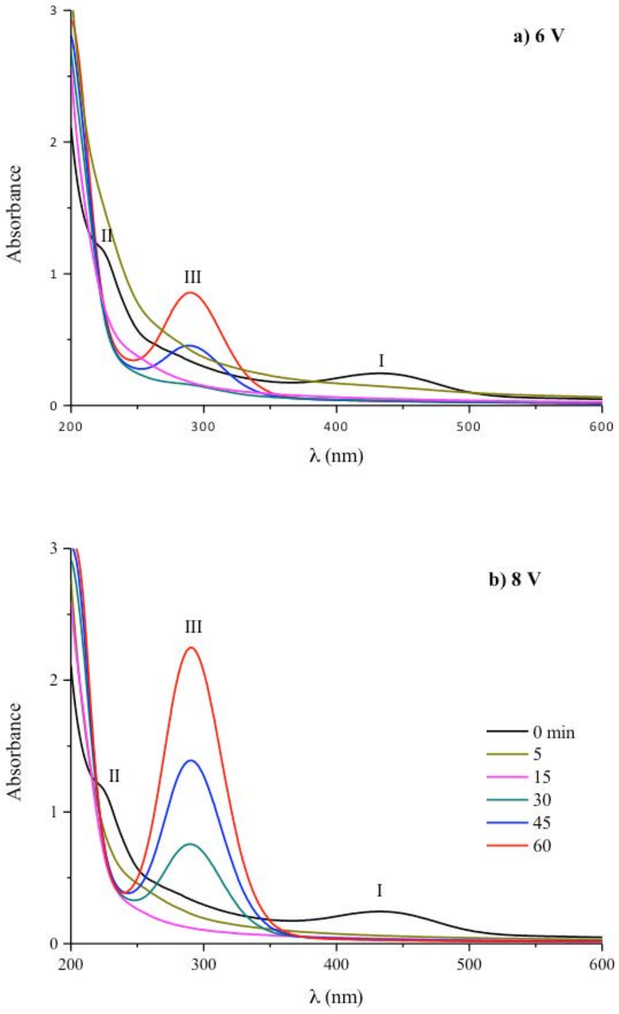

Fig. 4. UV-Vis spectra of the textile factory wastewater before and after an electrochemical oxidation treatment. Anode: Ti/PtPd(10%)Ox, support electrolyte: 2.5 g/L NaCl, pH 6.7. Cell voltages: (a) 6 V and (b) 8 V.

The relative amount of hypochlorite ion in the wastewater after electrolysis is proportional to the absorbance maximum at 290 nm in the UV-Vis spectrum (peak III, Figs. 4(a) and (b)). To compare the relative numbers of hypochlorite ions generated in solution under the different cell voltage conditions and as a function of electrolysis time, plots of relative absorbance (A_{290}/A_{max}) versus electrolysis time were constructed (Fig. 5). Here, A_{max} corresponds to the maximum absorbance at 290 nm, which was obtained with a cell voltage of 8 V and 60 min of electrolysis; we here assumed this A_{max} to be equivalent to the maximum number of generated hypochlorite ions. The relative absorbance was found to increase in direct relation to the electrolysis time, and the slope of the curve increased in proportion to the applied cell voltage. This result indicated that the concentration of hypochlorite ions generated increased with the electrolysis time and cell voltage. Consequently, a greater amount of active chlorine (hypochlorite) was produced for higher applied potentials and longer durations of electrolysis. Therefore, the production of active chlorine occurred simultaneously with the removal of organic matter through the indirect mechanism involving mediation by active chlorine.

3.2.3. Influence of the NaCl concentration

The electro-oxidation process of the textile factory wastewater was analyzed as a function of the concentration of NaCl at pH 6.7. The wastewater was subjected to electrolysis using the Ti/PtPd(10%)Ox anode with a constant cell voltage (7 V) and various electrolysis times. Figs. 6(a) and (b) show, respectively, the relative absorbance at 429 nm and the COD removal percentage, each as a function of the electrolysis time at various concentrations of NaCl. The relative absorbance decreased sharply in the first 5 min of electrolysis and remained below 0.1 as the electrolysis time was increased. Moreover, this behavior was independent of the NaCl concentration (between 2.5 and 4.5 g/L).

Therefore, the inclusion of NaCl as the electrolyte in the textile factory wastewater, besides favoring the conductivity of the medium, reduced the absorbance at 429 nm (and hence color) relatively rapidly. For each NaCl concentration tested, the COD removal percentage increased with the electrolysis time and eventually plateaued at a value close to 100%, which implied a nearly complete removal of organic matter. It took about 30 min of electrolysis to reach the COD removal maximum when the NaCl concentration was either 3.5 or 4.5 g/L and about 45 min when the NaCl concentration was 2.5 g/L. A similar behavior was reported by Costa and Olivi [19] when they studied the effect of chloride concentration on the electrochemical treatment of synthetic tannery wastewater: they found that higher chloride concentrations led to a decrease in total organic carbon as well as of COD and absorbance values at 228 nm, consistent with our results.

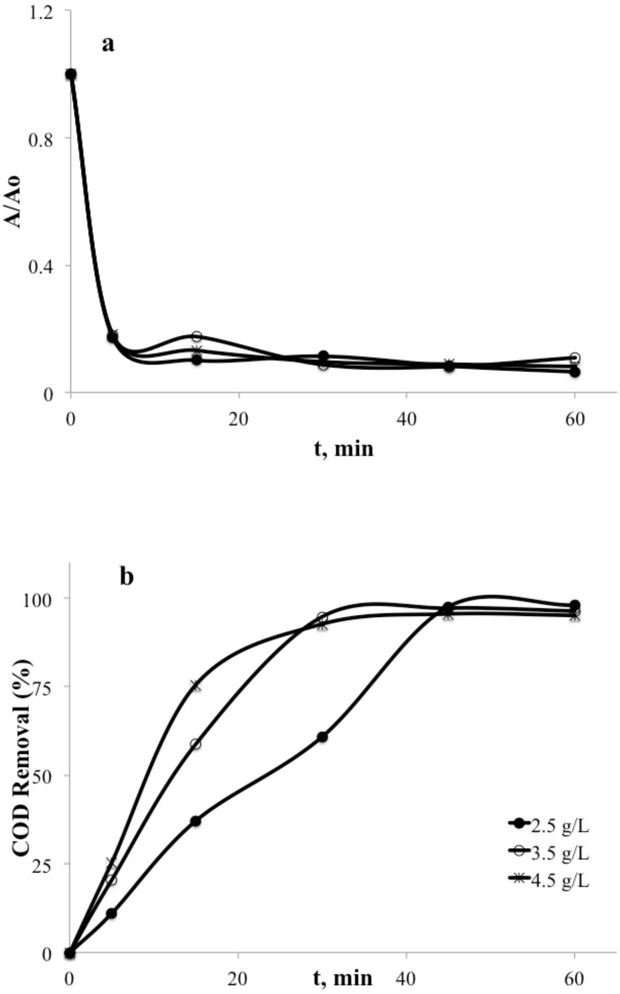

Fig. 6. (a) Relative absorbance (λ = 429 nm) and (b) percent removal of the COD from the textile factory wastewater as a function of the electrolysis time at various concentrations of NaCl. Anode: Ti/PtPd(10%)Ox, pH 6.7, and cell voltage: 7 V.

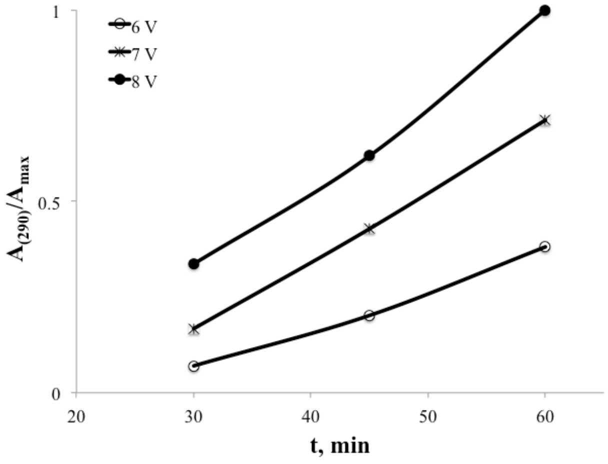

Fig. 5. Relative absorbance at λ = 290 nm of the textile factory wastewater as a function of the electrolysis time for different cell voltages. Anode: Ti/PtPd(10%)Ox, support electrolyte: 2.5 g/L NaCl, and pH 6.7.

Figs. 7(a)–(c) show UV-Vis absorption spectra of the textile factory wastewater with various concentrations of NaCl, after being subjected to electrolysis for various durations with a constant cell voltage of 7 V. At each of the NaCl concentrations tested, absorption bands I and II disappeared rapidly, after only 5 min of electrolysis, indicating a rapid

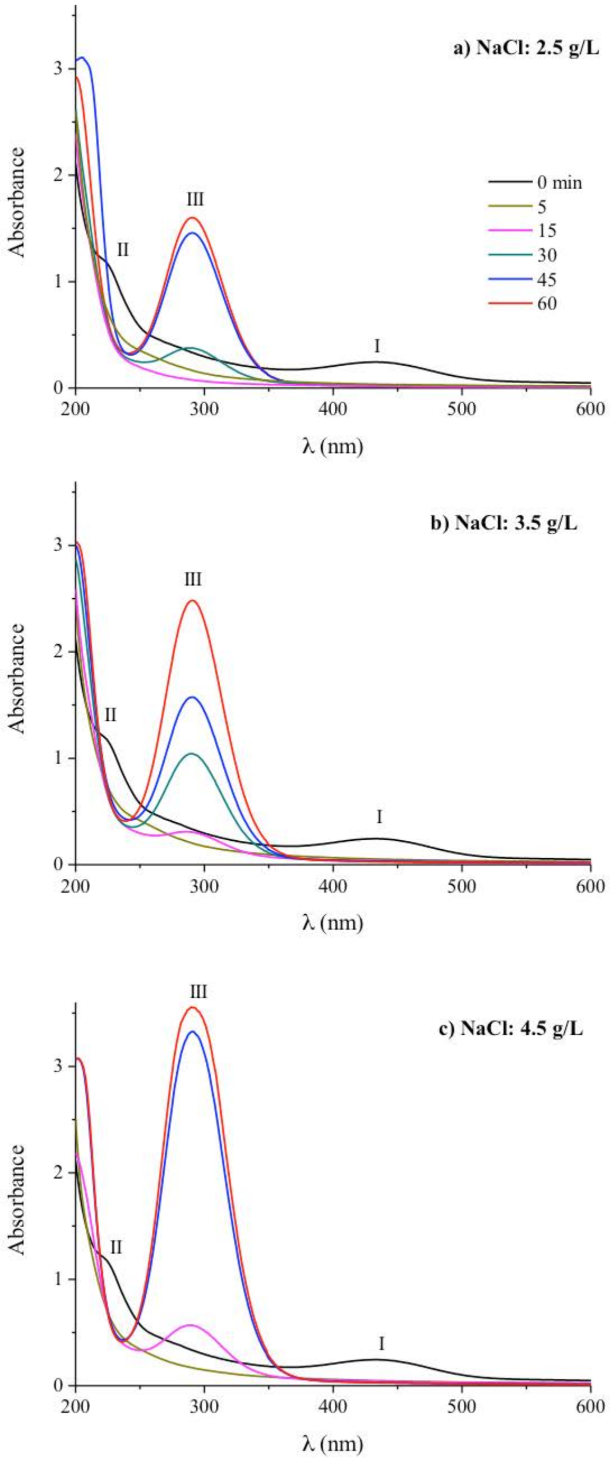

Fig. 7. UV-Vis absorption spectra of the textile factory wastewater before and after electrochemical oxidation treatment for various concentrations of NaCl: (a) 2.5, (b) 3.5, and (c) 4.5 g/L. Anode: Ti/PtPd(10%)Ox, cell voltage: 7 V, and pH 6.7.

removal of color from the wastewater. Absorption band III at 290 nm started to appear at 15 min of electrolysis when 4.5 g/L of NaCl was used, and soon thereafter for the other cases, indicating the presence of hypochlorite ions during the oxidation of the wastewater. Absorption peak III at 290 nm was observed to increase in intensity with increasing electrolysis time, as described earlier. But here, the intensity of peak III was also found to depend strongly on the concentration of NaCl in the solution. Fig. 8 shows the relative absorbance at λ = 290 nm as a function of the electrolysis time for the different concentrations of NaCl. The relative absorbance at this wavelength increased with the electrolysis time. At any given electrolysis time, the intensity of the absorbance was found to be proportional to the concentration of NaCl. Therefore, the amount of hypochlorite generated was proportional to electrolysis time and chloride ion concentration in the solution.

The wastewater became colorless after short electrolysis times regardless of the NaCl concentration. The complete removal of the COD from the wastewater required prolonged electrolysis times, but the time required to reach values close to 100% COD removal decreased as the NaCl concentration was increased. This behavior was consistent with the production of hypochlorite ions since at higher concentrations of NaCl, a greater amount of active chlorine (hypochlorite) would be expected to be produced, which in turn would promote the removal of organic matter through the indirect mechanism described earlier [18,19].

3.2.4. Effect of pH

The electrolysis of the textile factory wastewater was carried out at various pH values between 2 and 10 under the following conditions: NaCl concentration of 2.5 g/L, cell voltage of 7 V, and electrolysis time of 60 min. The percent reduction of the absorbance at λ = 429 nm and of the COD in the wastewater are shown in Fig. 9. These values were both above 95% for all pH levels, with the exception of the percent reduction of the COD at pH 10, which was only 78%, indicating that alkaline conditions did not favor the removal of organic matter as was observed at pH < 10. The low removal of the COD in alkaline media may have been caused by the formation of chlorate or perchlorate as has been suggested by

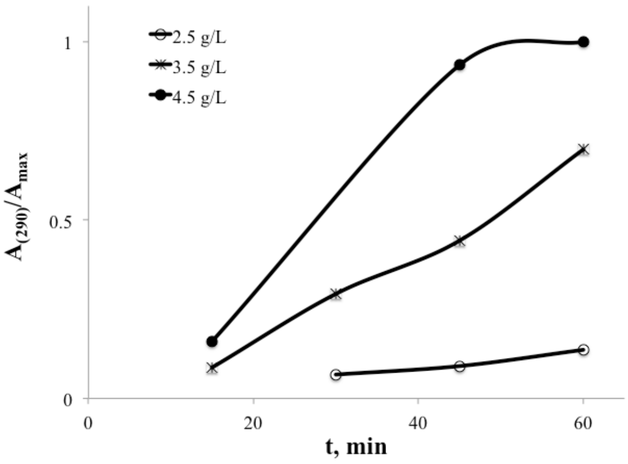

Fig. 8. Relative absorbance at λ = 290 nm of the textile factory wastewater as a function of the electrolysis time at various concentrations of NaCl; pH 6.7. Anode: Ti/PtPd(10%)Ox and cell voltage: 7 V.

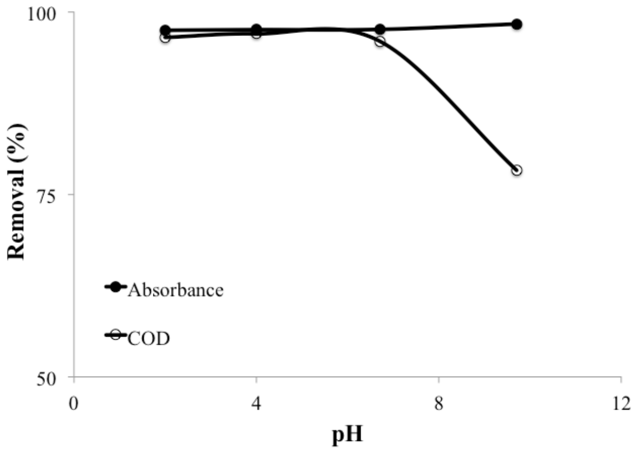

Fig. 9. Percent reduction of the intensity of the absorbance at λ = 429 nm and of the COD as a function of pH. Cell voltage: 7 V, electrolysis time: 60 min, and NaCl concentration: 2.5 g/L.

others [29]. On the other hand, Oliveira and colleagues [18] observed a dramatic decrease in the rate of decoloration of a solution of Acid Red 29 at pH 12, and they argued that such an effect could be due to the increased generation of oxygen associated with the OER, which renders chlorine formation more difficult.

UV-Vis spectra of the textile factory wastewater after it was oxidized at various pH conditions are shown in Fig. 10. Absorption bands I and II totally disappeared, regardless of the pH of the solution, indicating that the removal of the color of the wastewater did not depend on pH. Absorption band III, associated with the presence of the hypochlorite ion, was observed at pH > 2, consistent with previously reported results [18,29]. The relative amounts of each of the active chlorine species have been indicated to depend not only on temperature but also on the pH: chlorine, $Cl_{2(aq)}$, is the dominant species under very acidic conditions, HClO predominates at 3.3 < pH < 7.5, while ClO^- is the main species at pH > 7.5 [17]. However, the increase in the intensity of peak III (λ = 290 nm) at pH = 6.7, shown in Fig. 10, was due to the increase in the pH (>7.5) during the electrolysis experiments, where ClO^- is the predominant specie. While the hypochlorite ion is the dominant species in basic media, our results showed a drop in the COD removal at pH 10 that could nevertheless be justified by considering the interference of some undesirable side reactions such as formation of chlorate or perchlorate, water electrolysis and OER, should compete with the electrooxidation of the contaminant [29–31].

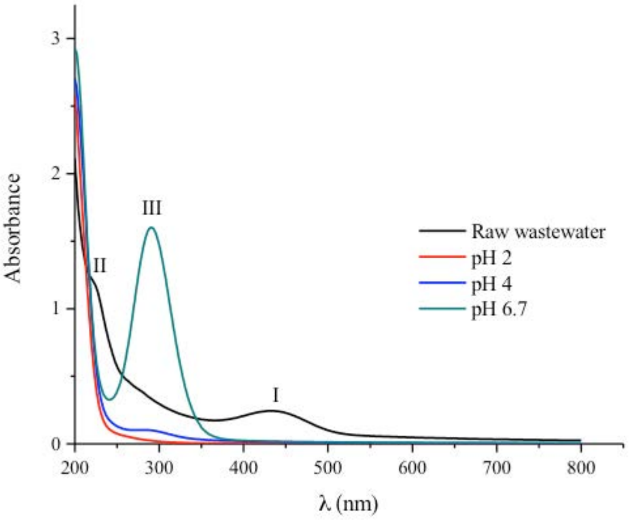

Fig. 10. UV-Vis spectra of the textile factory wastewater after oxidation with the Ti/PtPd(10%)Ox anode at various pH levels. Cell voltage: 7 V, Electrolysis time: 60 min, and NaCl concentration: 2.5 g/L.

4. Conclusions

The electrochemical oxidation of textile industry wastewater in a medium containing chlorides was studied using DSA-type anodes, specifically Ti/PtPb(1%)Ox and Ti/PtPd(10%)Ox. The effects of the electrode composition, cell voltage, electrolyte (NaCl) concentration, and pH were studied. The UV-Vis spectroscopy results showed that the hypochlorite ion was generated in the electrooxidation process at pH ≥ 4. The generation of hypochlorite ions depended on the chemical composition of the anode. Under the same electrolysis conditions, the Ti/PtPd(10%)Ox anode was found to favor the formation of the hypochlorite ion, but this ion was not detected in the wastewater when the Ti/PtPb(1%)Ox anode was used. The absence of hypochlorite ions during the electrolysis of the wastewater using the Ti/PtPb(1%)Ox anode prolonged the amount of time required to remove the COD, and in this case only ~25% of the COD was removed. In contrast, the generation of hypochlorite ions using the Ti/PtPd(10%)Ox anode resulted in the decoloration of the wastewater with relatively short electrolysis times (≤ 15 min) and a 97% removal of the COD with 45 min of electrolysis. The relative number of hypochlorite ions generated, determined by measuring the relative absorbance at a wavelength of 290 nm, was directly associated with the voltage of the applied cell, concentration of chloride ions, and electrolysis time. The results obtained from the electrochemical oxidation of textile industry wastewater using the Ti/PtPd(10%)Ox anode are consistent with an indirect mechanism involving mediation by active chlorine species.

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References

[1] A.B. Dos Santos, F.J. Cervantes, B. Jules van Lier, Review paper on current technologies for decolourisation of textile wastewaters: perspectives for anaerobic biotechnology, Bioresour. Technol., 98 (2007) 2369–2385.
[2] T. Robinson, G. McMullan, R. Marchant, P. Nigam, Remediation of dyes in textile effluent: a critical review on current treatment technologies with a proposed alternative, Bioresour. Technol., 77 (2001) 247–255.
[3] O. Türgay, G. Ersöz, S. Atalay, J. Forss, U. Welander, The treatment of azo dyes found in textile industry wastewater by anaerobic biological method and chemical oxidation, Sep. Purif. Technol., 79 (2011) 26–33.

[4] Z. Wang, M. Xue, K. Huang, Z. Liu, Textile Dyeing Wastewater Treatment, P. Hauser, Ed., Advances in Treating Textile Effluent, In Tech China, Shanghai, China, 2011.

[5] C. Comninellis, G. Chen, Electrochemistry for the Environment, Springer, New York, Dordrecht, Heidelberg, London, 2010.

[6] E. Brillas, C.A. Martínez-Huitle, Decontamination of wastewaters containing synthetic organic dyes by electrochemical methods. An updated review, Appl. Catal., B, 166–167 (2015) 603–643.

[7] J. Kim, C. Yeom, Y. Kim, Electrochemical degradation of organic dyes with a porous gold electrode, Korean J. Chem. Eng., 33 (2016) 1855–1859.

[8] M. Panizza, G. Cerisola, Direct and mediated anodic oxidation of organic pollutants, Chem. Rev., 109 (2009) 6541–6569.

[9] M. Panizza, Importance of Electrode Material in the Electrochemical Treatment of Wastewater Containing Organic Pollutants, C. Comninellis, G. Chen, Eds., Electrochemistry for the Environment, Springer, New York, Dordrecht, Heidelberg, London, 2010, p. 25.

[10] D. Shao, X. Li, H. Xu, W. Yan, An improved stable Ti/Sb–SnO_2 electrode with high performance in electrochemical oxidation processes, RSC Adv., 4 (2014) 21230–21237.

[11] T. Kim, G.-P. Kim, D. Lee, Y. Kim, S.E. Shim, S.-H. Baeck, Electrochemical oxidation of organic matter in the presence of chloride over Ti/SnO_2–Sb_2O_5 prepared via sol–gel methods, J. Nanosci. Nanotechnol., 16 (2016) 10892–10897.

[12] H. Xu, Q. Zhang, W. Yan, W. Chu, L. Zhang, Preparation and characterization of PbO_2 electrodes doped with TiO_2 and its degradation effect on azo dye wastewater, Int. J. Electrochem. Sci., 8 (2013) 5382–5395.

[13] M. Panizza, G. Cerisola, Electrochemical degradation of methyl red using BDD and PbO_2 anodes, Ind. Eng. Chem. Res., 47 (2008) 6816–6820.

[14] F. Bonfatti, A. De Battisti, S. Ferro, G. Lodi, S. Osti, Anodic mineralization of organic substrates in chloride-containing aqueous media, Electrochim. Acta, 46 (2000) 305–314.

[15] F. Bonfatti, S. Ferro, F. Lavezzo, M. Malacarne, G. Lodi, A. De Battisti, Electrochemical incineration of glucose as a model organic substrate. II. Role of active chlorine mediation, J. Electrochem. Soc., 147 (2000) 592–596.

[16] M. Panizza, G. Cerisola, Electrochemical oxidation of 2-naphthol with in situ electrogenerated active chlorine, Electrochim. Acta, 48 (2003) 1515–1519.

[17] Y. Feng, D.W. Smith, J.R. Bolton, Photolysis of aqueous free chlorine species (HOCl and OCl^-) with 254 nm ultraviolet light, J. Environ. Eng. Sci., 6 (2007) 277–284.

[18] F.H. Oliveira, M.A. Osugi, F.M.M. Paschoal, D. Profeti, P. Olivi, V. Boldrin Zanoni, Electrochemical oxidation of an acid dye by active chlorine generated using Ti/$Sn_{(1-x)}IrxO_2$ electrodes, J. Appl. Electrochem., 37 (2007) 583–592.

[19] C.R. Costa, P. Olivi, Effect of chloride concentration on the electrochemical treatment of a synthetic tannery wastewater, Electrochim. Acta, 54 (2009) 2046–2052.

[20] S. Neodo, D. Rosestolato, S. Ferro, De A. Battisti, On the electrolysis of dilute chloride solutions: influence of the electrode material on Faradaic efficiency for active chlorine, chlorate and perchlorate, Electrochim. Acta, 80 (2012) 282–291.

[21] C.A. Martínez-Huitle, E. Brillas, Decontamination of wastewaters containing synthetic organic dyes by electrochemical methods: a general review, Appl. Catal., B, 87 (2009) 105–145.

[22] C.A. Martínez-Huitle, S. Ferro, Electrochemical oxidation of organic pollutants for the wastewater treatment: direct and indirect processes, Chem. Soc. Rev., 35 (2006) 1324–1340.

[23] F.A. Rodríguez, M.R. Cruz-Díaz, S. Gómez, J.A. Calderón, A. Ortega, E.P. Rivero, Generation of active chlorine in acid and alkaline medium using a 3D anode in an electrochemical reactor for Reactive Black 5 degradation, J. Adv. Oxid. Technol., 21 (2018) 149–158.

[24] L. Szpyrkowicz, S.N. Kaul, R.N. Neti, S. Satyanarayan, Influence of anode material on electrochemical oxidation for the treatment of tannery wastewater, Water Res., 39 (2005) 1601–1613.

[25] M. Hepel, J. Luo, Photoelectrochemical mineralization of textile diazo dye pollutants using nanocrystalline WO_3 electrodes, Electrochim. Acta, 47 (2001) 729–740.

[26] C. Comninellis, A. Nerini, Anodic oxidation of phenol in the presence of NaCl for wastewater treatment, J. Appl. Electrochem., 25 (1995) 23–28.

[27] O. Scialdone, S. Randazzo, A. Galia, G. Silvestri, Electrochemical oxidation of organics in water: role of operative parameters in the absence and in the presence of NaCl, Water Res., 43 (2009) 2260–2272.

[28] C. Comninellis, Electrocatalysis in the electrochemical conversion/combustion of organic pollutants for wastewater treatment, Electrochim. Acta, 39 (1994) 1857–1862.

[29] N. Nordin, S.F. Mohd, M. Riyanto Rozali, Textile industries wastewater treatment by electrochemical oxidation technique using metal plate, Int. J. Electrochem. Sci., 8 (2013) 11403–11415.

[30] S. Trasatti, Electrocatalysis in the anodic evolution of oxygen and chlorine, Electrochim. Acta, 29 (1984) 1503–1512.

[31] C.J. Patton, S.R. Crouch, Spectrophotometric and kinetics investigation of the Berthelot reaction for the determination of ammonia, Anal. Chem., 49 (1977) 464–469.