

Electrochemical oxidation of textile azo dye reactive orange 16 on the Platinum electrode

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Abstract: This study focused mainly on the color removal of textile azo dye Reactive Orange 16 (RO16) by electrochemical oxidation. The effect of supporting electrolyte (H₂SO₄ and NaOH), RO16 concentration (from 0.5 to 10 mM) and potential scan rate (between 20 and 500 mV/s) was performed with cyclic voltammetry using platinum (Pt) wire as working electrode. The anodic peak current density was linear to RO16 concentrations. This allows the lowest concentrations to be determined voltammetrically in the two electrolytic media, acid (H₂SO₄ 1 M) and alkaline (NaOH 0.1 M). Linearity between the current density and the square root of the potential scan rate was observed in both electrolytes. This means that the electrochemical reaction at the electrode-electrolyte interface is controlled by the diffusion process. The slope of the logarithm of peak current density versus the logarithm of potential scan rate was found to be 0.43 for RO16 in H₂SO₄ and 0.48 in NaOH these values of slope are close to the theoretical value of 0.5 which confirms the diffusion process. The removal efficiency of the dye in acid electrolyte reached 40%, while it is 18% in the basic media after 4 hours of electrolysis by chronoamperometry.

Keywords: Reactive orange 16, Electrooxidation, Azo dyes, Cyclic voltammetry, Chronoamperometry.

1. Introduction

Dyes are colored substances, and resistant to fading on exposure to light, water and many chemicals due to their complex chemical structure and synthetic origin ^{1,2}, hence they persist in nature. More than 10,000 different commercially available dyes are used in textile industry for dyeing and printing purposes ^{3,4}. The estimated dyes concentration in the textile effluent has been reported to be in the range of 10–200 mg L⁻¹ ^{3,5}. The discharge of dye-containing effluents into receiving waters without appropriate treatment limits aquatic plant growth by creating anaerobic conditions ^{6,7}. Textile dyes are chemically diverse and are broadly divided into azo, reactive, triphenylmethane, heterocyclic, polymeric structures, etc ^{8,9}. The color of dyestuff in effluent interrupts the aquatic environment by reducing light penetration, gas solubility and interference of phytoplankton's photosynthesis ¹⁰. In addition, the discharge of untreated effluent into usable water resources like rivers and lakes alters pH scale and will increase biological oxygen demand (BOD), chemical oxygen demand (COD) and total organic carbon (TOC) values ^{11,12}.

Azo dyes are the largest and most versatile dyes and are widely used in the textile processing, cosmetics, food, leather, and plastics industries ^{13,14}. More than 60% of dyestuffs manufactured around the world are azo dyes ¹⁵. During the dyeing process, a large quantity of these dyes is released into wastewater streams ^{16,17}, which are recalcitrant, no biodegradable, carcinogenic, mutagenic, and toxic ¹⁸.

Azo dyes represent about 70% of the world dye production and are extensively used in textile industries. They contain one or more azo bonds (–N=N–) as chromophore group in association with aromatic structures containing functional groups such as –OH and –SO₃H ^{19,20}. Azo dyes are now classified as an environmentally hazardous material ²¹, so their release into wastewater streams without proper treatment could have serious environmental implications ^{22–24}. The environmental legislation about the appearance of color in discharged effluent has forced the industries to treat dyestuff containing effluent themselves ²⁵.

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Additionally, limited supply and increasing cost of water for the industrial sector have made the treatment and reuse of dyeing effluent mandatory to avoid environmental pollution and reduce production cost. A variety of typical Physico-chemical strategies such as coagulation, flocculation, activated carbon adsorption and reverse osmosis technique are used for the removal of color from textile effluent ²⁶⁻²⁹.

However, excessive use of chemicals in such conventional treatments produces a large amount of sludge and does not remove all dyes ³⁰, thus preventing recycling of treated effluent.

In addition, excess use of chemicals requires high cost and results in secondary pollution ^{31,32}. Besides

its environmental compatibility, the electrochemical process presents important advantages related to its versatility, high energy efficiency, amenability of automation and safety because it operates at mild conditions ³³⁻⁴⁵. The objective of this study was to investigate the efficiency of decolorization of the widely used textile azo dye with the electrochemical oxidation. In this context, RO16 an anionic sulphonated reactive azo dye was selected as a model pollutant because it is difficult to biodegrade ⁴⁶. It has molecular formula $C_{20}H_{17}N_3Na_2O_{11}S_3$ (Molecular weight: 617.5 g/mol) with Color Index Number (C.I. 17757). The structural formula of RO16 is shown in Fig.1 ⁴⁷⁻⁴⁹.

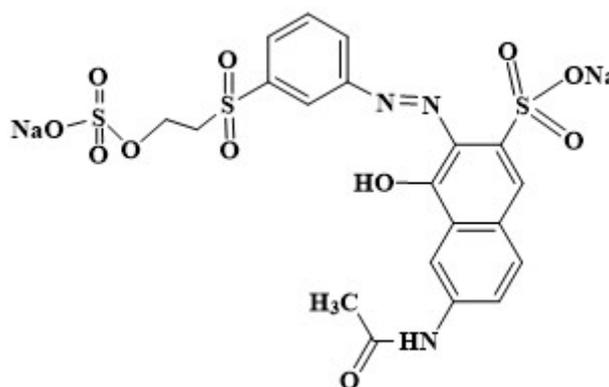


Figure 1. Structural formula of the Reactive Orange 16 (RO16) azo dye

2. Results and Discussion

2.1. Effect of electrolyte in RO16 electrooxidation

Fig.2 shows the voltammograms of 1 M H_2SO_4 (pH=0) and 0.1 M NaOH (pH=13) with and without 10 mM RO16 dye at a potential scan rate of 100 mV/s on Pt electrode.

For the voltammogram of H_2SO_4 without RO16 dye a wide anodic peak-like is observed from 0.8 V/SCE, due to the Pt oxidation, whereas one peak is observed at 0.5 V/SCE in the cathodic region, due to the Pt oxides reduction ⁵⁰. For the voltammogram of H_2SO_4 containing RO16 dye, two anodic peaks can be observed at 0.4 V/SCE and 1.35 V/SCE, which is attributed to the oxidation reaction of RO16 dye. In addition, a broad cathodic peak-like is observed over the potential range 0.7-0.9 V/SCE and a cathodic peak at -0.1 V/SCE (Fig.2a).

For the black voltammogram of NaOH, a wide anodic peak-like is observed from -0.1 V/SCE, due to the Pt oxidation, whereas one peak is observed at

-0.45 V/SCE in the cathodic region, due to the Pt oxides reduction ⁵¹.

For the blue voltammogram, two anodic peaks are observed, the first at -0.2 V/SCE and the second at 0.5 V/SCE, and in the cathodic region there is a large peak in the potential range 0-0.2 V/SCE and a peak at -0.9 V/SCE (Fig.2b).

In both electrolytes, the first anodic peak only appeared during the next scan after the reduction step, so this peak was obviously due to the corresponding oxidation of the reduction products.

As reported in previous studies ^{52,53}, azo dyes with a hydroxyl group adjacent to an azo bridge were reduced, producing a corresponding amine, which was more susceptible to reoxidation in the return analysis.

The presence of peaks in both electrolytes means that RO16 oxidizes easily on the Pt electrode surface.

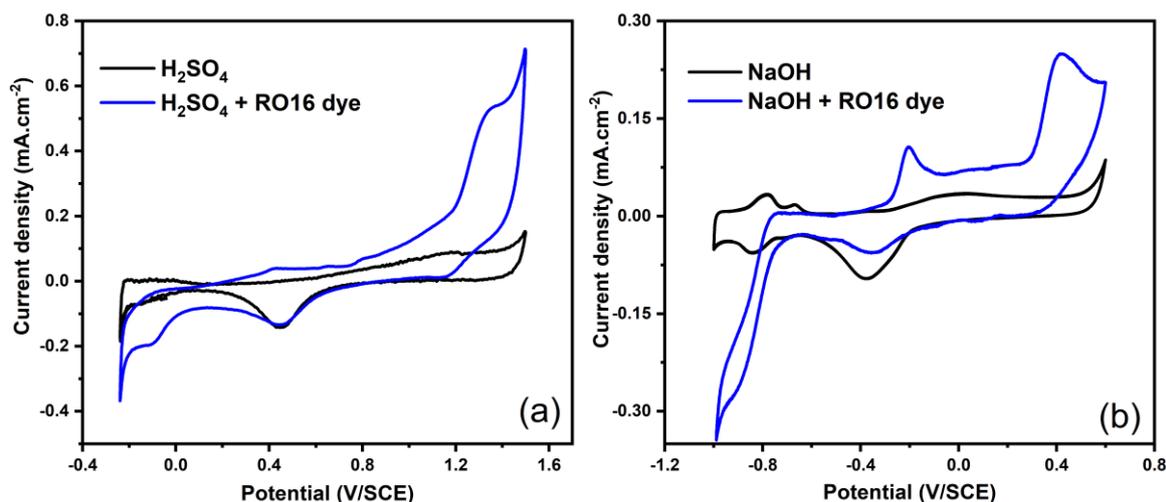


Figure 2. Cyclic voltammograms plotted on Pt electrode at 100 mV/s of 10 mM RO16 dye in: (a) H₂SO₄ (1 M) and (b) NaOH (0.1 M)

2.2. Effect of RO16 concentration

Fig.3 shows cyclic voltammograms recorded for different concentrations (0.5, 1, 2, 5, 10 mM) of RO16 dye in H₂SO₄ (1 M) and NaOH (0.1 M) at a potential scan rate of 50 mV/s.

In the potential range of -0.24 and 1.5 V/SCE, it is observed that as the RO16 dye concentration increases the anodic peaks current density increases and their position shifts to higher potential values (Fig.3a). The inset plot shows the linear relation between the peak current (I_p) and RO16 dye concentration in the range 0.5-10 mM. Hence, the corresponding linear regression equation is $I_p = 0.02 C + 0.13$ with the correlation coefficient of $R^2 = 0.99$.

From Fig.3b, we can be seen that the anodic peak currents are increased and their position shifts to higher potential values with increasing the RO16 concentration. The inset in panel shows that the oxidation peak current density varies linearly with the dye concentration: ($I_p = 0.02 C + 0.01$, $R^2 = 0.99$).

These results indicate that even RO16 dye concentrations lower than the millimolar can be detected by Pt electrode as well as used for the determination and analysis of the dye during its degradation.

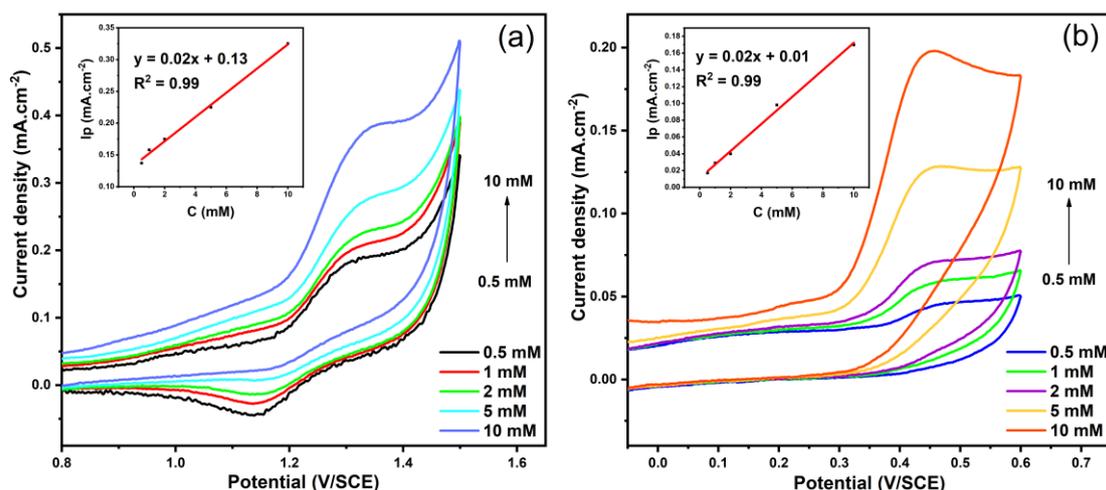


Figure 3. Cyclic voltammograms recorded at Pt electrode with scan rate of 50 mV/s for different concentrations of RO16 dye in: (a) H₂SO₄ and (b) NaOH. Inset current density versus RO16 dye concentration

2.3. Effect of potential scan rate

The relationship between peak current and potential scan rate provides useful information on the electrochemical mechanism. At different potential scan rates, the electrochemical behavior of RO16 was studied by applying a cyclic voltammetric

technique. Fig.4 and Fig.5 show the voltammograms recorded on a Pt electrode by varying the potential scan rate from 20 to 500 mV/s of 10 mM RO16 dye in H₂SO₄ (1 M) and NaOH (0.1 M), respectively.

From Fig.4a, as the potential scan rate increased, the oxidation peaks current (I_p) also increased, and the

peak potential (E_p) shifts to higher potential values, typical of irreversible systems (Fig.4a). The graph of peak current versus square root of scan rate is linear over the range of potential scan rate studied (Fig.4b), which indicates that it is a typical diffusion-controlled current system, and the equation can be expressed as $I_p = 1.12 v^{1/2} + 0.06$, $R^2 = 0.99$.

A logarithm of peak current, $\log(I_p)$, versus the logarithm of potential scan rate, $\log v$, was also studied (Fig.4c). This relationship was found to be linear, ($\log I_p = 0.43 \log v + 0.06$, $R^2 = 0.99$) with a slope, 0.43, which is near to the theoretical value of 0.5 for a diffusion controlled process⁵⁴.

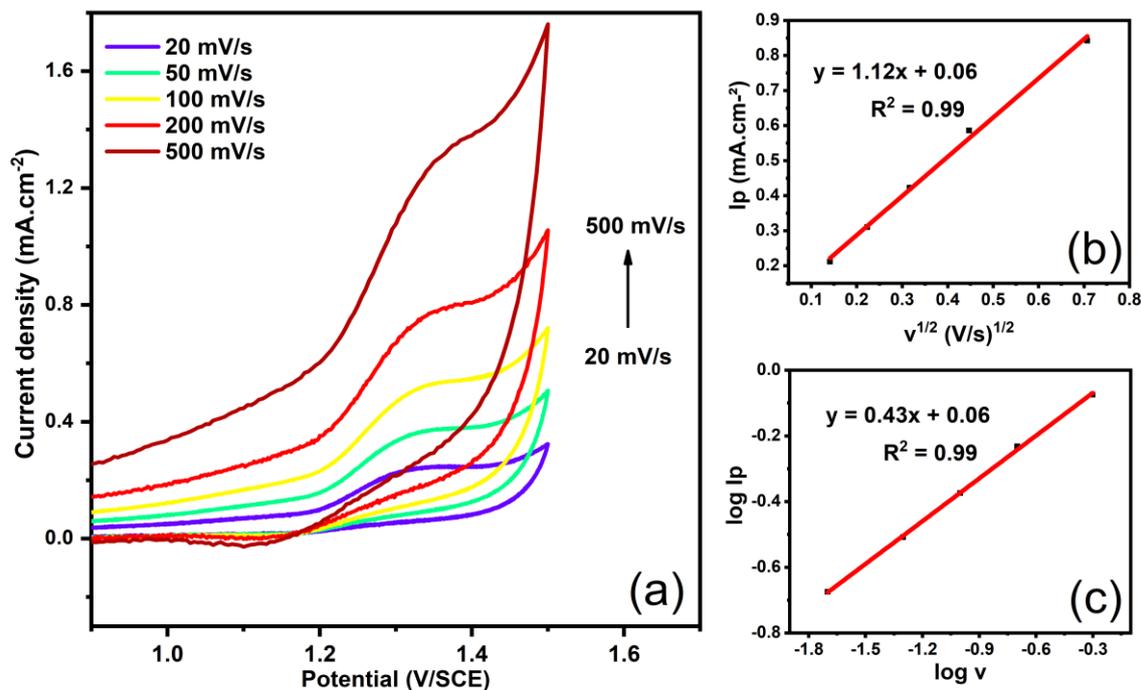


Figure 4. (a) Cyclic voltammograms recorded at scan rates between 20 mV/s and 500 mV/s in H_2SO_4 (1 M) containing 10 mM RO16 dye. (b) Graph of peak current versus square root of scan rate. (c) Graph of the logarithm of peak current versus the logarithm of scan rate

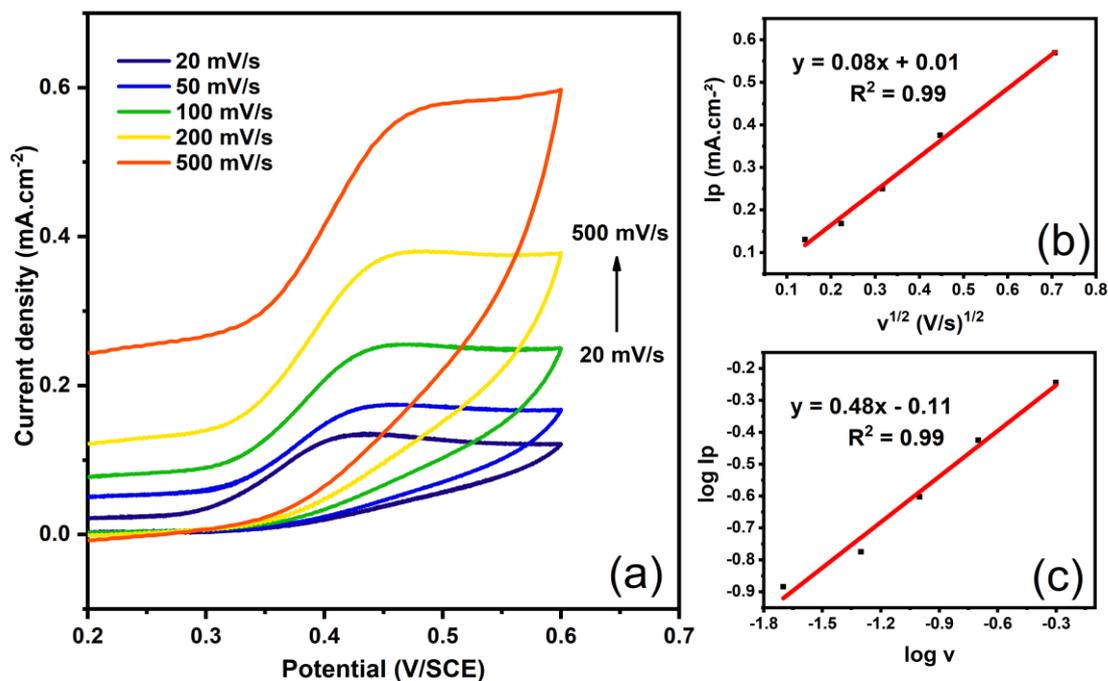


Figure 5. (a) Cyclic voltammograms recorded at potential scan rates between 20 mV/s and 500 mV/s in NaOH (0.1 M) containing 10 mM RO16 dye. (b) Graph of peak current versus square root of scan rate. (c) Graph of the logarithm of peak current versus the logarithm of scan rate

According to Fig.5a, as the potential scan rate increased, the oxidation peaks current (I_p) also increased, and the peak potential (E_p) moves towards higher potential values, typical of irreversible systems. The graph of peak current versus square root of scan rate is linear over the range of scan rate studied (Fig.5b), which indicates that it is a typical diffusion-controlled current system, and the equation can be expressed as $I_p = 0.08 v^{1/2} + 0.01$, $R^2 = 0.99$.

2.4. Electrolysis of RO16 dye by chronoamperometry

The RO16 dye electrolysis experiment was performed using chronoamperometry at a fixed potential (1.4 V/SCE for H_2SO_4 and 0.6 V/SCE for NaOH) for 4 hours (Fig.6). The curves exhibit the typical current drop in the very first seconds

A logarithm of peak current, $\log(I_p)$, versus the logarithm of potential scan rate, $\log v$, was also studied (Fig.5c). This relationship was found to be linear, ($\log I_p = 0.48 \log v - 0.11$, $R^2 = 0.99$). The value of the slope is close to the theoretical value of 0.5 for a diffusion-controlled mechanism⁵⁴. The results of these experimental studies suggest that the electrooxidation of RO16 dye on the Pt electrode is mainly controlled by diffusion, associated to the oxidation of RO16 adsorbed on the catalyst thin layer, followed by a slower variation with time, ascribed to the oxidation of RO16 under steady-state conditions. The linear relationship between current density and the reciprocal of the square root of time for both electrolytes was shown in Fig.6 (Insert). This indicates that the transient current must be controlled by a diffusion process.

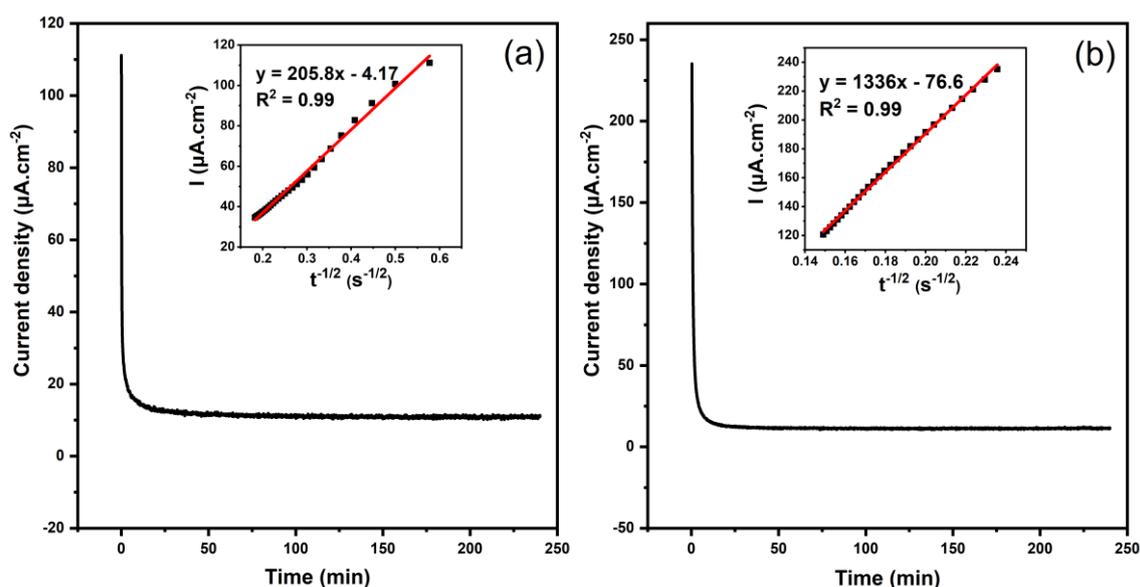


Figure 6. Chronoamperometry curve of 10 mM RO16 dye dissolved in: (a) H_2SO_4 (1 M) for 4h at 1.4 V/SCE and (b) NaOH (0.1 M) for 4h at 0.6 V/SCE. Insert plot of I versus $t^{-1/2}$ obtained from chronoamperogram

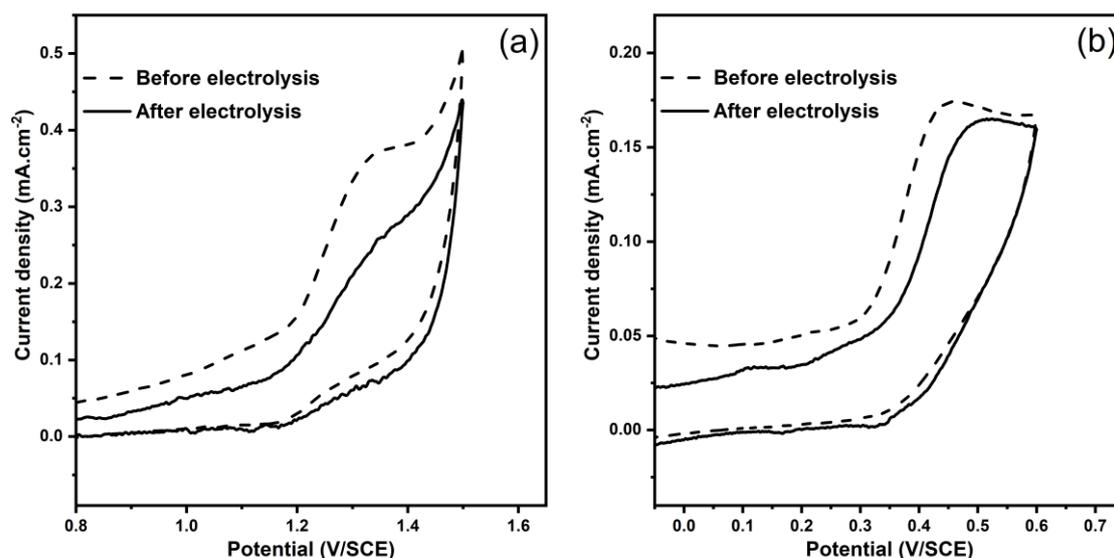


Figure 7. Cyclic voltammograms recorded before (solid line) and after (dashed line) the chronoamperometry at potential scan rate of 50 mV/s of 10 mM RO16 dye dissolved in: (a) H_2SO_4 (1 M) and (b) NaOH (0.1 M)

The evaluation of RO16 dye concentration after chronoamperometric treatment using a Pt electrode after 4 hours of electrolysis was performed using cyclic voltammetric detection with the same electrode. Fig.7 shows cyclic voltammograms recorded for initial RO16 dye concentration and after chronoamperometry applying. The percentage of dye removal was calculated according to the following equation ⁵⁵:

$$R\% = \frac{C_0 - C}{C_0} \times 100$$

Where C_0 and C are the initial and after electrolysis concentrations of the dye (mol/L), respectively.

After electrolysis, a sharp decrease in the RO16 peak was observed for both medium; it means that the concentration is reduced after the treatment. In acidic medium, the dye removal efficiency is 40%, however, 18% in alkaline medium. We can affirm that the H_2SO_4 (1 M) solution showed an excellent electrolytic performance towards the electrooxidation of RO16 compared to NaOH (0.1 M) solution.

3. Conclusion

The present work is devoted to the electrochemical oxidation of textile azo dye RO16 in both acid and basic mediums at Pt electrode. Cyclic voltammetry technique was used to perform the effect of supporting electrolyte, RO16 concentration and potential scan rate. The electrochemical process is diffusion-controlled and the oxidation peak current density of RO16 was linearly proportional to its concentration in a range from 0.5 mM to 10 mM. For the same operating variables, the acid medium proved to be the most favorable medium for active degradation of RO16 dye. The percentage of dye removal was found to be 40% in acidic medium and about 18% in the alkaline medium after 4h of electrolysis. Thus, electrochemical technology is an effective method for the removal of RO16 dye from the effluents of the textile industry.

4. Experimental

The electrochemical oxidation was carried out in a three-electrode cell (50 ml) with the Platinum (Pt) wire (0.2 cm²) as a working electrode (WE), a saturated calomel electrode (SCE) as a reference electrode (RE) and glassy carbon as a counter electrode (CE). The cyclic voltammetry measurements and chronoamperometry were performed using a PGZ 301 Potentiostat/Galvanostat monitored by VoltaMaster 4 software.

Sulphuric acid (96%, Sigma-Aldrich) and sodium hydroxide (99.99%, Sigma-Aldrich) were used for the preparation of the base electrolytes: 1 M H_2SO_4 and 0.1 M NaOH, respectively. All solutions were prepared with ultrapure water (18 M Ω .cm-1). Before each scan the electrode was prepared to

ensure a reproducible surface by polishing, rinsing with distilled water and then electrochemically cleaned by cyclic voltammetry in 1 M of the sulfuric acid solution until a reproducible voltammogram was obtained. All the electrochemical experiments were carried out at 25°C.

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