Electrochemical decolorization of the Reactive Orange 16 dye using a dimensionally stable Ti/PtOₓ anode

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Abstract: The electrochemical decolorization of Reactive Orange 16 in a chloride containing solution was studied using a dimensionally stable Ti/PtOₓ anode. Different reaction parameters, agitation speed, applied current, sodium chloride concentration, and dye concentration were varied and the optimum electrolysis conditions were suggested. Hypochlorous acid was suggested to be the active species in the electrochemical decolorization. Moreover, the reaction was studied using UV–Vis spectrophotometry, high-pressure liquid chromatography (HPLC), total organic carbon (TOC) and total nitrogen (TN) analyses.

Keywords: reactive dye; azo dye; electrolysis, hypochlorite; hypochlorous acid.

INTRODUCTION

The wastewaters from the textile industry contain, among other chemicals, unreacted dyestuffs. Even a small amount of dye in water (~1 ppm) is highly visible and affects the water transparency, the gas solubility, and possesses potential carcinogenic and mutagenic properties. Textile dyes can be classified based on the method of fixation to the textile fiber (e.g., reactive, direct, acid) or chemical structure (e.g., azo, anthraquinone, indigoid).

Azo dyes are synthetic organic colorants with a chromophoric azo group (–N=N–). On the one side, the azo group is attached to an aromatic or heterocyclic nucleus and on the other, to an unsaturated molecule of the carbocyclic, heterocyclic or aliphatic type. Azo colorants are the most widespread and versatile class of organic dyestuffs. As published in the Kirk–Othmer Encyclopedia of Chemical Technology in 2003, there are more than 10,000 Color Index (CI) generic names assigned to commercial colorants. Approximately 4,500 of them are in use, and over 50 % belongs to the azo group of compounds. The broad

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usage range of the azo dyes is due to the number of variations in chemical structure and methods of application, which are not complex in general.\(^3\)

Most dyes are resistant to biodegradation or physico-chemical treatments (e.g., chemical precipitation and separation of pollutants, coagulation, elimination by adsorption, etc.).\(^4\)\(^–\)\(^7\) These methods are not destructive, leading to the formation of sludge, and thus transferring pollutant from one phase to another, causing a new kind of pollution. An alternative to the mentioned processes are the advanced oxidation processes (AOPs), which are able to decolorize and mineralize dyestuffs and other organic pollutants.\(^8\)\(^–\)\(^13\)

Different electrochemical methods, such as direct or indirect anodic oxidation, cathodic reduction or electrocoagulation, could be used for decolorization and/or degradation of dyes.\(^14\)\(^–\)\(^18\) In order to achieve better fixation and exhaustion of reactive, direct or substantive dyes, an electrolyte, NaCl or Na\(_2\)SO\(_4\), is usually added. The salt also acts as an electrolyte during the further electrochemical treatment.\(^17\) Due to its low price and the formation of strong oxidizing electrolysis products, sodium chloride is considered as one of the best choices.\(^18\) During the electrolysis, depending on the reaction conditions, strong oxidizing species – chlorine, hypochlorous acid and/or hypochlorite are formed on the anode. At pH > 6, hypochlorous acid dissociates to hypochlorite and H\(^+\), and at pH lower than \(\approx 3.5\), HOCl reacts with Cl\(^–\) to yield Cl\(_2\). A mixture of these species is commonly called “active chlorine”.\(^17\)\(^–\)\(^19\)

Cl Reactive Orange 16 (RO16, \(M = 617.5 \text{ g mol}^{-1}\)), with the structural formula shown in Fig. 1, was the subject of electrochemical degradation studies. The electro-oxidation of RO16 dye was studied using boron-doped diamond (BDD) and dimensionally stable anode (DSA) type electrodes in acidified 0.1 M K\(_2\)SO\(_4\).\(^20\) The results showed that the BDD electrode had superior characteristics for color removal and in the mineralization of organic materials present in the dye. Decolorization was achieved within 90 min, following the pseudo-first order reaction kinetics with rate constants ranging from 0.02 to 0.08 min\(^{-1}\) for the applied current densities from 75 to 200 mA cm\(^{-2}\). For a commercial DSA electrode, the values of the rate constants were not obtained, because only a 10% decrease in the initial dye concentration was observed at 200 mA cm\(^{-2}\) after 90

![Fig. 1. Structure of CI Reactive Orange 16.](image-url)
Electrochemical decolorization of Reactive Orange 16 dye was performed in an electrochemical flow-cell, using a Pt electrode. The influences of the process variables, i.e., flow-rate, NaCl concentration, applied potential and pH, were studied. Using 1.0 g dm⁻³ NaCl as the supporting electrolyte at 2.2 V vs. RHE, the determined first order rate constant was ≈0.025 min⁻¹, and a color removal of 93% was achieved after 60 min electrolysis. The best TOC removal of 57% was at 1.8 V, without a membrane, indicating that the ideal conditions for color removal are not necessarily the same as those for TOC. Dimensionally stable Ru(Ta, Sn)O₂-based anodes were used for the electrochemical oxidation of different reactive dyes, including RO16. The reactions were performed in either the presence or absence of NaCl. At a low chloride concentration (0.01 M), total color removal was obtained after 10 min of electrolysis, and a significant increase in total dye degradation was achieved (reaching ca. 80%, chemical oxygen demand, COD, decrease).

The oxidation was studied using a combination of electrochemical and photo-electrochemical methods in 0.02 M Na₂SO₄ at a current density of 50 mA cm⁻² in a photo-electrochemical flow-cell. The photo-electrochemical method was demonstrated to be more efficient considering the specific energy consumption, TOC removal and a slightly higher first order rate constant of ≈0.012 min⁻¹ compared to the one obtained for the electrochemical method, ≈0.009 min⁻¹. The photo bleaching of RO16 in aqueous solution using TiO₂ thin-film electrodes prepared by the sol–gel method was also studied. The best conditions for maximal photo-electrocatalytic degradation was found to be pH > 10 for a Na₂SO₄ medium and pH < 6 for a NaCl medium, but only for the low dye concentrations. In both cases, 100% color removal was obtained after 20 min. Oxalic acid was identified by HPLC and UV-Vis spectrophotometric methods as the main degradation product generated after 180 min of photoelectrocatalysis.

In this paper, a study of the electrochemical decolorization of RO16 in sodium chloride-containing solutions using for the first time DSA Ti/PtOₓ is reported. The influences of the basic operational parameters, such as hydrodynamic conditions, applied current, and the initial concentrations of RO16 and NaCl, were studied in order to optimize the process of electrochemical decolorization of RO16.
EXPERIMENTAL

Materials

The textile dye, CI Reactive Orange 16, was obtained from Aldrich (dye content 50 %) and used without purification. Sodium chloride was p.a. grade (Merck). Acetonitrile (HPLC grade) was purchased from J.T. Baker. Deionized water was obtained from a Millipore Waters Milli-Q purification unit.

Electrochemical decolorization

The electrochemical decolorization process was investigated in a cylindrical glass batch reactor, with an electrolyte volume of 500 cm³. The electrolyte was prepared from distilled water, NaCl and RO16. A 5 cm² DSA Ti/PtOx anode obtained by thermal decomposition of H₂PtCl₆ in 2-propanol with 1 mg cm⁻² of platinum loading was used, while the cathode was 10 cm² plate made from austenite 18Cr/8Ni stainless steel series 304. The electrodes with a 3-mm gap between them were immersed at the top of the electrolyte. A PAR M273 potentiostat/galvanostat operated in the galvanostatic mode was used for the electrolysis of solution. Mixing of the electrolyte was accomplished by a magnetic stirrer. At certain times during the electrolysis, 3 cm³ of the solution was taken with a micropipette and its UV-Vis spectrum was instantly recorded. The concentration of dye was followed by measuring the absorption of the solution at 493 nm using a Shimadzu UV-Vis model 1700 spectrophotometer.

HPLC analysis

For HPLC determination, all samples were filtered through 0.45 μm syringe filters and analyzed at 245 nm and at ambient temperature (25 °C) on a SpectraSYSTEM P4000 liquid chromatograph with a SpectraSYSTEM UV1000 detector, equipped with a reversed phase column type Zorbax SB C8 (150 mm×4.6 mm i.d., 5 μm particle size). The mobile phase (flow rate 1.0 cm³ min⁻¹) was a mixture of acetonitrile and water (30:70, V/V), 0.1 % formic acid solution. The sample injection volume was 20 μL.

Total organic carbon (TOC) and total nitrogen (TN) analyses

The TOC and TN analyses during the electrolysis were performed using an Elementar liquiTOC II instrument.

RESULTS AND DISCUSSION

UV–Vis spectral changes

The UV–Vis spectral changes during the electrolysis are shown in Fig. 2. Several peaks were observed in the spectrum of the RO16 at the beginning of the reaction. The peak at 295 nm corresponds to the gamma acetylated acid structure, which is a precursor in the synthesis of RO16. The peak at 254 nm is indicative of benzene ring, and the peak at 386 nm could be associated with the azo group.24 Finally, the peak at 493 nm corresponds to the hydrazone form of the dye because an azo-hydrazone tautomerism is possible in the RO16 molecule.17,26 The decreases in the absorption peaks at 386 and 493 nm during electrolysis indicate fast decolorization of RO16 dye over time (Fig. 2). Complete decolorization was observed after ≈10 min of electrochemical treatment, insert in Fig. 2. At the end of the oxidation reaction, the spectrum showed small
peaks at 254 and 295 nm. Considering that the reaction was very fast, the concentrations of hypochlorite and hypochlorous acid are very low and cannot be observed in the spectra (the absorption maximum of hypochlorite is at 292 nm and the absorption maximum for hypochlorous acid is at 236 nm).27

**Effect of the applied current**

In order to investigate the influence of the current on the electrochemical decolorization of the RO16 dye, currents in the range from 50 to 250 mA were applied. The dependence of the relative dye concentration over time for different values of applied current is shown in Fig. 3a. More than 95 % decolorization was achieved within ten minutes for applied currents greater than 50 mA. Examining different pseudo-\(n\)-orders, the first-order gave the best linearity, and pseudo first-order decolorization rate constants, \(k_d\), \(\text{min}^{-1}\), were determined in accordance with the kinetic equation:

\[
\ln \frac{c_t}{c_0} = -k_d t
\]  

(1)

From the slopes of the straight lines, Fig. 3, the rate constants were determined and are shown in Fig. 3b. The decolorization rate constant practically linearly increased from 0.14 to 0.33 \(\text{min}^{-1}\) in the investigated range of applied currents, while electrolysis voltage increased from 3.5 to 5 V. The faster reaction was achieved with current of 250 mA, but considering that the specific energy consumptions with reaction rate increase, some optimum current lies at 100–150 mA. For example, an increase of current from 100 to 250 mA increases the reac-
tion rate 1.5 times, while the specific energy consumption is increased 2.5 times, from 1.1 to 2.8 Wh g\(^{-1}\), calculated using the cell voltage shown in Fig. 3b.

![Fig. 3. The logarithmic plot of the relative RO16 concentration vs. the electrolysis time for different values of applied current (marked in the figure) under the conditions \(m(\text{NaCl}) = 10 \text{ g dm}^{-3}, m(\text{RO16}) = 60 \text{ mg dm}^{-3}, \omega = 250 \text{ rpm}\). Insets: a) the dependence of the relative RO16 concentration over time for different values of the applied current; b) the dependence of the pseudo first-order reaction rate constants and the electrolysis voltage on the values of the applied current.](image)

The influence of the hydrodynamic conditions

The influence of the solution mixing (rpm of magnetic stirrer) on the RO16 decolorization is shown in Fig. 4. The apparent decolorization rate constant of \(\approx 0.24 \text{ min}^{-1}\) are practically independent of the agitation speed, as shown in Fig. 4. During the first five minutes of the electrolysis, the pH increased relatively fast from the initial \(\approx 5.5\) to 8, and reached a steady state value of \(\approx 8.5\) after 10 min, Fig. 4b. The changes in pH provoked changes in the relative ratio of the different active chlorine species in the solution (see Section: Possible active chlorine species).

Considering that diffusion, heterogeneous or homogeneous oxidation rate was highly dependent on the hydrodynamic conditions,\(^{28}\) the possible explanation is that the rate determining step is an activation controlled (charge transfer) reaction. The only activation-controlled reaction could be the oxidation of the chloride anions to the solvated chlorine, given by Eq. (3).

Effect of the initial sodium chloride concentration

The influence of the initial NaCl concentration on the reaction rate was investigated in the range from 10 to 30 g dm\(^{-3}\) and the results are shown in Fig.
5. The determined reaction rate constants increased with increasing salt concentration up to 25 g dm\(^{-3}\), and above that concentration, a small change in the reaction rate is observed, as shown in the insert of Fig. 5.

![Fig. 4](image-url)  
**Fig. 4.** The logarithmic plot of the relative concentration of the dye vs. the electrolysis time for different agitation speeds (marked in the figure), \(m(\text{NaCl}) = 10\) g dm\(^{-3}\), \(I = 100\) mA, \(m(\text{RO16}) = 60\) mg dm\(^{-3}\). Insets: a) the dependence of the relative RO16 concentration over time for different agitation speeds; b) the change in the pH value during electrolysis.

![Fig. 5](image-url)  
**Fig. 5.** The logarithmic plot of the relative RO16 concentration vs. the electrolysis time for different sodium chloride concentrations (marked in the figure), and in 10 g dm\(^{-3}\) Na\(_2\)SO\(_4\) during continuous electrolysis. Inset: the dependence of the pseudo first-order reaction rate constants on the sodium chloride concentration, \(I = 100\) mA, \(m(\text{RO16}) = 60\) mg dm\(^{-3}\), \(\omega = 250\) rpm.
According to the Faraday law, the amount of the produced active chlorine should be proportional to the passed charge (It) and the rate should remain constant independently of the chloride concentration. However, the oxygen evolution:

$$4\text{OH}^- = \text{O}_2 + 2\text{H}_2\text{O} + 4e^- \quad (2)$$

and the production of active chlorine (Eqs. (3)-(5)) compete.\textsuperscript{19,29} Thus, the current efficiency of active chlorine production is connected with the chloride concentration. Namely, as determined by Kraft et al.\textsuperscript{19} in the concentration range of NaCl from 1 to 20 g dm\textsuperscript{-3}, the current efficiency of active chlorine production on a Ti/PtO\textsubscript{x} electrode linearly increases from \approx 5 to 75\%. Therefore, in the solution with a NaCl concentration in the range of 10 to 20 g dm\textsuperscript{-3}, the oxygen evolution reaction proceeds at a relatively high rate. In the solution with higher NaCl concentrations, the current efficiency steady state conditions are attained and the amount of the active chlorine production becomes nearly constant.

**Possible active chlorine species**

In order to resolve which of the active chlorine species are the most active, the following experiment was performed: a solution of 5 g NaCl in 500 cm\textsuperscript{3} of water was pre-electrolyzed for 1 and 5 min at 100 mA, and then, 30 mg of RO16 dye was added. The results of these experiments are presented in Fig. 5. It can be seen that decolorization occurred practically with a similar rate as during the electrolysis with higher currents (Fig. 3a). The rate in the electrolyte pre-electrolyzed during 5 min was \approx 20\% faster than in the electrolyte pre-electrolyzed for 1 min.

In Fig. 3, the results obtained during electrolysis with current of 100 mA in a solution containing 10 g dm\textsuperscript{-3} of Na\textsubscript{2}SO\textsubscript{4} and 60 mg of RO16 is also shown, because of the possibilities that anodic water oxidation could result in the formation of hydroxyl radicals, which can easily oxidize RO16\textsuperscript{17,30} Under such conditions, no activity was observed. Hence, it could be concluded that hydroxyl radicals were not involved in the reaction mechanism. One more important conclusion from this experiment is that RO16 is not cathodically reduced during electrochemical degradation.

The oxidation of the chloride anions to the hydrated chlorine is given by the complex overall reaction:

$$2\text{Cl}^- = \text{Cl}_2(\text{aq}) + 2e^- \quad (3)$$

which is followed by the fast disproportionation of the hydrated chlorine to HOCl and its dissociation to OCl\textsuperscript{-}:\textsuperscript{13,19}

$$\text{Cl}_2(\text{aq}) + \text{H}_2\text{O} = \text{HClO} + \text{Cl}^- + \text{H}^+, K_1 = 5.1 \times 10^{-4} \text{ M}^2 \quad (4)$$

$$\text{HClO} = \text{ClO}^- + \text{H}^+, K_a = 2.9 \times 10^{-8} \text{ M} \quad (5)$$
The distribution of different active chlorine species in a solution containing chloride as a function of pH can be calculated starting from the chemical equilibrium equations given above. Assuming that concentration corresponds to activity and that water has unity activity, the following procedure was used starting from the mass balance equation:

\[ c(\text{Cl}_2, \text{act})_T = c(\text{Cl}_2) + c(\text{HOCl}) + c(\text{OCl}^-) \]  

(6)

The total active chlorine concentration in solution can be calculated using the Faraday law:

\[ c(\text{Cl}_2, \text{act})_T = \frac{n(\text{Cl}_2)}{0.5 \text{dm}^3} = \frac{It}{F} \eta_I \]  

(7)

where \( \eta_I \) is the current efficiency for chlorine formation. By rearranging Eq. (6), the concentration of hydrated chlorine is obtained:

\[ c(\text{Cl}_2) = c(\text{Cl}_2, \text{act})_T \left[ 1 + \frac{c(\text{HOCl})}{c(\text{Cl}_2)} + \frac{c(\text{OCl}^-)}{c(\text{Cl}_2)} \right]^{-1} \]  

(8)

Using a mathematical procedure, it can be evaluated that:

\[ \frac{c(\text{HOCl})}{c(\text{Cl}_2)} = \frac{K_I}{c(\text{H}^+) c(\text{Cl}^-)} \]  

(9)

and:

\[ \frac{c(\text{OCl}^-)}{c(\text{Cl}_2)} = \frac{K_I K_d}{c^2(\text{H}^+) c(\text{Cl}^-)} \]  

(10)

Introducing Eqs. (9) and (10) into Eq. (8), the free solvated chlorine concentration as a function of pH could be calculated. Once the pH dependence of the free chlorine concentration is known, it is possible to calculate, by a similar procedure, the pH dependence of the concentrations of all the other species in the solution. Taking into account that for the NaCl concentration of 10 g dm\(^{-3}\) (0.17 M), current efficiency is 0.45\(^{19}\) and using Eq. (7), the total active chlorine concentration for 1 and 5 min of electrolysis was calculated to be 0.028 and 0.125 mM. Applying the above-described mathematical treatment, the distribution of different active chlorine species in solution as a function of pH was calculated and shown in Fig. S-1 (Supplementary material to this paper). The pH for 1 and 5 min of electrolysis was \( \approx 6 \) and 8, respectively, Fig 4b. At these pH values, corresponding concentrations of HOCl are 29 and 37 \( \mu \)M, and for OCl\(^-\) \( \approx 0 \) and 0.1 mM, respectively. Therefore, the \( \approx 20\% \) higher rate in the electrolyte pre-electrolyzed during 5 min than in the electrolyte pre-electrolyzed for 1 min corresponds to the ratios of HOCl concentration, suggesting that hypochlorous acid is the active species in RO16 decolorization.
Effect of the initial dye concentration

The dependence of logarithm of the relative concentrations over time for different RO16 concentrations, 20–80 mg dm\(^{-3}\), is shown in Fig. 6. As it could be seen in the insert of Fig. 6, increasing the dye concentration decreased the reaction rate. This trend could be connected with the pH distribution of the suggested active HOCl species. Namely, for a low RO16 concentration, e.g., 20 mg dm\(^{-3}\), the decolorization was practically completed within 3 to 4 min and corresponding pH was lower than 7.5. At this pH value, the dominant species is practically pure HOCl. Increasing the dye concentration, the decolorization time and pH increased as well, which is connected with a decrease in HClO concentration and a slower reaction rate. However, the observed behavior could also be explained by taking into consideration that the overall rate of RO16 decolorization was controlled by active chlorine production, as was inferred in the previous section. It could be postulated that the rate of active chlorine production was approximately the same independently of the initial concentration of RO16, because in all the measurements current was the same, \(I = 100\) mA, as well as the chloride concentration, \(m(\text{NaCl}) = 10\) g dm\(^{-3}\). Consequently, in the solutions with a lower initial dye concentration, proportionally lower relative concentrations of RO16 were to be expected for the same electrolysis time (Fig. 6). The concentration of generated HOCl active species during the electrolysis is unknown, but from the kinetics point of view, it is reasonable to assume that it was lower in the solutions with a higher initial concentration of RO16. Taking into account that the concentration of active chlorine was included in the pseudo first-order rate constants, the dependence shown in the inset of Fig. 6 was anticipated.

![Fig. 6. The logarithmic plot of the relative RO16 concentration against electrolysis time for different initial dye concentrations. Inset: dependence of the pseudo first-order reaction rate constants on RO16 concentration, \(m(\text{NaCl}) = 10\) g dm\(^{-3}\), \(I = 100\) mA, \(\omega = 250\) rpm.](image-url)
**HPLC and TOC/TN analyses**

High-performance liquid chromatography (HPLC) was used to obtain a better insight in the decolorization process of the RO16 dye. As suggested by Miglierioni et al.,\(^2^1\) the reaction was followed at 245 nm using HPLC with a UV detector because the appearance of signal at this wavelength is related to the \(\pi \rightarrow \pi^*\) transition of conjugated systems, which is characteristic for aromatic compounds. The chromatograms of the RO16 azo dye solution before the electrochemical treatment (0 min) and after 16 min of electrochemical treatment at 100 mA are presented in Fig. S-2 (Supplementary material). The chromatogram for the RO16 azo dye solution before the electrochemical treatment showed four peaks related to aromatic compounds with different polarities and retention times. These aromatic peaks were named in the chromatogram from A to D. The highest intensity peak C is probably related to the RO16 dye while the less intense peaks are probably related to impurities in the 50% RO16 dye solution.

After the electrochemical treatment at 100 mA with DSA Ti/PtO\(_x\) electrode (16 min), peak C had almost disappeared while peaks D and B were reduced. At the same time, new peaks emerged (peaks E–J) due to the reaction indicating the presence of smaller, less polar aromatic molecules.

**TOC and TN analyses** were also performed in order to assess the effectiveness of used electrochemical method in the mineralization of the RO16 dye. The UV-Vis absorption spectrum (Fig. 2) shows that absorption in the visible part of the spectra was almost completely removed. However, the absorption in the UV region was not removed, which indicates the presence of intermediate compounds after color removal. The TOC and TN changes during the reaction are shown in Fig. S-3 (Supplementary material). As could be seen, ≈10% of the dye was mineralized. The obtained results confirm that the degradation of RO16 was only partial, but the rate of the achieved decolorization is much faster than in photocatalytic processes,\(^3^1,^3^2\) except when H\(_2\)O\(_2\) was added.\(^3^3\)

**CONCLUSIONS**

The dimensionally stable Ti/PtO\(_x\) anode was found to be effective in the decolorization process of CI Reactive Orange 16 dye solutions containing chloride. The decolorization proceeded via a pseudo-first order reaction with hypochlorous acid as the main active chlorine species. Depending on the electrolysis conditions, the apparent first-order reaction constant was in the range of 0.2 to 0.5 min\(^{-1}\). Complete decolorization within 15 min could be successfully realized with currents in the range of 100 to 200 mA (20–40 mA cm\(^{-2}\)), sodium chloride concentrations in the range of 10 to 30 g dm\(^{-3}\) and low (few mg dm\(^{-3}\)) and medium (~0.1 g dm\(^{-3}\)) contents of dye. A negligible effect of the hydrodynamic conditions on the RO16 decolorization was recorded. The specific power consumption was estimated in the range of 1 to 3 kWh kg\(^{-1}\), depending on the
applied current. Some optimum electrolysis conditions can be suggested: 10–15 g dm$^{-3}$ of NaCl, with anodic current density of 20–25 mA cm$^{-2}$ under moderate steering.

HPLC analysis revealed the formation of smaller aromatic molecules, which were less polar than the starting molecule. The obtained results of TOC/TN analyses confirmed that the degradation of RO16 was only partial.

**SUPPLEMENTARY MATERIAL**

The distribution of different active chlorine species in solution as a function of pH, HPLC chromatograms and relative TOC and TN change during electrochemical treatment of the RO 16 dye solution are available electronically from http://www.shd.org.rs/JSCS/, or from the corresponding author on request.

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