



Color removal from dye-containing aqueous solutions by electrooxidation

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ABSTRACT

This study investigated the electrochemical decolorization of Reactive Blue 21 (RB21) dye in an aqueous solution on a platinum (Pt) electrode. The influence of operating variables on decolorization efficiency was studied including supporting electrolyte (Na_2SO_4 and KCl), current density (range 50–300 mA cm^{-2}) and initial pH (between 3–11). Within 20 min of electrochemical treatment, about 99.94% of the color was removed from the KCl and 39.90% from the Na_2SO_4 solutions. This degradation efficiency in the KCl solutions can be attributed to indirect electrochemical oxidation, where, in the presence of chlorides, the electrolyte generates strongly oxidizing species, which enhance the efficiency of the treatment at the Pt electrode. Optimal operating conditions to achieve an efficiency greater than 99% for the removal of the RB21 dye (0.1 mM) were a current density = 100 mA cm^{-2} , an initial pH between 3 and 11 during the electrolysis time = 20 min in KCl solution at room temperature (20°C).

Keywords: Reactive Blue 21; Phthalocyanine dyes; Decolorization; Electrochemical oxidation; Platinum

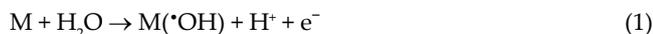
1. Introduction

Water pollution resulting from various industrial effluents is a worldwide environmental problem. With rapid industrialization, the use of chemical colorants such as dyes [1,2] is increasing every day. Currently, a total of 40,000 dyes and pigments with more than 7,000 different chemical structures have been reported [3,4]. It is estimated that more than 7×10^5 tons of dyes are produced worldwide each year and that 10%–15% of the dyes are released during the dyeing and manufacturing process [5]. As a result, a huge volume of colored wastewater is discharged and received by aquatic organisms annually [6]. Most dyes are synthetic and have a complex atomic structure that is very durable and resistant to biological degradation [7,8]. Reactive Blue 21 (RB21) is an organic phthalocyanine dye largely used

in the textile industry [9]. Besides the visual pollution of these colored effluents, phthalocyanine dyes have been reported to be toxic compounds and potentially mutagenic [10]. The phthalocyanine dyes that are widely used in the textile cannot be removed sufficiently by conventional processes involving adsorption [11–16], electrocoagulation [17,18], photocatalysis [19–21], membrane filtration [22], etc. Apart from its environmental compatibility, the electrochemical process has important advantages related to its versatility, high energy efficiency, ease of automation and safety because it operates in mild conditions [23–31]. Electrochemical oxidation processes use hydroxyl radicals produced by electrolysis for the mineralization of organic pollutants. From the production of hydroxyl radicals in the electrolytic system, the electrochemical oxidation processes can be divided into two categories: direct and

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indirect oxidation [32]. For direct electrochemical oxidation, hydroxyl radicals are produced on the surface of the anode by direct oxidation of water according to Eq. (1):



where M anode material. The main advantage of this process is that it doesn't require the external addition of reagents for the production of hydroxyl radicals [33,34]. For indirect electrochemical oxidation, the hydroxyl radical formation is based on Fenton chemistry, including in situ electrochemical generation (electro-Fenton) or external addition of the reagent (H_2O_2 or ferrous iron) [35]. The present study focused on the use of the electrochemical oxidation on Pt electrode for the decolorization of RB21 phthalocyanine dye. The influence of the reaction parameters such as the supporting electrolyte, the applied current density and the initial pH was optimized. The decolorization of the solution was monitored by UV-visible spectrophotometry.

2. Experimental

The electrochemical oxidation of the phthalocyanine dye RB21 (Fig. 1) widely used in the textile industry was performed using a Potentiostat/Galvanostat (PGZ 301) monitored by VoltaMaster 4 software with a three-electrode cell. For the working electrode, we employed a platinum sheet with an exposed apparent area of 1 cm^2 . The auxiliary electrode was a glassy carbon. The reference electrode was a saturated calomel electrode. The RB21 solutions were electrolyzed in galvanostatic mode at current densities between 50 and 300 mA cm^{-2} with an effective volume of 100 ml. The experimental set-up for the electrochemical decolorization system is shown in Fig. 2. For the preparation of the base electrolyte, two supporting electrolytes such as KCl (0.1 M) and Na_2SO_4 (0.1 M) were used. The solution was kept under agitation using a magnetic stirrer. Hydrochloric acid and sodium hydroxide of analytical grade were purchased from Aldrich and employed for pH adjustment. Double distilled water was used to prepare the desired concentration of dye solutions and of the reagents. All the electrochemical experiments were carried out at 20°C . Decolorization was calculated from the initial dye concentration and dye concentration at time t (C_0 and C_t , respectively) by measuring the absorbance at the visible maximum absorption wavelength (664 nm), using UV-vis spectrophotometer (Analytik Jena, Specord 210 plus). The percentage of decolorization in the treatment experiments was calculated as follows [36] (Eq. (2)):

$$\text{Decolorization (\%)} = \frac{C_0 - C_t}{C_0} \times 100 \quad (2)$$

3. Results and discussion

3.1. Effect of supporting electrolytes

The effect of the supporting electrolytes (KCl and Na_2SO_4) on RB21 (0.1 mM) decolorization efficiency with an electrolysis time of 20 min while maintaining the

current density at 100 mA cm^{-2} is shown in Fig. 3. We can see a rapid increase in decolorization efficiency in the presence of KCl after 5 min of electrolysis reaching 88.68% of decolorization. This observation could be attributed to the mediated oxidants rather than the direct electron transfer reaction at the surface of the anode. Cl^- is expected to oxidize at anode surface by direct electron transfer reaction which can be explained by the reaction between the generated chlorine/hypochlorite and the dye molecule (Eqs. (3)–(5)), or by consuming $\cdot OH$ which are accumulated in the vicinity of the electrode surface (Eq. (1)) [37].



For both electrolytes, the maximum variation in color is between 0 and 5 min and it is within this range that decolorization of the solution was observed. After 20 min of electrochemical treatment, color removal was approximately 99.94% for KCl and 39.90% for Na_2SO_4 . Consequently, no trace of color can be seen with the naked eye for the KCl electrolyte. Charlys Wilton dos Anjos Bezerra et al. [38] reported a study on RB21 dye degradation by applying 25 mA cm^{-2} in 0.1 mol L^{-1} Na_2SO_4 solution and with the use of different NaCl concentrations. The use of 0.01 mol L^{-1} NaCl shows a significant treatment, reaching 100% of color removal after 120 min of electrolysis with Ti/RuO₂-IrO₂ anode.

3.2. Effect of current density

The effect of applied current density values on the decolorization rates of the RB21 in KCl (0.1 M) solution was studied by setting the current density at 50, 100, 200, 300 mA cm^{-2} (Fig. 4). The results showed that when the current density increased, the dye removal rate increased. At current

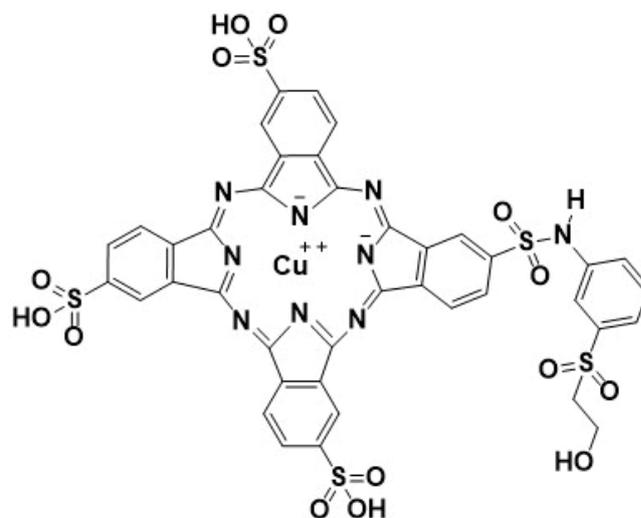


Fig. 1. Structural formula of the Reactive Blue 21 phthalocyanine dye.

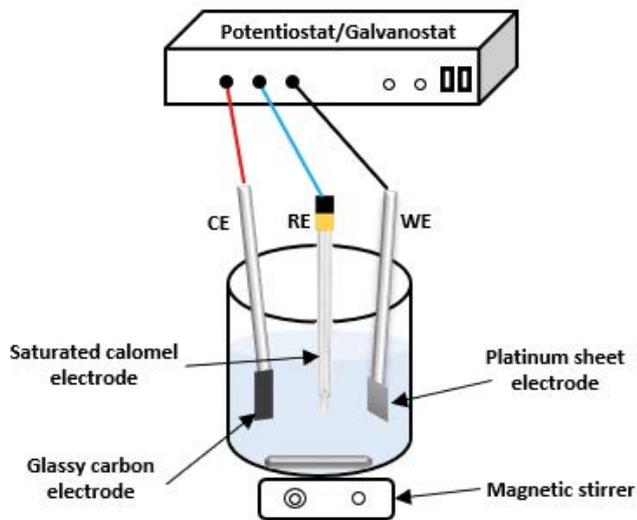


Fig. 2. Schematic diagram of the experimental setup.

densities of 100, 200 and 300 mA cm⁻², more than 99% of dye removal was observed after only 10 min of electrolysis, compared to 91.31% at a current density of 50 mA cm⁻². However, after 20 min of electrolysis, greater than 99% of dye removal was observed for all current densities studied. As estimated, increasing applied current density caused a faster decolorization of the RB21 solution, this can be attributed to a greater charge incoming into the cell involving an electro-generating of more oxidizing chlorine species in KCl medium [39]. Baddouh et al. [40] described the effect of applied current densities (range 20–40 mA cm⁻²) on the color degradation of Rhodamine B dye in 0.1 mol L⁻¹ Na₂SO₄ and 0.05 mol L⁻¹ NaCl as electrolyte during electrolysis at 25°C, using SnO₂ and DSA anodes. At 40 mA cm⁻², 100% of the color was removed in 90 min of treatment for SnO₂ anode and in 40 min for DSA anode.

3.3. Effect of initial pH

To investigate the effect of initial pH on the decolorization of RB21, the pH of the solution was changed from 3 to 11 by the addition of 0.1 M HCl or NaOH solution. The experiments were carried out for 20 min with a dye concentration of 0.1 mM and a KCl concentration of 0.1 M, a current density of 100 mA cm⁻² at room temperature (Fig. 5). Based on the results, after 5 min of electrolysis, more than 92% of the decolorization obtained at pH values between 3 and 9. However, only 35.19% of the decolorization for pH 11. Greater than 92% of the decolorization was obtained after 5 min (pH between 3 and 9) by means of indirect chlorine oxidation resulted in the best removal rates. This can be explained by the fact that the standard potential of Cl₂ and HOCl is higher than that of OCl⁻. In addition, the order of species formation at different pH ranges is as follows: OCl⁻ (pH > 8) > HOCl (8 > pH > 3) > Cl₂ (pH ~ 3) [41,42]. OCl⁻ ions may be present in higher concentrations than other chlorine species in an alkaline environment. The elimination of the dye is reduced under alkaline conditions, which can be attributed to the low oxidation potential of OCl⁻ species compared to Cl₂ and HOCl [43]. Higher than 99% of the decolorization was obtained in all pH values after 20 min of electrolysis. Therefore, the initial pH (5.5) of the electrolyte solution (KCl 0.1 M and RB21 0.1 mM) was kept in future experiments without any adjustment. According to previous studies [40,44], it has been shown that a lower initial pH provides better and faster removal efficiency.

4. Conclusion

The electrochemical oxidation of an aqueous solution of RB21 dye has been explored in this work using a Pt electrode as an anode. The findings revealed that the KCl electrolyte solution showed good performance towards the decolorization of solutions containing this dye in a short time, in contrast to Na₂SO₄. The species generated by the

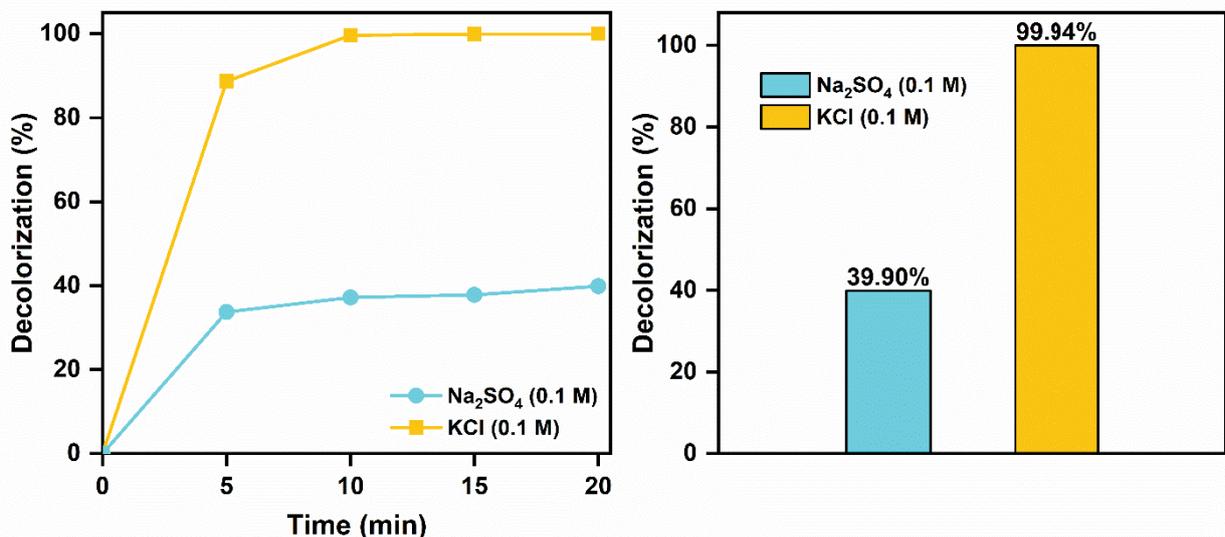


Fig. 3. Effect of electrolyte solution on the % decolorization of Reactive Blue 21 (0.1 mM) during electrolysis treatment on Pt electrode; applied current density = 100 mA cm⁻².

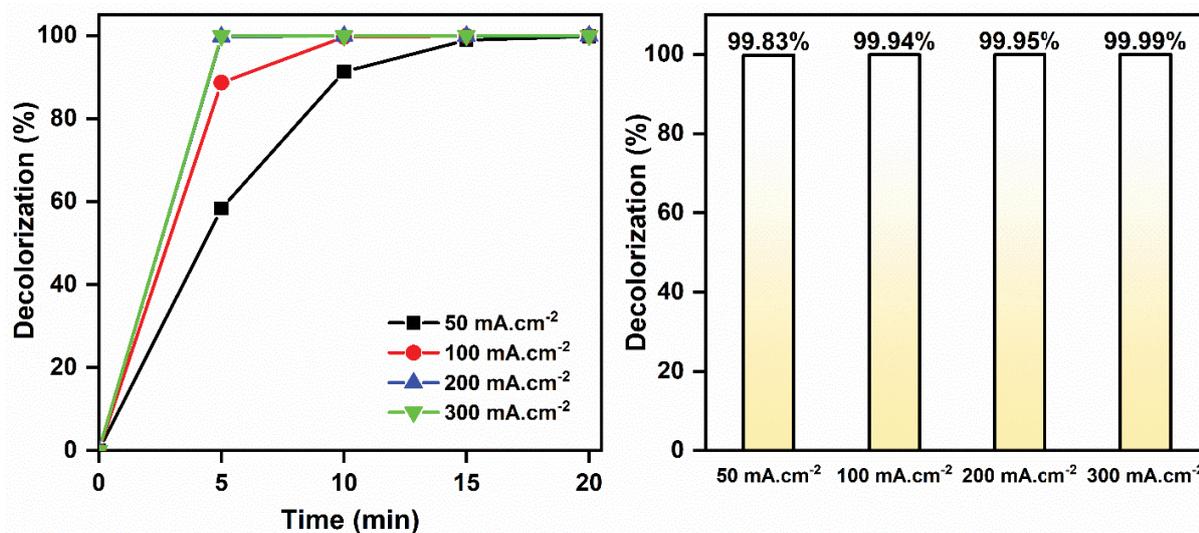


Fig. 4. Effect of the applied current density on the % decolorization of Reactive Blue 21 (0.1 mM) during electrolysis treatment on Pt electrode.

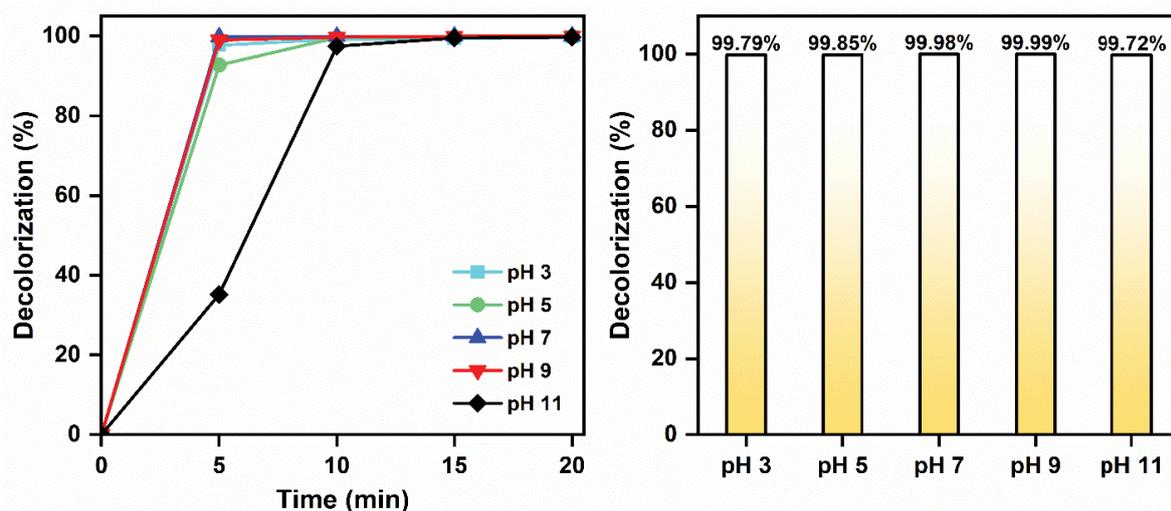


Fig. 5. Effect of initial pH on the % decolorization of Reactive Blue 21 (0.1 mM) during electrolysis treatment on Pt electrode; applied current density = 100 mA cm⁻².

anodic oxidation of chloride ions play an important role in the efficiency of the electrochemical process. Higher than 99% color removal obtained with a current density between 50 and 300 mA cm⁻² and a pH between 3 and 11. We have demonstrated the applicability of electrochemical technology, which proposes, as an alternative for the removal of dyes from textile wastewater, to eliminate their strong color and reduce their environmental and toxicological consequences for the aquatic environment.

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