THE INFLUENCE OF THE BACKGROUND ELECTROLYTE CONCENTRATION ON THE REMOVAL OF CRYSTAL VIOLET BY ELECTROCHEMICAL OXIDATION ON THE PLATINUM ANODE

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The subject of this paper is the removal of Crysta Violet from the model wastewater by electrochemical oxidation on Pt anode. The aim of the study was to investigate the effect of the concentration of the background electrolyte Na₂SO₄ on the process rate and the energy consumption. Cyclic voltammogram of the Pt anode in the Crystal Violet solution was recorded. Dye oxidation was performed by electrolysis in a two-electrode cell. The dye concentration was determined spectrophotometrically. It was found that the optimal Na₂SO₄ concentration was 0.5 mol dm⁻³, which provided the solution decolorization in 30 minutes with the energy consumption of 23.8 kWh/kg dye.

Keywords: Crystal Violet, electrochemical oxidation, background electrolyte.

Introduction

Industry releases huge amounts of colored effluents into the environment. Various dyes and colorants which are used in different industries and science could be very harmful to the receiving water sources because of the toxicity towards many aquatic organisms and because colored compounds reduce water transparency, which, in turn, affects a photosynthetic activity, thus causing severe damage to the ecosystems [1].

Electrochemical technology has been largely developed for its alternative use for wastewater remediation. It currently offers promising approaches for the prevention of the pollution problems from industrial effluents. The main advantage of this technology is its environmental compatibility and other advantages are related to its versatility, high energy efficiency, amenability of automation and safety because it operates at mild conditions. Electrochemical oxidation is the most popular electrochemical procedure for removing organic pollutants from wastewaters and it has been widely used for decolorizing and degrading dyes from aqueous solutions. The oxidation of pollutants can be done as the direct anodic oxidation and a direct electron transfer to the anode, which yields poor decontamination; or by the chemical reaction with electrogenerated species from water discharge at the anode surface such as “active oxygen”, i.e. hydroxyl radical •OH, which is considered to be a responsible species for the electrochemical degradation of organic pollutants [2]. The anode material is a very important factor determining the extent of decolorization, and various materials are used as anodes: Pt [3], boron-doped diamond [4], graphite [5] activated carbon fiber [6] and the electrodes based on metal oxides, such as PbO₂, RuO₂, IrO₂, SnO₂, SbO x etc. and their mixtures [7 – 12].

In this paper, the effect of the concentration of the background electrolyte Na₂SO₄ on the removal of Crystal Violet from the model wastewater by electrochemical oxidation on Pt anode was studied.

EXPERIMENTAL

Chemicals

All chemicals were of reagent grade and used without further purification. Crystal Violet, Na₂SO₄, H₂SO₄ and NaOH were purchased from Sigma Aldrich. All solutions were prepared with deionized water.

Instruments

All electrochemical experiments were carried out using Amel 510 DC potentiostat (Materials Mates, Italy) furnished with VoltaScope software package. The dye concentrations were determined by using UV-vis spectrophotometer Shimadzu UV-1650 PC (Shimadzu, Japan). The pH of the solutions was measured by sension3 (HACH, Colorado USA) pH-meter.

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Table 1. Main characteristics of Crystal Violet

<table>
<thead>
<tr>
<th>Name</th>
<th>Chemical structure</th>
<th>IUPAC name</th>
<th>Molar mass (g mol⁻¹)</th>
<th>λ_{max} (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystal Violet</td>
<td><img src="image" alt="Chemical structure" /></td>
<td>Tris(4- (dimethylamino)phenyl)methyllum chloride</td>
<td>407.98</td>
<td>590</td>
</tr>
</tbody>
</table>

Dye decolorization

Dye decolorization experiments were carried out at room temperature, in a two-electrode cell, at constant current density of 40 mA cm⁻², by using Pt sheet as the anode and Au sheet as a cathode. Model wastewater Crystal Violet solutions of 50 mg dm⁻³ of the dye, pH 7.0±0.1, were prepared separately by dissolving the proper amounts of the powdered dye and Na₂SO₄ in water. During the decolorization experiments, dye solutions were stirred on a magnetic stirrer. At required time intervals, the samples were taken and determined spectrophotometrically at a wavelength of 590 nm, where Crystal Violet exhibits the absorption maximum, with the molar extinction coefficient of 87.000 M⁻¹cm⁻¹. In the range of the concentrations used in this study, the absorbance of the solutions linearly depended on the solution concentration, with the R² value of 0.997. The dye is considered degraded when more than 99.9% of its initial concentration is removed. Electrolysis energy consumption was determined by using the following equation:

\[
\text{Energy consumption (kWh)/(kg dye)} = \frac{IVt}{\Delta m_{\text{dye}}} \quad \ldots(1)
\]

where \( I \) is the average applied current (A), \( V \) is the average cell voltage (V), \( t \) is the electrolysis time (h) and \( \Delta m_{\text{dye}} \) is the dye mass removed (g).

Recording the cyclic voltammogram

Before the dye degradation experiments, cyclic voltammogram of the Pt anode was recorded in the solution which contained 50 mg dm⁻³ of the dye and 0.5 mol dm⁻³ Na₂SO₄, by scanning from 1.2 V to 3.2 V at a scan rate of 20 mV s⁻¹ using saturated calomel electrode as a reference electrode and Au sheet as an auxiliary electrode. All the potentials in this work are given versus standard hydrogen electrode.

RESULTS AND DISCUSSION

Cyclic voltammogram

Cyclic voltammogram of Pt anode recorded in the 50 mg dm⁻³ Crystal Violet solution is presented in Figure 1.

Scanning was performed in anodic direction and the changes of current were observed. No significant changes of current values were observed up to about 2.5 V, and only the weak, nonfaradaic current was detected. However, when the electrode potential reached 2.5 V, the current started to increase more significantly, and when the potential reached 2.8 V, a rapid, linear growth of the current was observed and further increase of the potential up to 3.2 V caused a linear increase of the current. A rapid growth of the current in the potential range of 2.6 – 2.8 V indicated the beginning of the electrochemical reaction at the electrode in that region and it can be attributed to a formation of “active oxygen”, i.e., hydroxy radical •OH, a strong oxidant, with standard formation potential of \( E_0=2.80 \text{ V} \) [2], which further oxidized the dye molecule. The cyclic voltammogram was recorded in the same conditions in the solution which did not contain the dye, and the corresponding curve had the same shape, i.e., the same processes were observed in that system as well (picture not shown). This further confirmed that the oxidation of the dye did not proceed directly at the anode, but through a formation of hydroxy radical •OH, which further oxidized the dye molecule. When the scanning potential decreased, a rapid decrease of the current was observed as well, and when the potential dropped...
below 2.6 V, the current also decreased to negligible values.

Dye decolorization

The effect of the background electrolyte on the decolorization rate of Crystal Violet is shown in Figure 2, where \(C_0\) is the initial dye concentration and \(C\) is the dye concentration after the electrolysis time \(t\). The concentration of 50 mg dm\(^{-3}\) is in the common initial dye concentrations range used in the electrochemical dye degradation experiments, since those concentrations of dyes are present in the industry effluents [2]. The working pH was adjusted using Na\(_2\)SO\(_4\) and NaOH. It was selected based on the preliminary investigation which showed that the decolorization time decreased with increasing pH from 2.0 to 9.0; the decolorization times of the dye for the pH values 2.0±0.1, 3.0±0.1, 4.0±0.1, 7.0±0.1 and 9.0±0.1 were: 55, 50, 46, 30 and 29 minutes, respectively. Since the increasing pH above 7.0±0.1 did not provide a significant decrease of the decolorization time, pH 7.0±0.1 was selected as the optimal pH for this process in order to avoid the addition of excessive base.

The background electrolyte was added to the dye solution in order to increase its electrical conductivity, i.e. to decrease its electrical resistance and thus the energy consumption. Na\(_2\)SO\(_4\) is the most commonly used background electrolyte due to its high electrochemical stability and neutrality in the broad potential region, good electrical conductivity, low cost and environmental compatibility. As shown in Figure 2, for the \(C_{Na2SO4}\) 0.10 – 0.50 mol dm\(^{-3}\), the rate, and thus the efficiency of the Crystal Violet removal significantly increases with the increase of \(C_{Na2SO4}\). Decolorization times for 0.10, 0.20, 0.50 i 1.0 mol dm\(^{-3}\) Na\(_2\)SO\(_4\) are 57±1, 45±1, 35±1 i 32±1 minutes, respectively, and during the first 5 minutes, the amount of the dye removed was: 40, 53, 65 i 67 % of its initial concentration, respectively. However, in the presence of 1.0 mol dm\(^{-3}\) Na\(_2\)SO\(_4\), the increase of the dye removal rate was only negligible, compared to the removal rate in the presence of 0.50 mol dm\(^{-3}\) Na\(_2\)SO\(_4\), though its concentration was twice as high. It can be assumed that the increase of the Na\(_2\)SO\(_4\) concentration causes the increase of the dye decolorization rate, but only up to 0.50 mol dm\(^{-3}\) Na\(_2\)SO\(_4\), and its further increase does not have much effect on the decolorization rate. The reason for this might be the addition of excess SO\(_4^{2-}\) anions, which are able to react with hydroxyl radicals, leading to inorganic radical ions which exhibit a much lower reactivity than •OH, hence they do not participate in the dye decolorization [13].

For 0.10, 0.20, 0.50 i 1.0 mol dm\(^{-3}\) Na\(_2\)SO\(_4\), the energy consumption values for the process were: 130.1, 65.2, 23.8 and 17.3 kWh kg\(^{-1}\) dye, respectively.

As shown in Figure 3, the energy consumption decreased with the increase of \(C_{Na2SO4}\), because the electrical resistance decreased as well, but the effect was significant only up to 0.50 mol dm\(^{-3}\) Na\(_2\)SO\(_4\). Further increase of its concentration to 1.0 mol dm\(^{-3}\) caused only a slight decrease of the energy consumption. It can be assumed that the increase of the background electrolyte concentration not only increased the decolorization rate, but it also decreased the reaction energy consumption. However, the effect was significant only up to 0.50 mol dm\(^{-3}\) Na\(_2\)SO\(_4\), which is assumed to be an optimal concentration for this process.

**CONCLUSION**

In this paper, the removal of Crysta Violet from the wastewater by electrochemical oxidation on Pt anode and the effect of the concentration of the background electrolyte, Na\(_2\)SO\(_4\), on the process rate and the energy consumption were investigated. The dye was completely decolorized by the »active oxygen«, electrogenerated at the anode. The decolorization rate increased and the pro-
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cess energy consumption decreased with the increase of Na₂SO₄ concentration, but the effects were significant only up to 0.50 mol dm⁻³ Na₂SO₄, which was found to be the optimal background electrolyte concentration. With 0.50 mol dm⁻³ Na₂SO₄ the complete dye removal was achieved in 30 minutes with the energy consumption of 23.8 kWh/kg dye. The optimal pH of the process was found to be 7.0±0.1.

ACKNOWLEDGEMENT

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REFERENCES


UTICAJ KONCENTRACIJE POMOĆNOG ELEKTROLITA NA UKLANJANJE BOJE CRYSTAL VIOLET ELEKTROHEMIJSKOM OKSIDACIJOM NA PLATINSKOJ ANODI

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Izvod

Predmet ovog rada je uklanjanje boje Crystal Violet iz modelne otpadne vode elektrohemijskom oksidacijom na Pt anodi. Cilj je ispitivanje uticaja koncentracije pomoćnog elektrolita, Na₂SO₄, na brzinu procesa i utrošak električne energije. Snimljen je ciklični voltamogram Pt elektrode u rastvoru Crystal Violet. Oksidacija boje je izvedena elektrolizom u dvoelektrodnoj celiji. Koncentracija boje je merena spektrofotometrijski. Nađeno je da je optimalna koncentracija Na₂SO₄ 0.5 mol dm⁻³, pri kojoj se rastvor obezboji za 30 minuta, uz utrošak električne energije od 23.8 kWh/kg boje.

Ključne reči: Crystal Violet, elektrohemijska oksidacija, pomoćni elektrolit.