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DEGRADATION OF RECALCITRANT ORGANIC COMPOUNDS BY ELECTROCHEMICAL METHOD

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ABSTRACT

Degradation of recalcitrant organic compounds such as azo dyes is difficult to accomplish because of their complex structure. This paper deals with the electrochemical oxidation of C.I. Reactive Black 5 (RB5) azo dye at dimensionally stable anodes (DSA). The Ti/RuO₂/SnO₂-Sb₂O₅-Bi₂O₃ electrodes were prepared by thermal decomposition of the appropriate precursors and they were characterized by scanning electron microscopy (SEM) and cyclic voltammetry (CV). The SEM image revealed a surface morphology with mud-like cracks and the cyclic voltammograms suggested that the dye oxidation might occur simultaneously with oxygen evolution. The electrochemical oxidation of the dye was carried out in a cell with two anodes of Ti/RuO₂/SnO₂-Sb₂O₅-Bi₂O₃ and three cathodes of stainless steel. The electrolyte solution consisted of 0.1 g/L dye in 0.1 M Na₂SO₄ as supporting electrolyte at pH 5.8, 11 and 3. The degradation of the dye was assessed by recording UV-VIS spectra of the electrolysed solutions. Colour removal efficiency higher than 96% was obtained for an applied current density of 100 A/m² and electrolysis time of 120 minutes at any value of the pH.

INTRODUCTION

Azo dyes are extensively used for dyeing of cotton fabrics and have a world market share of 60-70% [1,2]. Azo dyes due to their poor exhaustion properties as much as 30% of the initial dye applied remain unfixed and finally by dyebath effluent, this group of synthetic dyes are discharged into the environment [3].

Discharge of azo dyes is undesirable for aesthetic reasons and because many azo dyes and their degradation products are toxic to the aquatic life or they have carcinogenic effects [4,5]. The degradation of dyes, especially azo dyes, is difficult to accomplish because of their complex structure and synthetic nature. It is well known that textile dyes are designed to resist biological, photolytic and chemical degradation.

Electrochemical methods are promising for degradation of recalcitrant organic compounds such as azo dyes. Researches have been focused on degradation by electrochemical oxidation by using different electrodic materials that show high overpotential towards the oxygen discharge [6-8].

The aim of this paper was the degradation of RB5 azo dye by electrooxidation at DSA type electrodes prepared by thermal decomposition of the appropriate precursors. The composition of the anodes was Ti/RuO₂/SnO₂-Sb₂O₅-Bi₂O₃ with molar ratio Sn:Sb:Bi in precursors solution 94:3:3.

MATERIALS and METHODS

SEM analysis

The morphology of the electrocatalytic film of DSA electrodes was examined by SEM. The SEM images were obtained at 2,200 magnification by using a Philips CM30T scanning electron microscope. The microscope was operated at an accelerating voltage of 20 kV.

Electrochemical measurements

The cyclic voltammetric experiments were performed by using an EcoChemie Autolab-PGSTAT 302 computer-controlled potentiostat-galvanostat. A saturated calomel electrode was used as a reference electrode. A Ti/RuO₂/SnO₂-Sb₂O₅-Bi₂O₃ wire with active surface area of 1 cm² was used as working electrode and a platinum plate of 1 cm² as a counter electrode. Experiments were carried out at 50 mVs⁻¹ scan rates at room temperature in solution of 0.1 M Na₂SO₄ supporting electrolyte and RB5. The pollutant concentration in the working solutions was 0.1 g/L.

Electrolysis

The electrochemical oxidation of RB5 was carried out in galvanostatic conditions. Two Ti/RuO₂/SnO₂-Sb₂O₅-Bi₂O₃ anodes and three stainless steel cathodes were used at 1 cm gap. Active surface area was 38 cm². Experiments were carried out applying current densities of 25, 50, 75 and 100 A/m² at electrolysis time of 120 minutes and values of pH 5.8, 11 and 3. Experiments were carried out in solutions of 0.1 g/L RB5 prepared in 0.1 M Na₂SO₄ as supporting electrolyte. The dye was used without any previous purification. The solutions were prepared with distilled water and reagent grade Na₂SO₄ (Chimopar București).

UV-VIS spectra

A Jasco V-530 spectrophotometer controlled by computer recorded the UV-VIS spectra. The UV-VIS spectra of RB5 are shown in Fig.1 and 2. RB5 exhibits at pH 5.8 and 3 four peaks at 229 nm, 256 nm, 310 nm, 597 nm and a shoulder at 487 nm. RB5 exhibits for pH 11 three peaks at 229 nm, 317 nm and 607 nm. The azo dye has in its structure benzene and naphthalene rings. In UV range the assignments, in accordance with the literature data [9], are the following: benzene ring at 229 nm (pH 5.8, 11 and 3) and naphthalene ring at 310 nm (pH 5.8 and 3), and 317 nm (pH 11), respectively. The maximum in visible range are due to azo bond.

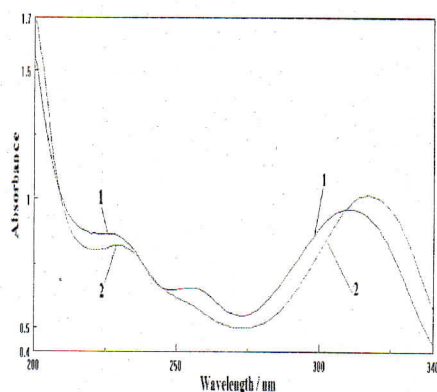


Fig.1. UV spectra of RB5
1. pH – 5.8 and 3; 2. pH – 11

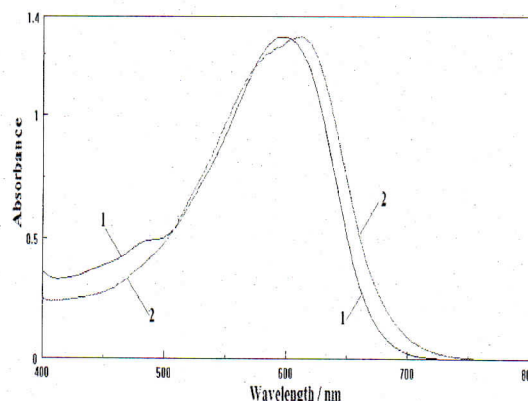


Fig.2. Visible spectra of RB5
1. pH – 5.8 and 3; 2. pH – 11

RESULTS

SEM analysis

The SEM image (Fig. 3) exhibited a relative compact surface morphology, the coating having few mud-like cracks and pores. The presence of the cracks will facilitate the formation of TiO_2 with poor conductivity. As a result, the resistance of the anode surface during the electrolysis will increase and the activity of the electrode would be also reduced.

Electrochemical measurement

CV was used to characterise the electrochemical properties of electrocatalytic film of $\text{Ti/RuO}_2/\text{SnO}_2\text{-Sb}_2\text{O}_5\text{-Bi}_2\text{O}_3$ electrode. The cyclic voltammograms recorded in 0.1 M Na_2SO_4 supporting electrolyte and in the presence of RB5, in the potential range from 0 V to 1.5 V and pH 5.8, 11 and 3, are shown in Fig. 4-6.

It can be observed that the voltammograms recorded without and in the presence of the azo dye overlap that suggests the oxidation of the pollutant could occur in the O_2 evolution potential range. The electrode exhibited the same electrochemical behaviour at any value of the pH (5.8, 11 and 3).

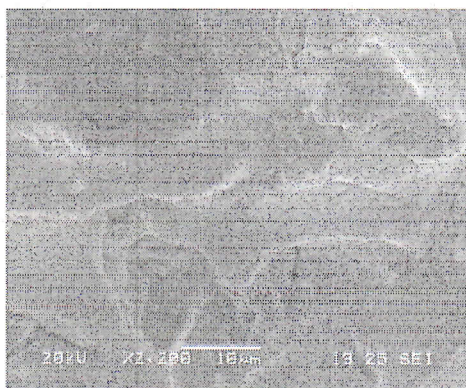


Fig.3. SEM image of $\text{Ti/RuO}_2/\text{SnO}_2\text{-Sb}_2\text{O}_5\text{-Bi}_2\text{O}_3$

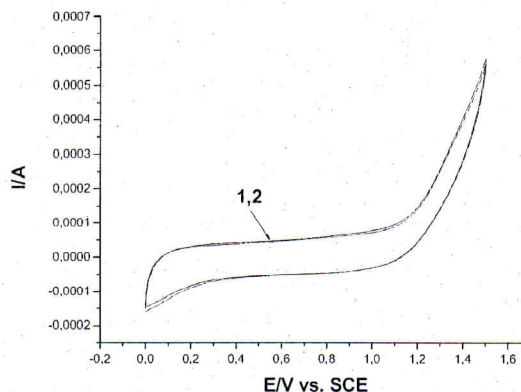


Fig.4. Cyclic voltammograms of $\text{Ti/RuO}_2/\text{SnO}_2\text{-Sb}_2\text{O}_5\text{-Bi}_2\text{O}_3$; scan rate 0.05 V/s; potential range: 0 V to 1.5 V vs. SCE; pH=5.8; 1- 0.1 M Na_2SO_4 ; 2 - 0.1 g/L RB5 in 0.1 M Na_2SO_4

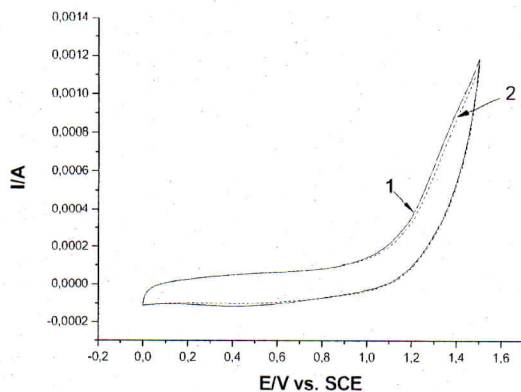


Fig.5. Cyclic voltammograms of $\text{Ti/RuO}_2/\text{SnO}_2\text{-Sb}_2\text{O}_5\text{-Bi}_2\text{O}_3$; scan rate 0.05 V/s; potential range: 0 V to 1.5 V vs. SCE; pH=11; 1- 0.1 M Na_2SO_4 ; 2 - 0.1 g/L RB5 in 0.1 M Na_2SO_4

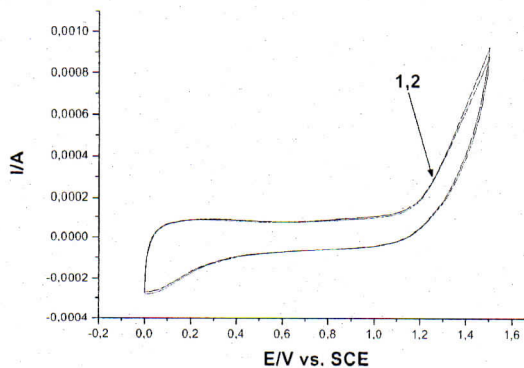


Fig.6. Cyclic voltammograms of $\text{Ti/RuO}_2/\text{SnO}_2\text{-Sb}_2\text{O}_5\text{-Bi}_2\text{O}_3$; scan rate 0.05 V/s; potential range: 0 V to 1.5 V vs. SCE; pH=11; 1- 0.1 M Na_2SO_4 ; 2 - 0.1 g/L RB5 in 0.1 M Na_2SO_4

Electrolysis and UV-VIS spectra analysis

The examination of the UV spectra shows the shift and the flattening of the peaks corresponding to the aromatic rings at pH 5.8, 11 and 3, and also the disappearance of the peak from 256 nm at pH 5.8 and 3. The spectra of the electrolysed solutions kept the shape at any applied current density, and the flattening of the peaks was more emphasised as the applied current density was higher (Fig.7 shows the spectra for pH 5.8; the spectra for pH 11 and 3 are not shown as part of this paper). This findings lead to the hypothesis of the aromatic rings opening and the oxidation to carbon dioxide during the degradation of RB5 at modified SnO₂ anodes. In accordance with the literature data, the electrochemical oxidation of organic compounds on anodes which exhibits a high overpotential for oxygen evolution, such as Ti/SnO₂ or Ti/SnO₂-Sb₂O₅, leads to carbon dioxide [10].

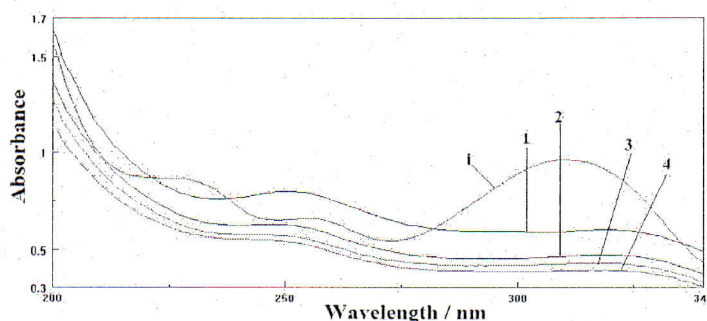


Fig.7. UV spectra of RB5 electrolysed solutions at various current densities: pH=5.8; RB5 concentration – 0.1 g/L; electrolysis time - 120 minutes; i – initial solution; applied current densities: 1 – 25 A/m²; 2- 50 A/m²; 3 – 75 A/m²; 4 – 100 A/m²

The colour removal efficiency was calculated from the relative decrease of absorbance at 597 nm for pH 5.8 and 3, and 607 nm for pH 11, values of wavelength that presents maximum of absorbance of the azo dye in the visible region (Fig. 2). It can be easily observed (Table 1) the increase of colour removal efficiency when the applied current density increased for any value of pH.

Table 1. Working conditions, absorbance and colour removal efficiency for RB5; electrolysis time: 120 min; $A_{i, \text{pH}=5.8 \text{ and } 3} = 3,30$; $A_{i, \text{pH}=11} = 3,27$

pH	Current density/ A/m ²	Cell voltage/ V	A_{597}	A_{607}	Colour removal efficiency / %
5,8	25	3,2	0,25	-	92,42
	50	3,5	0,08	-	97,57
	75	3,8	0,07	-	97,87
	100	4,0	0,06	-	98,18
11	25	3,1	-	0,22	93,27
	50	3,5	-	0,17	94,80
	75	3,8	-	0,15	95,41
	100	4,0	-	0,13	96,02
3	25	3,2	0,20	-	93,93
	50	3,5	0,08	-	97,57
	75	3,7	0,04	-	98,78
	100	4,0	0,04	-	98,78

CONCLUSIONS

This study deals with the degradation of C.I. Reactive Black 5 azo dye by electrochemical oxidation at DSA type electrodes. The electrodic composition Ti/RuO₂/SnO₂-Sb₂O₅-Bi₂O₃ was prepared by thermal decomposition method. The molar ratio Sn:Sb:Bi in the precursors solution was 94:3:3. The morphology of the electrocatalytic film of DSA type electrodes was examined by SEM and the characterization of electrochemical properties was accomplished by CV.

The cyclic voltammograms were recorded in the potential range from 0 V to 1.5 V for a scan rate of 0.05 V/s in 0.1 M Na₂SO₄ supporting electrolyte and in presence of 0.1 g/L RB5. The degradation experiments were carried out in 0.1 g/L RB5 in 0.1 M Na₂SO₄ as supporting electrolyte, applied current densities of 25, 50, 75 and 100 A/m², pH values of 5.8, 11 and 3 at 120 minutes electrolysis time.

The SEM image exhibited a relative compact surface morphology, the coating having few mud-like cracks and pores. The voltammograms recorded in the presence and absence of RB5 suggests that the oxidation of the pollutant at any pH could occur in the oxygen evolution potential range.

The UV spectra suggested that the anodic oxidation of RB5 on Ti/RuO₂/SnO₂-Sb₂O₅-Bi₂O₃ led to the opening of aromatic rings and the oxidation to carbon dioxide for any working pH. The best result for the colour removal efficiency was obtained for an applied current density of 100 A/m² and 120 minutes of electrolysis and they were about 98% at pH 5.8 and 3, and about 96% at pH 11.

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