

Electrochemical Degradation of Aromatic Compounds at Modified SnO₂ Anodes

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Abstract. The purpose of this study was the electrochemical degradation of a mixture of Reactive Black 5 (RB5) azo dye and nonylphenol ethoxylate with 9 ethoxy units (NP9EO) at modified SnO₂ anodes. Ti/RuO₂/SnO₂-Sb₂O₅-RuO₂ and Ti/RuO₂/SnO₂-Sb₂O₅-Bi₂O₃ anodes were prepared by thermal decomposition of appropriate precursors. Both NP9EO and RB5 concentrations were 0.1 g/L in 0.1 M Na₂SO₄ as supporting electrolyte. The electrolysis were conducted under galvanostatic regime at applied current densities of 50, 75 and 100 A/m² and electrolysis time of 30, 60 and 120 minutes. The electrolysed solutions were characterised by UV-VIS spectroscopy. The spectral data revealed the aromatic ring opening and they were also used to assess the colour removal efficiency. Based on the spectral data, it was assessed the colour efficiency and some aspects of oxidation process were discussed.

Keywords: aromatic compounds, electrochemical degradation, modified SnO₂ anodes

1. Introduction

Textile wastewaters contain aromatic compounds like dyes and nonionic surfactants. Usually, dyes are not treatable by biological organisms. Nonylphenol ethoxylates, which are nonionic surfactants, require a very long time to be broken down by bacteria. Consequently, their release in the environment is undesirable.

Electrochemical methods are promising concerning the treatment of wastewaters containing dyes and nonylphenol ethoxylates. Researches have been conducted by using dimensionally stable anodes (DSA) to degrade organic pollutants [1-3].

An appropriate choice of anode material can allow complete elimination of total organic carbon with high current efficiency. One of these materials could be DSA having electrocatalytic layer of modified SnO₂. Studies have been reported the use of modified SnO₂ anodes for the electrochemical oxidation of organic compounds [4, 5].

The aim of this paper was electrochemical degradation of a mixture of RB5 and NP9EO at modified SnO₂ anodes, Ti/RuO₂/SnO₂-Sb₂O₅-RuO₂ and Ti/RuO₂/SnO₂-Sb₂O₅-Bi₂O₃.

2. Experimental

2.1. Modified SnO₂ anodes preparation

The following anodes: Ti/RuO₂/SnO₂-Sb₂O₅-RuO₂ and Ti/RuO₂/SnO₂-Sb₂O₅-Bi₂O₃ were prepared by using titanium plates as a support. The plates were treated by sand-blasting followed by a chemical treatment with technical hydrochloric acid 15 % for 20 minutes under boiling. Then, the plates were washed with

water, distilled water and absolute ethylic alcohol reagent degree Chimopar Bucuresti) followed by drying in open air. The precursors solution was brushed onto plates surface.

The intermediate layer of RuO₂ was obtained by thermal decomposition of a precursor solution obtained by dissolving RuCl₃·nH₂O (Fluka) in isopropanol reagent degree (Chimopar Bucuresti) at 450 °C.

The electrocatalytic layer of SnO₂-Sb₂O₅-RuO₂ and SnO₂-Sb₂O₅-Bi₂O₃ was prepared as follows: the precursors solution was obtained by dissolving the appropriate amount of SnCl₄·5H₂O (Aldrich), SbCl₃ (Aldrich) and RuCl₃·nH₂O (Fluka) or Bi(NO₃)₃·5H₂O (Chimopar Bucuresti) in the solution containing hydrochloric acid (37%) and isopropanol reagent degree (Chimopar Bucuresti). The molar ratio Sn:Sb:Ru or Sn:Sb:Bi in precursors solution was 94:3:3.

The anodic material was further treated by heating to 110 °C in a drying cabinet. After that, the electrode was treated at 550 °C for 10 minutes to decompose the salts from precursors solution. This cycle brushing – drying – thermal decomposition was repeated 15 times. Finally, a thermal treatment was applied for 1 hour to stabilize the oxide film.

2.2. Electrolysis

Electrochemical degradation of pollutants was carried out in a plexiglass cell at modified SnO₂ anodes. Two anodes and three stainless steel cathodes were inserted at 1 cm gap. The active surface area was 38 cm². Experiments were carried out by applying current densities of 50, 75, 100 and 300 A/m² at various electrolysis times: 30, 60 and 120 minutes.

Experiments were carried out in working solutions that contained a mixture of 0.1 g/L RB5 and 0.1 g/L NP9EO (RB5-NP9EO) in 0.1 M Na₂SO₄ as supporting electrolyte. For comparison purposes, experiments were carried out only in solutions of 0.1 g/L RB5 in 0.1 M Na₂SO₄ as supporting electrolyte. The pH of initial solutions (RB5-NP9EO or only the dye) was 5.8. RB5 and NP9EO were technical products and they were used as suppliers provided them. Solutions were prepared with distilled water and Na₂SO₄ (Chimopar București) reagent grade.

Chemical structure of RB5 and NP9EO is shown in figures 1 and 2.

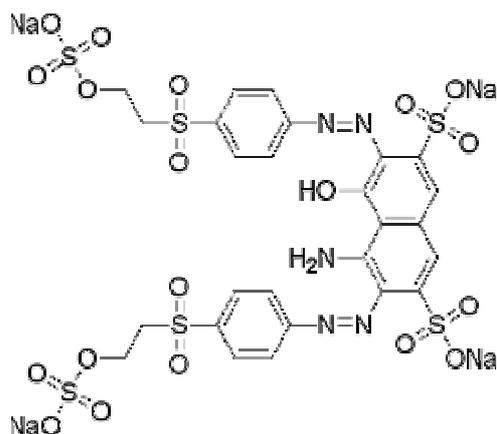


Figure 1. Chemical structure of RB5

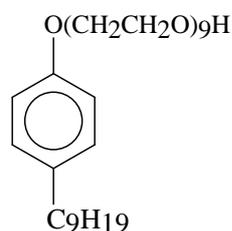


Figure 2. Chemical structure of NP9EO

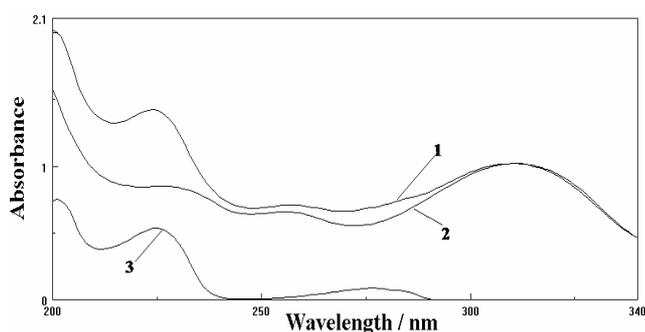


Figure 3. UV spectra of the individual components and the mixture (dilution 1:2.5)

1. RB5-NP9EO in 0.1 M Na₂SO₄; pH=5.8; 2. RB5 in 0.1 M Na₂SO₄; c_{ini} = 0.1 g/L; pH=5.8 3. NP9EO in 0.1 M Na₂SO₄; c_{ini} = 0.1 g/L

2.3. UV-VIS spectra

The UV-VIS spectra were recorded by a Jasco V-530 spectrophotometer controlled by computer.

The individual UV spectra of the RB5 and NP9EO and also the spectrum of the RB5-NP9EO are shown in figure 3.

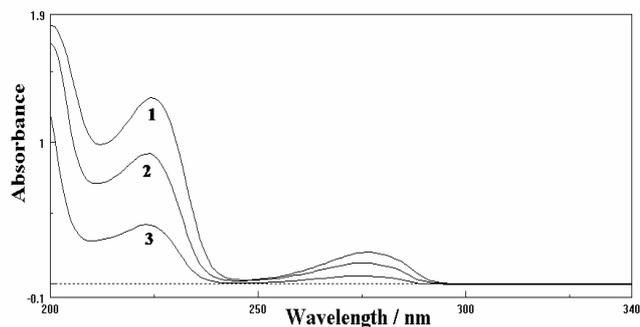


Figure 4. UV spectra of nonylphenols ethoxylates in 0.1 M Na₂SO₄: 1. NP9EO 2. NP16EO 3. NP40EO NPnEO concentration: 0.1 g/L

The spectrum in the visible range of the RB5-NP9EO is shown in figure 5.

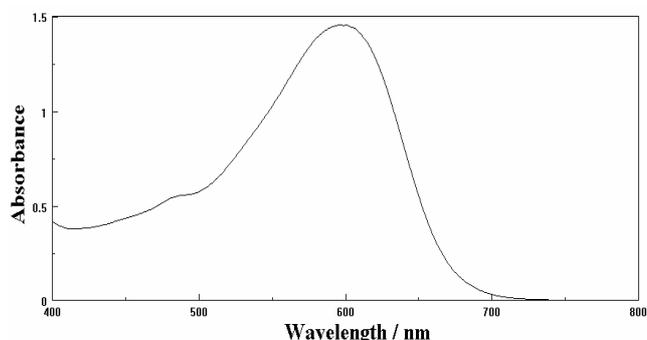


Figure 5. Spectra in visible range of RB5-NP9EO in 0.1 M Na₂SO₄; pH=5.8; dilution 1:2.5

3. Results and discussion

3.1. UV spectra analysis

At pH 5.8 the UV spectra of RB5 exhibits three absorbance peaks at 229 nm, 256 nm and 310 nm. In accordance to the literature data [6], the absorbance peak at 229 nm was assigned to benzene ring, while those of 310 nm to naphthalene ring.

The absorbance peaks at 225 nm and 276 nm in the UV spectrum of the NP9EO were assigned to the benzene ring, as it can be inferred from Fig. 4. Thus, it can be observed that the absorbance peaks appeared at the same wavelength for any nonylphenol ethoxylate. Because the absorbance decreased as the number of the ethoxy units increased for any peaks and the weight of the benzene ring in the molecular weight of the nonylphenol ethoxylate decreased, the absorbance peaks at 225 nm and 276 nm in the NP9EO spectrum can be assigned to the benzene ring.

The spectrum of the RB5-NP9EO exhibits absorbance peaks at 225 nm, 258 nm and 310 nm. It can be observed that the absorbance peak of 310 nm appeared in the spectrum only as contribution of RB5.

3.2. Electrochemical degradation experiments

The electrochemical degradation experiments proved that as the electrolysis time increased for any applied current density and anodic composition the value of the absorbance at 225 nm and 310 nm decreased (Table 1).

TABLE 1. Working conditions, values of absorbance at 225 nm and 310 nm for RB5-NP9EO in 0.1 M Na₂SO₄; *A_{mi_225}=1.41; *A_{mi_310}=1.02

Anodic composition	Current density / (A/m ²)	Time / (min)	*A ₂₂₅	*A ₃₁₀
Ti/RuO ₂ /SnO ₂ -Sb ₂ O ₅ -RuO ₂	50	30	1.32	0.71
		60	1.28	0.63
		120	1.17	0.60
	75	30	1.38	0.69
		60	1.29	0.63
		120	1.10	0.58
	100	30	1.31	0.68
		60	1.25	0.62
		120	0.98	0.52
Ti/RuO ₂ /SnO ₂ -Sb ₂ O ₅ -Bi ₂ O ₃	50	30	1.35	0.71
		60	1.27	0.60
		120	1.09	0.56
	75	30	1.35	0.69
		60	1.20	0.57
		120	0.96	0.48
	100	30	1.33	0.67
		60	1.16	0.55
		120	0.84	0.42

* dilution 1:2.5

As it is shown in figure 6 and 7, at 120 minutes of electrolysis, the absorbance peak flattening is more enhanced, as the applied current density is higher for both anodic compositions. However, it can be observed that the degradation process occurred more efficiently at Ti/RuO₂/SnO₂-Sb₂O₅-Bi₂O₃ anodes.

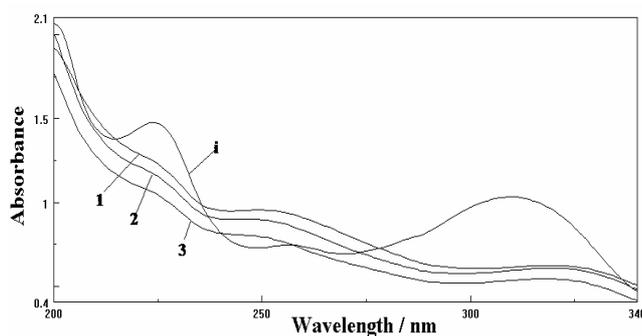


Figure 6. UV spectra of RB5-NP9EO in 0.1 M Na₂SO₄ (dilution 1:2.5) anodic composition: Ti/RuO₂/SnO₂-Sb₂O₅-RuO₂; electrolysis time: 120 min; current density: i - initial solution; 1 - 50 A/m²; 2 - 75 A/m²; 3 - 100 A/m²

Figures 6 and 7 show also that the shape of spectra of the electrolysed solutions was the same for both anodic compositions. In addition, the absorbance peaks attributed to the aromatic rings decreased as the applied current

densities increased and no additional peak absorbance appeared in the spectra.

The electrochemical degradation of RB5-NP9EO at Ti/RuO₂/SnO₂-Sb₂O₅-RuO₂ in the following conditions: 300 A/m² and 120 or 180 minutes led to almost disappearance of the absorbance peaks (figure 8). Also, no new peaks appeared in the electrolysed solutions spectra that could suggest the formation of additional compounds with aromatic structures.

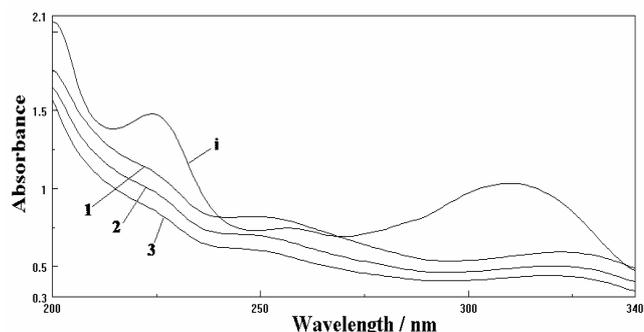


Figure 7. UV spectra of RB5-NP9EO in 0.1 M Na₂SO₄ (dilution 1:2.5) anodic composition: Ti/RuO₂/SnO₂-Sb₂O₅-Bi₂O₃; electrolysis time: 120 min; current density: i - initial solution; 1 - 50 A/m²; 2 - 75 A/m²; 3 - 100 A/m²

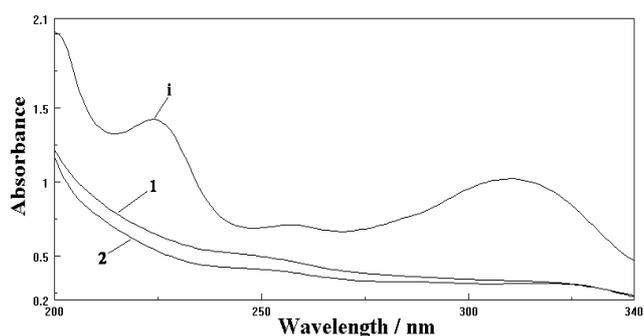


Figure 8. UV spectra of RB5-NP9EO in 0.1 M Na₂SO₄ (dilution 1:2.5) anodic composition: Ti/RuO₂/SnO₂-Sb₂O₅-RuO₂; current density: 300 A/m²; electrolysis time: i - initial solution; 1 - 120 min; 2 - 180 min

These findings suggest the aromatic ring opening and there are in accordance with the literature data [7 - 9]. The authors reported that the electrochemical oxidation of the organic compounds at anodes that exhibit high overpotential towards the oxygen evolution, such as Ti/SnO₂ or Ti/SnO₂-Sb₂O₅, leads to CO₂.

The 310 nm absorbance peak in the RB5-NP9EO spectrum is due exclusively to the RB5 presence. Therefore, it is possible a comparison between the degradation efficiency of the dye individual (Table 2) as well in the mixture (Table 1).

The data from Tables 1 and 2 revealed that the differences between the absorbance peak at 310 nm (assigned to the naphthalene ring) in the spectra of the solutions of the RB5-NP9EO and only the dye are insignificant. Consequently, the presence of NP9EO did not hamper the oxidation process of RB5 in relation to naphthalene ring.

TABLE 2. Working conditions and absorbance at 310 nm after electrolysis for RB5 in 0.1 M Na₂SO₄; c_{in RB5}=0.1 g/L; electrolysis time: 120 minutes

Anodic composition	Current density / (A/m ²)	Cell voltage / (V)	*A ₃₁₀
Ti/RuO ₂ /SnO ₂ -Sb ₂ O ₅ -RuO ₂	50	3.4	0.62
	75	3.5	0.57
	100	3.7	0.50
Ti/RuO ₂ /SnO ₂ -Sb ₂ O ₅ -Bi ₂ O ₃	50	3.5	0.46
	75	3.8	0.42
	100	4.1	0.39

* dilution 1:2.5

3.3. Colour removal efficiency

As it is shown in figure 5 the spectrum of the RB5-NP9EO presented a maximum of the absorbance in the visible range at 597 nm. The presence in the spectrum of this absorbance peak is due to RB5, as it is well known NP9EO is colourless.

The colour removal efficiency was calculated from the relative decrease of absorbance at 597 nm peaks and the results are listed in Tables 3 and 4.

TABLE 3. Working conditions, colour removal efficiency for RB5-NP9EO in 0.1 M Na₂SO₄ and RB5 (c_{in RB5}=0.1 g/L) in 0.1 M Na₂SO₄ at Ti/RuO₂/SnO₂-Sb₂O₅-RuO₂

Current density / A/m ²	Time / min	Cell voltage / V	Colour removal efficiency (mixture) / %	*Colour removal efficiency (individual) / %
50	30	3.3	70.05	-
	60	3.4	83.24	-
	120	3.4	93.68	97.27
75	30	3.5	69.23	-
	60	3.5	85.16	-
	120	3.5	95.32	97.27
100	30	3.7	73.07	-
	60	3.7	89.01	-
	120	3.7	98.07	97.57

* - no experiments were carried out

TABLE 4. Working conditions, colour removal efficiency for RB5-NP9EO in 0.1 M Na₂SO₄ and RB5 (c_{in RB5}=0.1 g/L) in 0.1 M Na₂SO₄ at Ti/RuO₂/SnO₂-Sb₂O₅-Bi₂O₃

Current density / A/m ²	Time / min	Cell voltage / V	Colour removal efficiency (mixture) / %	*Colour removal efficiency (individual) / %
50	30	3.6	63.73	-
	60	3.5	84.61	-
	120	3.5	94.78	97.57
75	30	3.8	63.73	-
	60	3.8	87.36	-
	120	3.8	97.52	97.87
100	30	4.0	71.70	-
	60	4.1	90.38	-
	120	4.1	98.62	98.18

* - no experiments were carried out

It can be easily observed that generally for both anodic compositions the colour removal efficiency from RB5-NP9EO solutions increase with the increase of the current density and the electrolysis time.

The colour removal efficiency was higher for the anodic composition with Bi₂O₃ in the electrocatalytic layer, excepting the 30 minutes of electrolysis time at any applied current density.

For both anodic compositions at 120 minutes of electrolysis and applied current densities of 50 and 75 A/m² the colour removal efficiency is higher for RB5 individual degradation than in the mixture.

4. Conclusions

In this study, the electrochemical degradation of a mixture of RB5 and NP9EO was investigated at modified SnO₂ anodes.

The Ti/RuO₂/SnO₂-Sb₂O₅-RuO₂ and Ti/RuO₂/SnO₂-Sb₂O₅-Bi₂O₃ anodes were prepared by thermal decomposition of the appropriate precursors.

The UV spectra analysis showed the aromatic ring opening in the working conditions of 50, 75 and 100 A/m² applied current densities at 30, 60 and 120 minutes of electrolysis for both anodic compositions.

The degradation of the naphthalene ring of RB5 from the mixture of pollutants at modified SnO₂ anodes was not hampered by the presence of NP9EO.

The best colour removal efficiencies (about 98%) were obtained for both anodic compositions at 100 A/m² and 120 minutes of electrolysis.

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