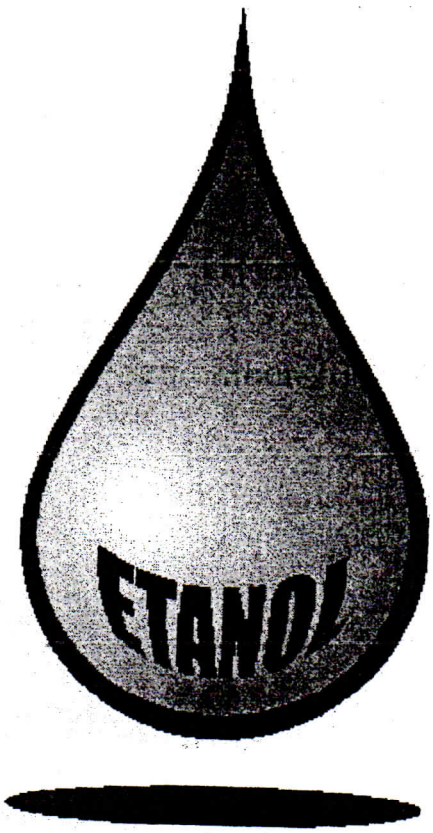
PROCEEDINGS OF

THE 14th SYMPOSIUM ON ANALYTICAL AND ENVIRONMENTAL PROBLEMS

24 September 2007

Edited by
Zoltán Galbács



SZAB

SZEGED, HUNGARY

THE 14th SYMPOSIUM ON ANALYTICAL AND ENVIRONMENTAL PROBLEMS

Organised by

SZAB Kémiai Szakbizottság Analitikai és Környezetvédelmi Munkabizottsága

ISBN

978-963-87720-0-8

Sponsors

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Galbács Zoltán

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UTILIZATION OF SnO_2 ANODES TO THE ELECTROCHEMICAL DEGRADATION OF BIOREFRACTORY DYES

Monica Ihos*, Gligor Bocea, Ladislau Andres*, Florica Manea*****

* National R&D Institute for Industrial Ecology – ECOIND, PO Box 254 Of.1, P-ta Victoriei Nr.2, Et.2, 300006 Timisoara, Romania, e-mail: monica.ihos@chim.upt.ro
** S.C. Catalysis Timisoara, Str. Stefan Octavian Iosif Nr.24, 300117 Timisoara, Romania, e-mail: catalysis@mail.dnttm.ro
*** "Politehnica" University of Timisoara, Faculty of Industrial Chemistry and Environmental Engineering, P-ta Victoriei Nr.2, 300006 Timisoara, Romania, e-mail: florica.manea@chim.upt.ro

ABSTRACT

This study deals with the characterization of electrochemical properties of doped SnO_2 anodes by cyclic voltammetry (CV) and their use for Reactive Blue 4 azo dye (RB4) degradation. The experiments were carried out by using Ti/RuO_2/SnO_2-Sb_2O_5-RuO_2 anodes (94:3:3 Sn:Sb:Ru molar ratio in precursors solution) prepared by thermal decomposition method. Cyclic voltammograms were recorded at a scan rate of 0.05 V/s and potential range from 0 V to 1.5 V vs. SCE in 0.1 M Na_2SO_4 and 0.1 g/L RB4. The supporting electrolyte was 0.1 M Na_2SO_4. Degradation experiments were carried out in solutions of 0.1 g/L dye in 0.1 M Na_2SO_4, applied current densities of 25, 50 75 and 100 A/m^2 at various electrolysis times and pH values: 6.2; 11 and 3. The cyclic voltammograms showed that the oxidation of dye could occur under conditions of simultaneous O_2 evolution. The best value for the colour removal efficiency was about 99% for an applied current density of 100 A/m^2 and 120 minutes of electrolysis at any pH value.

INTRODUCTION

Wastewater from dyeing and finishing factories is a significant source of environmental pollution. This wastewater is typically characterized by high levels of COD and colour. Furthermore, commercial dyes are resistant to biodegradation [1]. Dyes can be removed from wastewater by methods such as adsorption and advanced oxidation processes [2-5].
Over the recent years, there has been a growing interest for the application of electrochemical processes to the destruction of toxic or non-biodegradable organic pollutants from wastewater. The electrochemical oxidation of the organic pollutants has attracted a great deal of attention mainly because an appropriate choice of anode material can allow the oxidation of organic compounds to carbon dioxide.
Electrochemical oxidation of organic compounds by using SnO_2 anodes have been reported [6,7]. SnO_2 anodes exhibit a high over potential for oxygen evolution therefore they are suitable for organic compounds degradation.
The aim of this paper is the characterization by cyclic voltammetry (CV) of doped SnO_2 anodes and their use in the degradation process of RB4 azo dye.

MATERIALS and METHODS

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/RuO_2/SnO_2-Sb_2O_5-RuO_2 wire with active surface area of 1 cm^2 was used as working electrode and a platinum plate of 1 cm^2 as a counter electrode. Experiments were carried out at 50 mVs^{-1} scan rates at room temperature in solution of 0.1 M Na_2SO_4 (Chimopar Bucureşti) and 0.1 g/L RB4. The supporting electrolyte was 0.1 M Na_2SO_4.

Electrolysis

The anodic oxidation of RB4 was carried out in galvanostatic conditions. Two Ti/RuO_2/SnO_2-Sb_2O_5-RuO_2 anodes and three stainless steel cathodes were used at 1 cm gap. Active surface area was 38 cm^2. Experiments were carried out applying current densities of 25, 50, 75 and 100 A/m^2 at various electrolysis times and values of pH: 6.2, 11 and 3. Experiments were carried out in solutions of 0.1 g/L Reactive Blue 4 prepared in 0.1 M Na_2SO_4 as supporting electrolyte. The dye was used without any previous purification. The solutions were prepared with distilled water and reagent grade Na_2SO_4 (Reactivul Bucureşti).

UV-VIS spectra

A Jasco V-530 spectrophotometer controlled by computer recorded the UV-VIS spectra. The UV-VIS spectrum of RB4 is shown in Fig. 1 and the chemical structure of the dye is represented in Fig. 2. The azo dye exhibits for the pH values of 6.2, 11 and 3 the peaks at the same wavelength: 209, 320 and 593 nm and a shoulder at 238 nm.

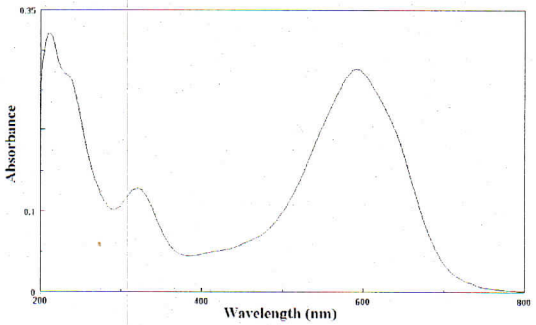

Fig.1. UV-VIS spectra of RB 4

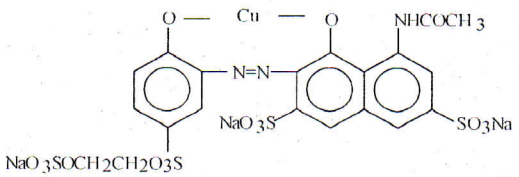

Fig. 2. Chemical structure of RB 4

RESULTS

Electrochemical measurement

CV was used to characterise the electrochemical properties of electrocatalytic film of Ti/RuO_2/SnO_2-Sb_2O_5-RuO_2 electrode. The cyclic voltammograms recorded in 0.1 M Na_2SO_4 in the potential range from 0 V to 1.5 V and pH=6.2 are shown in Fig3. The voltammograms overlaped and this showed the electrode stability under the experimental conditions. For pH=11 and pH=3 the electrode stabilisation began with the second scan (voltammograms are not shown as part of this paper).

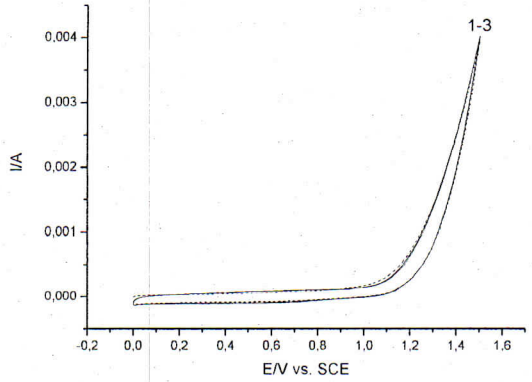

Fig.3. Cyclic voltammograms of $Ti/RuO_2/SnO_2$-Sb_2O_5-RuO_2 in 0.1 M Na_2SO_4; pH=6.2; scan rate 0.05 V/s; potential range: 0 V to 1.5 V vs. SCE; 1- first scan; 2 - second scan; 3-third scan

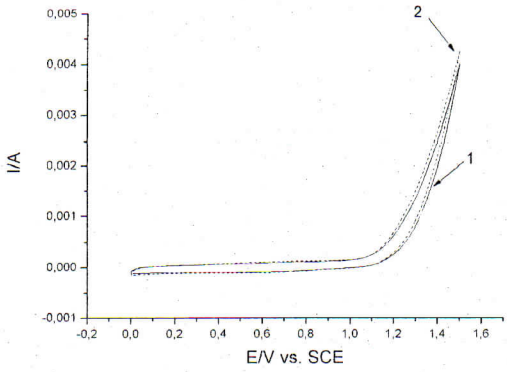

Fig.4. Cyclic voltammograms of $Ti/RuO_2/SnO_2$-Sb_2O_5-RuO_2; scan rate 0.05 V/s; potential range: 0 V to 1.5 V vs. SCE; pH=6.2; 1- 0.1 M Na_2SO_4; 2 - 0.1 g/L RB4 in 0.1 M Na_2SO_4

The electrochemical behaviour of $Ti/RuO_2/SnO_2$-Sb_2O_5-RuO_2 electrode in the presence of RB4 for pH=6.2 is presented in Fig. 4. It can easily be observed that the voltammograms recorded in the presence and absence of RB4 overlapped that suggested the oxidation of the pollutant could occur within O_2 evolution potential range. The electrode exhibited the same electrochemical behaviour for pH=11 and pH=3 (voltammograms are not shown as part of this paper).

Electrolysis and UV-VIS spectra analysis

The anodic oxidation of RB4 on $Ti/RuO_2/SnO_2$-Sb_2O_5-RuO_2 led to the disappearance of peaks assigned to aromatic structures (320 nm peak and 238 nm shoulder) from the UV spectrum of RB4 (Fig. 5). These spectra did not show any further peaks assigned to new compounds that suggested the opening of aromatic rings and the oxidation to carbon dioxide. In agreement with the literature, the anodic oxidation of organic compounds on anodes which exhibits a high overpotential for oxygen evolution leads to carbon dioxide [8]. The shape of the UV spectra of RB4 electrolysed solutions is the same for any working pH.

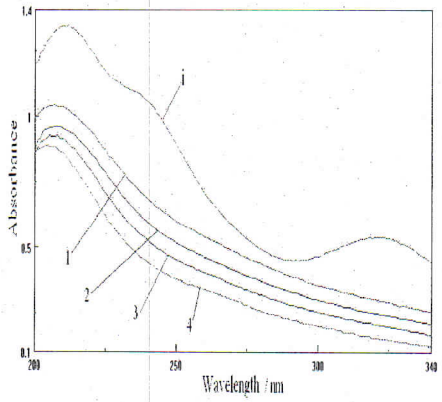

Fig.5. UV spectra of RB 4 electrolysed solutions at various current densities: initial pH=6,2; RB4 concentration – 0.1 g/L ; electrolysis time 120 minutes; i – initial solution; 1 – 25 A/m^2; 2- 50 A/m^2; 3 – 75 A/m^2; 4 – 100 A/m^2

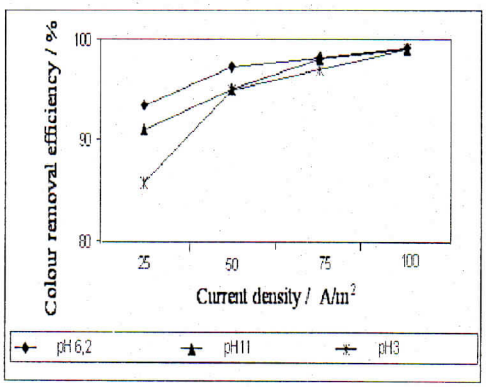

Fig. 6. Colour removal efficiency versus current density at 120 minutes of electrolysis

The colour removal efficiency was calculated from the relative decrease of absorbance at 593 nm, value of wavelength that presents maximum of absorbance of this azo dye in the visible region (Fig. 1). The absorbance of initial solutions, 0.1 g/L RB4 in 0.1 M Na_2SO_4, was not influenced by the pH. Fig. 6 shows the colour removal efficiency at pH values of 6.2; 11 and 3 and different current densities. The best result for the colour removal efficiency was about 99% for an applied current density of 100 A/m^2 for any value of pH.

CONCLUSIONS

This study deals with the characterization of electrochemical properties of doped SnO_2 anodes by CV and their use in the degradation of (RB4). The electrodic composition Ti/RuO_2/SnO_2-Sb_2O_5-RuO_2 was prepared by thermal decomposition method. The molar ratio Sn:Sb:Ru in the precursors solution was 94:3:3.

The cyclic votammograms 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 Na_2SO_4 and 0.1 g/L RB4. The supporting electrolyte was 0.1 M Na_2SO_4. The degradation experiments were carried out in 0.1 g/L RB4 in 0.1 M Na_2SO_4 as supporting electrolyte, applied current densities of 25, 50, 75 and 100 A/m^2, pH values of 6.2; 11 and 3 at various electrolysis time.

The voltammograms recorded in the presence and absence of RB4 suggest that the oxidation of the pollutant at pH values of 6.2; 11 and 3 could occur in the O_2 evolution potential range.

The UV spectra suggested that the anodic oxidation of RB4 on Ti/RuO_2/SnO_2-Sb_2O_5-RuO_2 led to the opening of aromatic rings and the oxidation to carbon dioxide. The shape of the UV spectra of RB4 electrolysed solutions was the same for any working pH.

The best result for the colour removal efficiency was about 99% for an applied current density of 100 A/m^{2}and 120 minutes of electrolysis for any value of pH.

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