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Electrochemical and photoelectrochemical treatment of C.I. Acid Violet 1

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Abstract

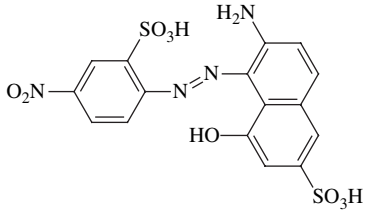
The electrochemical and photoelectrochemical oxidation of C.I. Acid Violet 1 using a titanium electrode coated with a mixture of TiO_2 and RuO_2 was investigated. Cyclic and differential pulse voltammetry was used to determine the kinetics of the process. Oxidation parameters such as current intensity, temperature, anode surface, pH and time were optimized. The combined electrochemical and photochemical oxidation of C.I. Acid Violet 1 increased the effectiveness of dye conversion to 57% based on TOC.

Keywords: C.I. Acid Violet 1; Electrochemical oxidation; Photoelectrochemical oxidation; $Ti/TiO_2/RuO_2$ electrode

1. Introduction

Industrial dye wastewater is usually purified by conventional methods such as biological oxidation [1], adsorption [2] or coagulation by aluminum or iron salts [3]. Although the colour of the wastewater can be satisfactorily eliminated by physico-chemical methods, this type of treatment generates very large amount of sludge. For this reason, recent trends are towards the use of biological treatment which lowers the extent of organic matter; however, these methods do not remove the colour entirely because most dyes are not easily biodegradable [4]. As a potential alternative [5–7] ozonization has been proposed; whilst this method has been found to be very effective in decolorizing textile wastewater, but it is not effective for COD (chemical oxygen demand) decrease. Recent years have seen the use of electrochemical methods for the treatment of industrial effluent [4]. Such processes are clean, operate at low temperatures and usually do not require the application of additional reagents. Commercial electrochemical technology for treating contaminated water was developed in the early 1970s [8,9]. Initially, electrochemical treatment was applied to the chemical reduction and removal of hexavalent chromium; more recently, the electrochemical destruction of organic compounds in textile effluent has been achieved by direct anode oxidation or/and by indirect oxidation through species generated at the anode. For colour removal, whilst many different anodes such as lead, platinum, graphite and lead dioxide can be used [10,11], titanium anodes, coated with metal oxides (titanium or ruthenium), have been found to be very effective [12,13].

This paper concerns about the application of electrochemical techniques for the removal of colour from C.I. Acid Violet 1 wastewater using a titanium electrode coated with a mixture of titanium and ruthenium oxides (70%/30%). RuO_2 shows metallic conductivity and electrocatalytic activity, whereas TiO_2 is photochemically active semiconductor.



C.I. Acid Violet 1

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2. Experimental

C.I. Acid Violet 1 was synthesized by the conventional diazotization of 2-amino-5-nitrobenzenesulfonic acid followed by coupling with 7-amino-1-hydroxy-3-naphthalenesulfonic acid (γ acid) under acidic conditions. The chemical structure of the dye was confirmed by FAB spectrometry (*m/z*: 489.1 $[M-2H+Na]^-$; *m/z*: 512.1 $[M-2H+2Na]^-$). The NaCl content was 25%. The concentration of aqueous C.I. Acid Violet 1 solutions was in the range from 1×10^{-3} to 1×10^{-4} mol L^{-1}. Solutions used for determination of pH effect were prepared by dissolving the dye in appropriate buffers; all the dye solutions were degassed by bubbling with argon using a blanket of argon over the solution.

Cyclic and differential pulse voltammetry [14,15] was employed in the electrochemical experiments using an AUTOLAB potentiostat; a three-electrode cell was used. Platinum or titanium coated with TiO_2/RuO_2 (70%/30%) was used as the anode (obtained from Department of Inorganic Chemistry and Technology of Silesian Technical University). The cathode was a platinum electrode. The potential of the working electrode was measured using a saturated calomel electrode (SCE). Differential capacity was measured using an electrochemical impedance spectroscopy (module FRA AUTOLAB). The electrode potential was changed every 50 mV in the applied potential range. Preparative oxidation of the dye was carried out in an electrochemical cell with undivided electrode compartments under galvanostatic conditions. Photochemical oxidation of the dye was carried out in the same electrochemical cell placed in a photochemical reactor (Rayonett RPR-200) equipped with eight lamps emitting radiation of 254, 300 and 350 nm. Results of oxidation were analyzed by the measurements of the changes of TOC (total organic carbon).

3. Results and discussion

Preliminary information about the electrochemistry of C.I. Acid Violet 1 was obtained from the dependence of the current on the potential. Examples of voltammograms of the dye oxidation and reduction under different conditions are presented in Figs. 1–3.

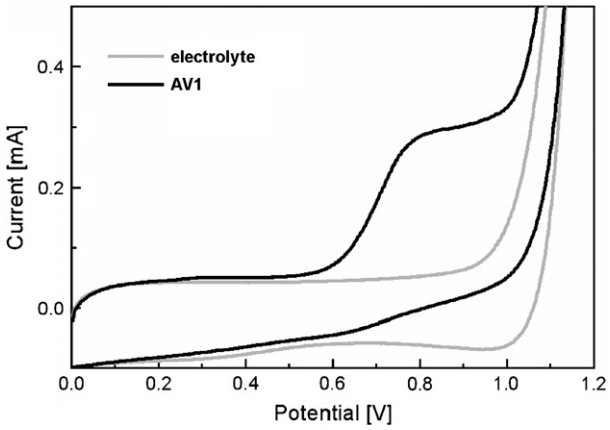

Fig. 2. Voltammogram of C.I. Acid Violet 1 oxidation recorded at titanium electrode coated with TiO_2/RuO_2: $c=1\times10^{-3}$ mol L^{-1} (0.1 mol L^{-1} $NaClO_4$), $v=0.01$ V s^{-1}.

The oxidation of the dye at the platinum electrode proceeds in at least one step before the potential reaches the value at which oxygen evolution begins and is irreversible (Fig. 1). The process commences at 0.6 V vs. SCE. In the reverse scan a current peak of 0.2 V was formed indicating the reduction of the products formed during oxidation. The dye was reduced at the platinum electrode in two irreversible steps before the potential reached a value at which hydrogen evolution began (Fig. 1). The first step of the reduction started at −0.35 V and the second one at −0.65 V.

Fig. 2 represents the oxidation voltammogram of the dye at the titanium electrode coated with TiO_2/RuO_2.

The oxidation proceeds in one step before the potential reaches the value at which oxygen evolution starts; the process began at 0.6 V.

The reduction of the dye at the mercury electrode (Fig. 3) proceeded in two irreversible steps before hydrogen evolution began.

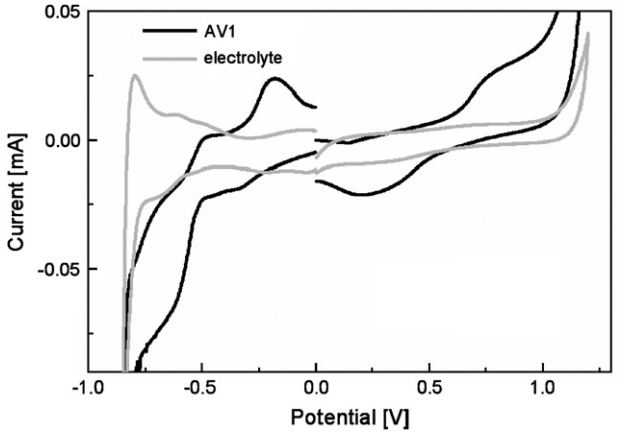

Fig. 1. Voltammograms of C.I. Acid Violet 1 oxidation and reduction recorded at platinum electrode: $c=1\times10^{-3}$ mol L^{-1} (0.1 mol L^{-1} $NaClO_4$), $v=0.01$ V s^{-1}.

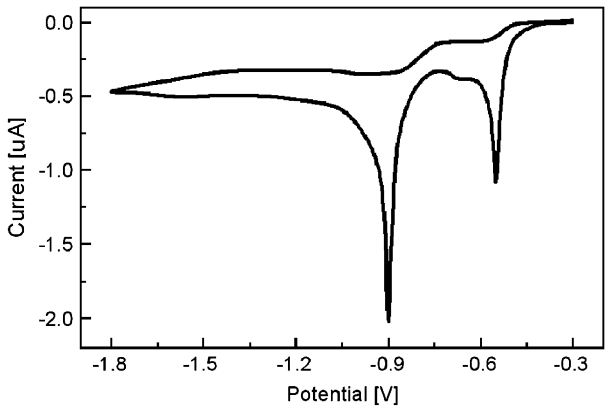

Fig. 3. Voltammogram of C.I. Acid Violet 1 reduction recorded at mercury electrode: $c=1\times10^{-3}$ mol L^{-1} (0.1 mol L^{-1} $NaClO_4$), $v=0.01$ V s^{-1}.

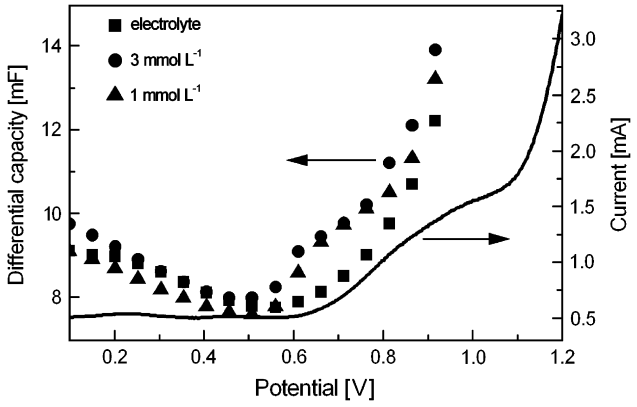

Fig. 4. Differential pulse voltammogram of C.I. Acid Violet 1 oxidation recorded at titanium electrode coated with TiO_2/RuO_2: $c = 1 \times 10^{-3}$ mol L^{-1} (0.1 mol L^{-1} $NaClO_4$), $v = 0.01$ V s^{-1}. Differential capacity dependence on the electrode potential.

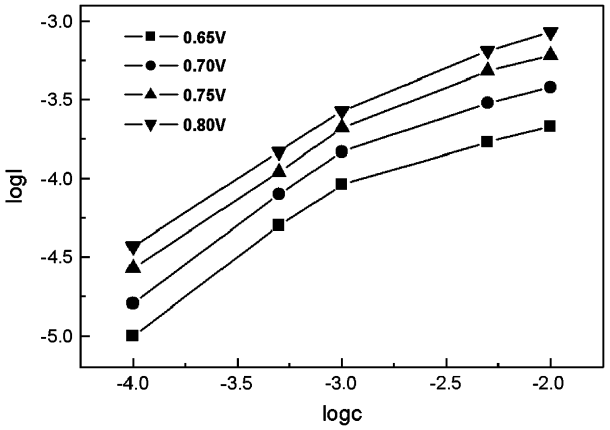

Fig. 6. Dependence of the current logarithm in C.I. Acid Violet 1 oxidation at a constant potential at the titanium electrode coated with TiO_2/RuO_2 on the logarithm of the substrate concentration; $v = 0.01$ V s^{-1}.

The first peak at −0.55 V is assigned to the reduction of NO_2 group, whereas the second one at −0.9 V corresponds to the reduction of the azo group.

Electrochemical impedance spectroscopy (Fig. 4) revealed that C.I. Acid Violet 1 was absorbed at the titanium electrode surface within the range of initial values of polarization potentials (0.0−0.6 V).

While Faradaic reaction started at 0.6 V, a pseudo-capacitive adsorptive−desorptive peak was observed in the curves $C = f(E)$ indicating desorption of the dye from the electrode surface. In addition, within the potential range where peaks of C.I. Acid Violet 1 oxidation are formed, there is a linear dependence of the peak current on the square root of the scan rate (Fig. 5).

The process is controlled by diffusion because the dependence crosses the origin of the coordinates.

As the concentration of dye in the wastewater can vary, its effect on the rate of oxidation is very important. A dependence of the logarithm of the current at the specified potential on the logarithm of the substrate concentration, shown in Fig. 6, presents the order of the reaction. It is evident that there is a change in the curve slope from 0.9 to 0.4 indicating the change in mechanism of the electrode reaction.

For the first step of oxidation the heterogeneous rate constant k_{bh} at titanium electrode coated with TiO_2/RuO_2 determined at a half-wave potential was calculated [15], which is equal to 2.06×10^{-5} cm s^{-1} .

The investigation of the pH effect on C.I. Acid Violet 1 oxidation was also carried out. Cyclic voltammograms of the dye oxidation at different pH values, shown in Fig. 7, clearly indicate that an increase in the pH of the solution causes the reaction to proceed easier.

In order to optimize the effectiveness of electrochemical treatment of C.I. Acid Violet 1 the electrolyses were carried out under different conditions in which parameters such as current intensity (A), temperature (°C), anode surface (cm^2) and time (h) were changed. The results of these experiments are shown in Table 1. The results obtained clearly indicate that current intensity of 0.5 A should be used in further experiments at constant electrode surface of 20 cm^2 which

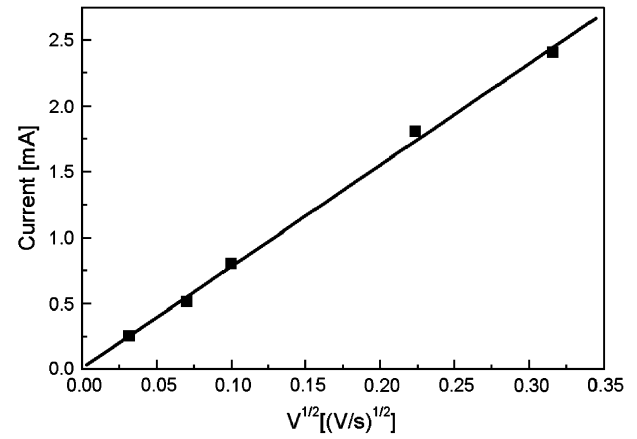

Fig. 5. Dependence of the peak current in C.I. Acid Violet 1 oxidation at titanium electrode coated with TiO_2/RuO_2 on the square root of the scan rate; $c = 1 \times 10^{-3}$ mol L^{-1}.

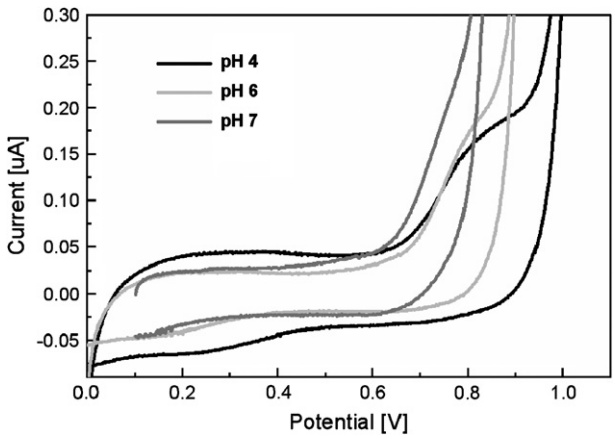

Fig. 7. Cyclic voltammograms of C.I. Acid Violet 1 oxidation at titanium electrode coated with TiO_2/RuO_2 at different pH; $c = 1 \times 10^{-3}$ mol L^{-1} (0.1 mol L^{-1} $NaClO_4$), $v = 0.005$ V s^{-1}.

Table 1
Dependence of C.I. Acid Violet 1 conversion on the electro-oxidation conditions[a]

Current density (A)	Conversion η_{TOC} (%)[b]	Time (h)	Conversion η_{TOC} (%)[b]	Temperature (°C)	Conversion η_{TOC} (%)[b]	Anode surface (cm^2)	Conversion η_{TOC} (%)[b]
0.2	19.0	1	7.3	30	27.5	2	21.3
0.4	23.0	2	19.8	40	29.0	4	32.7
0.5	31.0	3	31.3	50	33.0	20	39.6
0.6	28.0	4	26.1	60	41.0	40	38.5
0.8	34.0	5	26.8	70	40.0	60	39.1

[a] The concentration of C.I. Acid Violet 1 is 1×10^{-3} mol L^{-1}.
[b] Conversion of C.I. Acid Violet 1 is presented as a change in TOC − η_{TOC}.

corresponds to the current density 2.5×10^{-2} A/cm^2 for the specified cell geometry. In addition, it was found that the best substrate conversion (calculated as a change in TOC) was achieved when the electrolyses were carried out within 3 h at 60 °C.

In order to increase the yield of C.I. Acid Violet 1 conversion (based on TOC), a combined electrochemical and photochemical oxidation using optimal parameters for single electrochemical process was conducted. The results are shown in Table 2.

Table 2 shows that a single electrochemical oxidation of C.I. Acid Violet 1 results in 32% conversion, whereas a single UV irradiation causes only slight conversion of 6–10%, depending on the light used. On the other hand, when combined procedure with the use of 254 nm light was applied, the conversion of the dye increased to 57%. Comparing this value with the sum of conversions obtained in single electrochemical and photochemical procedures, it is evident that a synergic effect between both processes exists. However, this is not the case for photoelectrochemical procedures performed with 300 and 350 nm light, which results from a very small absorption of TiO_2 in this region [16].

4. Conclusions

The oxidation of C.I. Acid Violet 1 at titanium electrode coated with TiO_2/RuO_2 mixture proceeds in one step before the potential reach a value at which oxygen evolution begins. The results obtained indicate that optimum conversion of C.I. Acid Violet 1 (as indicated by a change in TOC) was achieved when the electrolyses were carried out with a current intensity of 0.5 A at a constant electrode surface of 20 cm^2 (corresponding to a current density of 2.5×10^{-2} A/cm^2) for 3 h at 60 °C. It is also evident that an increase in the pH of the dye solution enhances the reaction. The results clearly demonstrate that the efficiency of the electrochemical procedure can be significantly improved by simultaneously using a photochemical procedure. The extent of mineralization of C.I. Acid Violet 1 achieved was of the order of 57%, which is a promising alternative for the treatment of acid dye wastewater.

Table 2
Dependence of C.I. Acid Violet 1 conversion on the type of the process[a]

Process type	Conversion η_{TOC} (%)[b]
Electrochemical oxidation	32.0
Photochemical treatment with the use of 254 nm light	8.0
Photochemical treatment with the use of 300 nm light	6.0–8.0
Photochemical treatment with the use of 350 nm light	8.0–10.0
Photoelectrochemical oxidation with the use of 254 nm light	57.3
Photoelectrochemical oxidation with the use of 300 nm light	36.0
Photoelectrochemical oxidation with the use of 350 nm light	34.5

[a] The concentration of C.I. Acid Violet 1 is 1×10^{-4} mol L^{-1}.
[b] Conversion of C.I. Acid Violet 1 is presented as a change in TOC − η_{TOC}.

Acknowledgements

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