Use of Dimensionally Stable Anodes for the Electrochemical Treatment of Textile Wastewaters

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Abstract: This study deals with the treatment of textile wastewaters containing azo dyes by electrochemical oxidation at dimensionally stable anodes (DSA). Two anodic compositions were used: $Ti/Ru_{0.3}Ti_{0.7}O_2$ and $Ti/Ir_{0.3}Ti_{0.7}O_2$. The characteristics of the textile wastewater were: pH=8.3, Cl^-=653 mg/L, and the value of wavelength that corresponded to tha maximum of absorbance of textile wastewater in the visible region, $A_{595\ nm}$ = 1.35 (dil.=1:2.5). Experiments were carried out at applied current densities of 25, 50 and 75 A/m^2 and various electrolysis times: 5, 10, 15, 30 şi 60 minutes. UV-VIS spectra of the electrolysed solutions were recorded and colour removal efficiency was determined. The degradation of dyes by electrochemical oxidation was also assesed by the increase of absorbance at 253 nm (A_{253}). For both anodic compositions, colour removal efficiency was 100%. On the other hand, the formation of chlorinated organic compounds during the electrochemical treatment of textile wastewaters is a disadvantage of this method.

**Keywords:** azo dye, DSA, electrochemical oxidation, textile wastewaters

1. Introduction

The increase of environmental awarness has stimulated the development of new processes for pollutants removal. Electrochemical methods are taken into account in those situations where traditional method do not guarantee the limits concentration allowed by laws or they are more economically convenient. The electrochemical methods are suitable for the pre-treatment of biorefractory organic compounds and abatement of pollutants found at low concentration (when traditional methods are affected by slow kinetics) [1].

Guohua Chen [2] has accomplished an extensive review about the application of electrochemical methods in wastewater treatment. Electrodeposition, electrocoagulation and electrochemical oxidation have been reviewed. The last two methods proved to be effective in removal or degradation of refractory organic compounds, which also include dyes.

The colour fixation efficiency in textile industry could be less than 60%; therefore a significant amount of dyes can be found in wastewaters. The degradation of dyes can successfully be achieved by using electrochemical oxidation at oxide electrodes or metal plated Ti electrodes: $Ti/[(Ru +Pt) O_x]$ [3], Ti/Pt [4], Ti/RuO_2, Ti/Pt şi Ti/Pt/Ir [5], Ti/B – diamond and $Ti/Sb_2O_5 – SnO_2$ [6].

In the presence of chloride, a usual constituent of textile waters, dyes oxidation at DSA occurs to a large extent by generation of active chlorine, although direct electrochemical oxidation might be assumed.

Anodic oxidation of chloride ions to form chlorine molecules occurs according to the following reactions:

$$Cl^- \leftrightarrow Cl_{ads}{}^\bullet + e^- \qquad (1)$$
$$Cl^- + Cl_{ads}{}^\bullet \rightarrow Cl_2 + e^- \qquad (2)$$
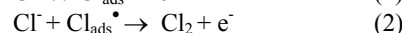
Hypochlorite ions are formed as the product of chlorine hydrolysis in the bulk of the aqueous solution:

$$Cl_2 + H_2O \leftrightarrow HClO + H^+ + Cl^- \qquad (3)$$
$$HClO \leftrightarrow H^+ + ClO^- \qquad (4)$$
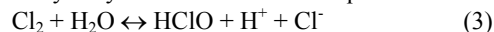
Processes of organic substances oxidation by active chlorine in the presence of a catalyst follow the mechanism of chain reactions, which can be explained by the concomitant existence of atomic oxygen and radicalic organic species [7].

The aim of this paper was the treatment of textile wastewaters by electrochemical oxidation at two DSA compositions ($Ti/Ru_{0.3}Ti_{0.7}O_2$ and $Ti/Ir_{0.3}Ti_{0.7}O_2$).

2. Experimental

2.1. Electrolysis

Azo dyes degradation from textile wastewaters by electrochemical oxidation was carried out in a plexiglass cell at DSA anodes with the following compositions: $Ti/Ru_{0.3}Ti_{0.7}O_2$ and $Ti/Ir_{0.3}Ti_{0.7}O_2$.

Two DSA anodes and three stainless steel cathodes were inserted at 1 cm gap. The active surface area was 38 cm^2. Experiments were carried out by applying current densities of 25, 50 and 75 A/m^2 at various electrolysis times: 5, 10, 15, 30 and 60 minutes. The electrolysis set-up (galvanostatic conditions) as well as the electrodes preparation was similar to that used for [8].

2.2. Textile wastewater

The textile wastewater was sampled from total effluent of a company which uses reactive azo dyes for the dyeing process. The characteristics of the textile wastewater were: pH = 8.3; Cl^- = 653 mg/L; $A_{595\ nm}$ = 1.35 (dil.=1:2.5). $A_{595\ nm}$ is the value of wavelength that corresponded to the maximum of absorbance of textile wastewater in the visible region. (Fig. 1).

2.3. UV-VIS spectra

The UV-VIS spectra were recorded by a Jasco V-530 spectrophotometer controlled by computer. The UV-VIS spectra recorded for the textile wastewater are shown in Fig. 1 and 2 .
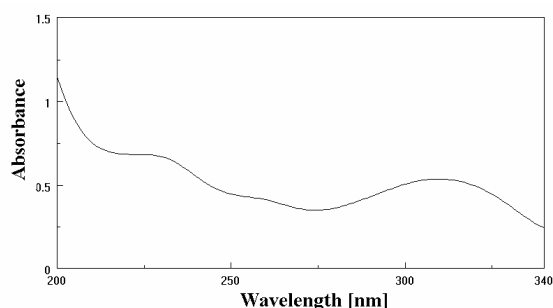

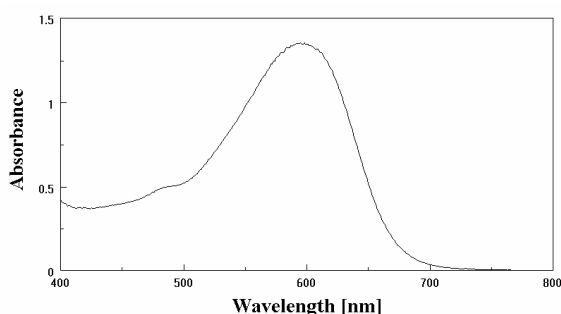**Figure 1.** UV spectrum of the textile wastewater

Figure 2. Visible spectrum of textile wastewater

3. Results and discussion

3.1. Colour removal efficiency

The colour removal efficiency was calculated from the relative decrease of absorbance at 595 nm peaks. The colour removal efficiency and cell operating conditions for the two anodic compositions are shown in Table 1 and 2.

For both anodic composition ($Ti/Ru_{0.3}Ti_{0.7}O_2$ and $Ti/Ir_{0.3}Ti_{0.7}O_2$), the colour removal efficiency was practically 100% and it was achieved after 10-30 minutes of electrolysis, as the applied current density was varied. The dark blue colour of the textile wastewater changed during electrolysis going by light blue – mauve – dark yellow – light yellow.

TABLE 1. Working conditions, absorbance and colour removal efficiency at $Ti/Ru_{0.3}Ti_{0.7}O_2$ anode

Current density (A/m^2)	Time (min)	Cell voltage (V)	A_{595}	Colour removal efficiency/ %
25	5	3.1	2.15	36.64
	10	3.1	0.83	75.46
	15	3.1	0.07	97.70
	30	3.1	< 0.002	100
50	5	3.7	0.34	89.72
	10	3.7	0.02	99.54
	15	3.7	0.01	99.69
	30	3.7	<0.002	100
75	5	4.5	0.02	99.27
	10	4.5	< 0.002	100

* 0.002 represents the background noise

TABLE 2. Working conditions, absorbance and colour removal efficiency at $Ti/Ir_{0.3}Ti_{0.7}O_2$

Current density (A/m^2)	Time (min)	Cell voltage (V)	A_{595}	Colour removal efficiency/ %
25	5	3.2	0.99	70.73
	10	3.2	0.12	96.48
	15	3.2	0.04	98.73
	30	3.2	<0.002	100
50	5	3.8	0.02	99.35
	10	3.8	<0.002	100
75	5	4.6	0.01	99.49
	10	4.6	<0.002	100

* 0.002 represents the background noise

These anodic compositions tested in textile wastewatwers treatment were effective for the colour removal process, but at $Ti/Ir_{0.3}Ti_{0.7}O_2$ the process occurred faster than at $Ti/Ru_{0.3}Ti_{0.7}O_2$. Thus, for an applied current density of 25 A/m^2 and 5 minute of electrolysis the colour removal efficiency was 36.64% at $Ti/Ru_{0.3}Ti_{0.7}O_2$, and 70.73 % at $Ti/Ir_{0.3}Ti_{0.7}O_2$. For the same compositions, an applied current density of 50 A/m^2 determined colour removal efficiency of 100% after 30 and 10 minutes of electrolysis, respectively.

3.2 UV spectra analysis

Fig. 3 - 8 show UV absorption spectra for the electrolysed textile wastewater under the operating conditions mentioned in section 2.1.

The dyes degradation during the electrolysis was also evaluated by the decrease of A_{253}, which is characteristic to the aromatics/olefinic carbon [9].

The UV spectrum of textile wastewater had two peaks at 230 nm and 310 nm (Fig. 2). For the anodic composition $Ti/Ru_{0.3}Ti_{0.7}O_2$ and 25 A/m^2 the UV spectra showed that the absorbance at 230 nm and 310 nm decreased gradually.
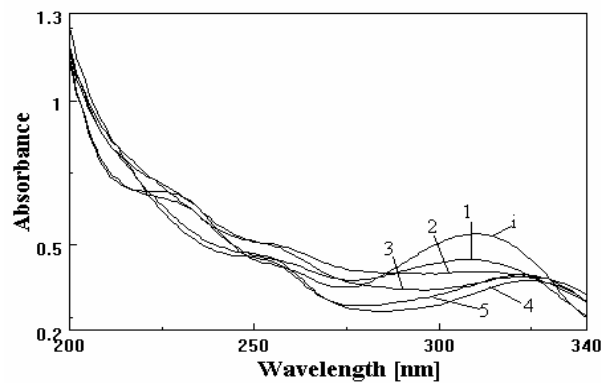
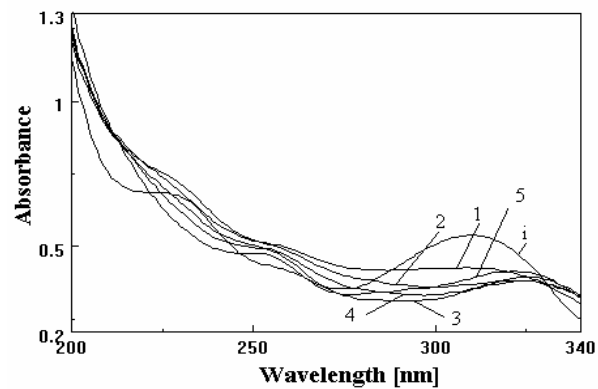**Figure 3.** UV spectrum of textile wastewater (dil. 1:5) after electrolysis in the following conditions: anodic composition $Ti/Ru_{0.3}Ti_{0.7}O_2$; applied current density 25 A/m²; electrolysis time: i - 0 min; 1 – 5 min; 2 – 10 min; 3 – 15 min; 4 – 30 min; 5 – 60 min
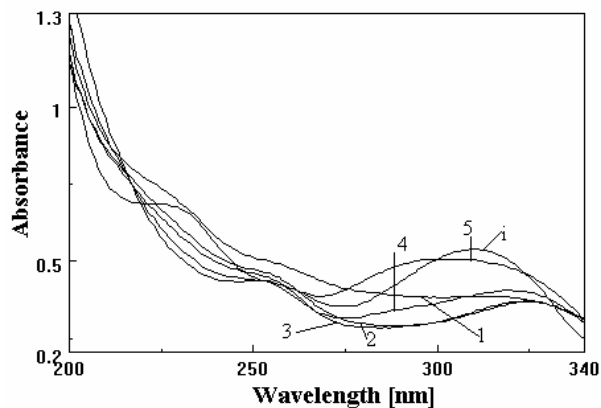

Figure 6. UV spectrum of textile wastewater (dil. 1:5) after electrolysis in the following conditions: anodic composition $Ti/Ir_{0.3}Ti_{0.7}O_2$; applied current density 25 A/m²; electrolysis time: i - 0 min; 1 – 5 min; 2 – 10 min; 3 – 15 min; 4 – 30 min; 5 – 60 min

Figure 4. UV spectrum of textile wastewater (dil. 1:5) after electrolysis in the following conditions: anodic composition $Ti/Ru_{0.3}Ti_{0.7}O_2$; applied current density 50 A/m²; electrolysis time: i - 0 min; 1 – 5 min; 2 – 10 min; 3 – 15 min; 4 – 30 min; 5 – 60 min

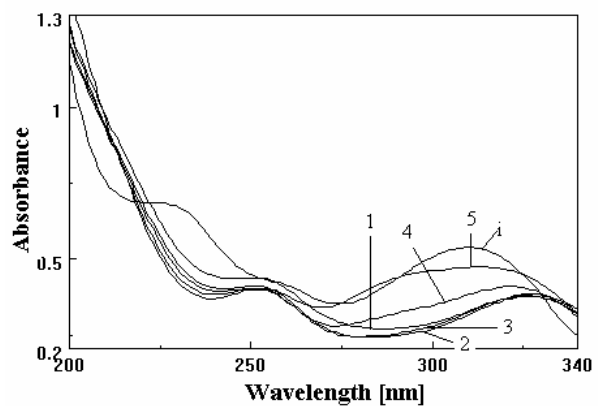**Figure 7.** UV spectrum of textile wastewater (dilution 1:5) after electrolysis in the following conditions: anodic composition $Ti/Ir_{0.3}Ti_{0.7}O_2$; applied current density 50 A/m²; electrolysis time: i - 0 min; 1 – 5 min; 2 – 10 min; 3 – 15 min; 4 – 30 min; 5 – 60 min
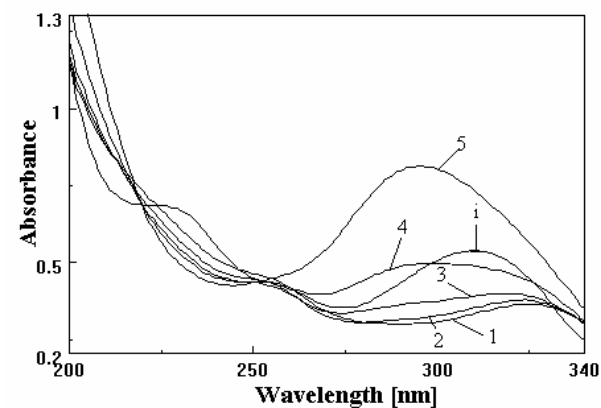

Figure 5. UV spectrum of textile wastewater (dil. 1:5) after electrolysis in the following conditions: anodic composition $Ti/Ru_{0.3}Ti_{0.7}O_2$; applied current density 75 A/m²; electrolysis time: i - 0 min; 1 – 5 min; 2 – 10 min; 3 – 15 min; 4 – 30 min; 5 – 60 min
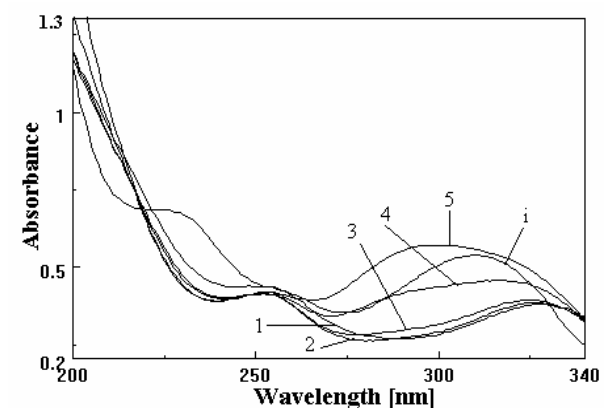

Figure 8. UV spectrum of textile wastewater (dil. 1:5) after electrolysis in the following conditions: anodic composition $Ti/Ir_{0.3}Ti_{0.7}O_2$; applied current density 75 A/m²; electrolysis time: i - 0 min; 1 – 5 min; 2 – 10 min; 3 – 15 min; 4 – 30 min; 5 – 60 min

By increasing the electrolysis time, these peaks disappeared and other two peaks were present at wavelength of 253 nm and 327 nm corresponding to other degradation products after electrolysis. The wavelength range of 240 nm – 265 nm is characteristic to the absorption of the chlorinated aromatic compounds [9].

The degradation process continued when the applied current density increased. Thus, for an applied current density of 75 A/m^2 and 60 minutes of electrolysis a new peak appeared at 295 nm. According to other studies [5], the GC – MS analyses has shown that most of degradation products have been especially chlorinated organic compounds.

The previous findings were also valid in the case of Ti/Ir$_{0.3}$Ti$_{0.7}$O$_2$. However, for an applied current density of 25 A/m^2 the peaks at 253 nm and 327 nm occured after shorter electrolysis time.

The complete decolourisation was accomplished in 10-30 minutes for both anodic compositions, as a function of the applied current density. The same fast decrease of the intensity absorption at 253 nm was not noticed. To destroy the aromatic/olefinic carbon (the characteristic band A$_{253}$ vanished), 60 minutes of electrolysis and an applied current density of 75 A/m^2 were necessary for Ti/Ru$_{0.3}$Ti$_{0.7}$O$_2$, while for Ti/Ir$_{0.3}$Ti$_{0.7}$O$_2$ longer electrolysis time were required.

4. Conclusions

Two DSA compositions: Ti/Ru$_{0.3}$Ti$_{0.7}$O$_2$ and Ti/Ir$_{0.3}$Ti$_{0.7}$O$_2$ were used for the electrochemical treatment of textile wastewater. The chloride concentration in the textile wastewater was Cl$^-$ = 653 mg/L and the value of wavelength that showed maximum of absorbance was A$_{595\ nm}$ = 1.35 (dil.=1:2.5). In the presence of chloride ions dyes oxidation at DSA occured to a large extent by generation of active chlorine, although direct electrochemical oxidation might also takes place in this process.

For both anodic compositions colour removal efficiency were 100%. The cleavage of the chromophore N=N bond occurred faster at Ti/Ir$_{0.3}$Ti$_{0.7}$O$_2$ for the same applied curent density; the colour removal efficiency of 100% was achieved after 30 minutes of electrolysis at Ti/Ru$_{0.3}$Ti$_{0.7}$O$_2$ and after 10 minutes at Ti/Ir$_{0.3}$Ti$_{0.7}$O$_2$.

The UV-VIS spectra showed the same degradation mechanism for the azo dyes within textile wastewater at both anodic compositions. To destroy the aromatic/olefinic carbon (the characteristic band A$_{253}$ vanished) a shorter time of electrolysis was needed at Ti/Ru$_{0.3}$Ti$_{0.7}$O$_2$.

During the electrochemical treatment of texile wastewater chlorinated organic compounds were formed, which is a disavantage of this process.

Acknowledgments

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