View metadata, citation and similar papers at core.ac.uk
brought to you by CORE
provided by Central Repository of the Institute of Chemistry, Technology and Metallurgy (CER)

*Int. J. Electrochem. Sci.*, 8 **(2013)** 168 - 183

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

# Study of the Electrochemical Oxidation of Reactive Textile Dyes Using Platinum Electrode

*Milica Jović, Dalibor Stanković, Dragan Manojlović, Ivan Anđelković, Anđelija Milić, Biljana Dojčinović[1], Goran Roglić[*]*

Faculty of Chemistry, University of Belgrade, Student Square 12-16, 11158 Belgrade, Serbia
[1]Institute of Chemistry, Technology and Metallurgy, Center of Chemistry, University of Belgrade, Njegoševa 12, 11000 Belgrade, Serbia
[*]E-mail: groglic@chem.bg.ac.rs

*Received:* 6 November 2012 / *Accepted:* 30 November 2012 / *Published:* 1 January 2013

Textile industries are widespread in developing countries. Among the various processes in the textile industry, the dyeing process uses large volumes of water for dyeing, fixing and washing. Textile industry wastewater is characterized by intensive color and high chemical oxygen demand (COD) concentrations that discarding of these toxic wastewaters to the environment will cause a major problem. In this study electrochemical oxidation of reactive textile dyes: Reactive Blue 52, Reactive Black 5, Reactive Green 15, and Reactive Yellow 125, using platinum anode was examined. Electrolysis is carried out in electrochemical cell containing membrane which is standard membrane in industry. Membrane separated anodic and cathodic area. Supporting electrolyte was 0.1M sodium sulfate which is also present in real textile effluents. Applied voltage of 6, 12 and 24V, and influence of membrane on electrolysis were examined on model dye (Reactive Blue 52). Highest degradation degree for model dye was achieved at 12V, so electrolysis of other dyes was done on this voltage. COD value of all dyes dropped after 60 minutes of electrolysis below a measurable level (<30mg/L $O_2$), except Reactive Black 5 whose COD reduction was 57.95% with membrane and 35.28% without membrane applied. Complete decolorization was achieved after 10 to 60 minutes for all dyes. Degradation products of model dye Reactive Blue 52 were monitored with HPLC, and influence of pH on decolorization was also examined on model dye.

**Keywords:** Electrochemical Oxidation, Reactive Blue 52, Reactive Black 5, Reactive Green 15, Reactive Yellow 125, Platinum electrode

## 1. INTRODUCTION

Textile industry is rated as one of the most polluting sector among the different human activities. [1] Approximately, one million tons of dyes are produce every year all around the world.

The majority (about 70% by weight) are azo dyes. [2] Up to 50% of the dyes are lost after the dyeing process and disposed out in the effluents. [3] The presence of unfixed dyes is perceived as one of the major environmental problems of textile wastewater and therefore they need to be removed from the wastewater before it is discharged to the environment. [4] Color is usually the first contaminant to be recognized in effluents. Very small amount of dyes in water (10 – 20 mg/1) is highly visible and affects water transparency and gas solubility of lakes, rivers and other water bodies. [5,6] Dyes contained in textile effluents retain their color and structural integrity under diverse weather conditions due to their design to persist under oxidizing and reducing conditions, washing and light exposure. [1]

Reactive dyes are one of the most significant technological innovations of the 20th century in the dyes field. [7] They are generally water soluble and used for dyeing cellulosic fibers, such as cotton and rayon, but are also used for silk, wool, nylon, and leather. [4] Reactive azo dyes have one or more azo groups (R1–N=N–R2) and aromatic rings mostly substituted by sulfonate groups. Their complex structure is responsible for their intensive color, high water solubility; resist fading on exposure to sweat, soap, water, light. [8] The most important property of reactive dyes is that they form a covalent bond with hydroxyl or amino groups present on the fiber. [9] However, the fixation reaction of dyes is hindered by competitive reaction consisting on the dye hydrolysis. Because of this they are one of the major responsible of colored rivers. [7] They are considered as recalcitrant xenobiotic compounds. [10]

Several techniques have been used for the removal of dyes from wastewaters. Wastewaters are usually treated by physical or chemical processes (i.e. adsorption, chemical transformation, incineration, electrocoagulation, photocatalysis or ozonation) and biological or enzymatic treatment. They are effective but rather costly. [11,12]

Over the past 10 years, the electrochemical techniques have been found of special interest for wastewater remediation. [7] Electrochemical techniques used for dye removal can be classified as electrocoagulation, electrochemical reduction, electrochemical oxidation, indirect electro-oxidation with strong oxidants (electro-oxidation with active chlorine, electro-Fenton), and photo-assisted electrochemical methods (photoelectro-Fenton, photoelectrocatalysis). [13] These techniques are compatible with the environment because the main reagent, the electron, is a clean one. [14] They have advantages such as simple equipment, easy operation, lower operating temperature, etc. [4] It is interesting to notice the high yields of removal of polluting substances with maximum energy resource management. [7] The electric current induces redox reactions upon the electrodes surface resulting in the transformation and destruction of the organic compound, and almost complete oxidation to $CO_2$ and $H_2O$. [10]

Electrochemical oxidation (EO) of dyes can be done in electrochemical cell by:

(1) Direct anodic oxidation (direct electron transfer to the anode), which yields very poor decontamination,

(2) Chemical reaction with electrogenerated species from water discharge at the anode, such as physically adsorbed ‘‘active oxygen’’ (physisorbed hydroxyl radical (*OH)) or chemisorbed ‘‘active oxygen’’ (oxygen in the lattice of a metal oxide (MO) anode). (Brillas et al., 2003) *OH radical is the second strongest oxidant known after fluorine, with a high standard potential ($E_0$ = 2.80 V vs. SHE).

The existence of oxidation with different electrogenerated species formed from water discharge has allowed the proposal of two main approaches for the wastewaters treatment by EO:

(i) The electrochemical conversion method, with chemisorbed ‘‘active oxygen’’ in which refractory organics are selectively transformed into biodegradable compounds, usually carboxylic acids,

(ii) The electrochemical combustion (or electrochemical incineration) method, with physisorbed *OH where organics are completely oxidized to $CO_2$ and inorganic ions. [15]

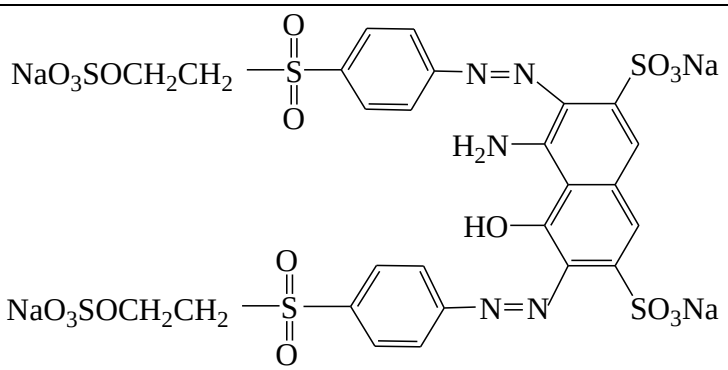
Due to the electrogeneration of hydroxyl radical as mediated oxidant, electrochemical oxidation is considered as EAOP (**E**lectrochemical **A**dvanced **O**xidation **P**rocesses).

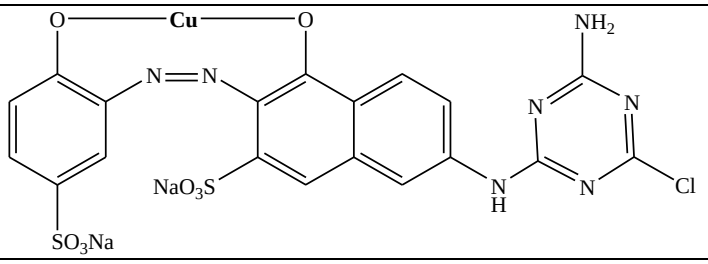
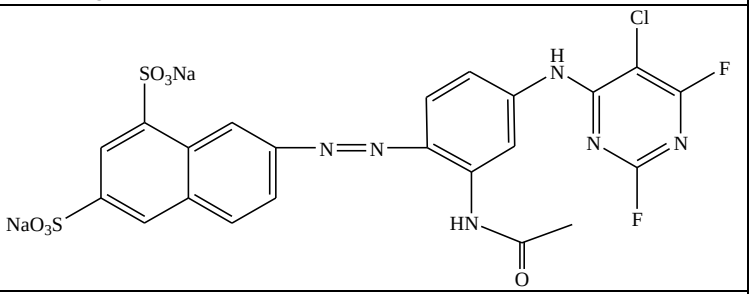
With the aim to solve two major problems that occur in textile wastewater, intense color and high COD values, electrochemical oxidation is used for decolorization and degradation of dyes. In this study electrochemical oxidation of reactive dyes: Reactive Black 5 (commercial name *Drimaren* Black *K-3B)*, Reactive Blue 52 (commercial name Drimaren Blue X-3LR), Reactive Yellow 125 (commercial name Drimarene Gold Yellow K-2R) and Reactive Green 15 (commercial name Drimarene Green X 2BL) were done in the presence of sodium sulfate. Sodium sulfate is already present in actual effluents from textile industry at considerable concentration. It cause easy sorption of dye by neutralization of electronegative potential of fiber, and reduces the repulsion between dye and fibers. [16] Fisher platinum electrodes were employed as anode and cathode. Applied voltage during electrolysis of 6, 12, and 24 V, with and without membrane and influence of pH on decolorization was examined for model dye (Reactive Blue 52, 200mg/L). Highest degradation degree was achieved at 12 V for model dye, so electrolysis of other dyes was done on this voltage. Decolorization was monitored spectrofotometrically and electrochemical degradation was monitored with cyclic voltammetry, by COD values and LC.

## 2. EXPERIMENTAL PART

### *2.1. Chemicals and material*

**Table 1**. Chemical structure and characteristics of dyes

| **C.I. (*Color Index*)**<br>**Commercial Name**<br>**CAS registration number**<br>**$\lambda_{max}$** | **Chemical Structure** |
|---|---|
| **C.I. Reactive Black 5**<br>***Drimaren* Black *K-3B***<br>CAS No.: 17095-24-8<br>$\lambda_{max}$ = 590 nm |  |

| | |
|---|---|
| **C.I. Reactive Blue 52**<br>**Drimaren Blue X-3LR**<br>CAS No.: 12225-63-7<br>$\lambda_{max}$ = 615 nm |  |
| **C.I. Reactive Yellow 125**<br>**Drimarene Gold Yellow K-2R**<br>CAS No.: 68155-62-4<br>$\lambda_{max}$ = 390 nm |  |
| **C.I. Reactive Green 15**<br>**Drimarene Green X 2BL**<br>CAS No.: 61969-07-1<br>$\lambda_{max}$ = 620 nm | |

Four commercial reactive azo dyes Reactive Blue 52, Reactive Black 5, Reactive Yellow 125 and Reactive Green 15 (*technical grade*, Clariant, Switzerland) were used without any further purification. The molecular structures of used dyes are shown in Table 1. Sodium sulfate (Merck, p.a.) was used as supporting electrolyte, tetrabutylammonium hydrogensulfate (97%, Sigma Aldrich) and acetonitrile (*HPLC grade*, Sigma Aldrich) were used as mobile phases, methanol (Sigma Aldrich, p.a.) and ammonia (Sigma Aldrich, p.a.) were used for SPE. All solutions were prepared using deionized water with conductivity between 1.0 and 1.5 μS/cm, except solutions for HPLC which were prepared with *HPLC grade* water (Sigma Aldrich).

*2.2 Methods*

All electrochemical measurements were carried out using electrochemical workstation METROHM 797 (VA Computrace). The three electrode system consisted of Hanging Mercury Drop Electrode (HMDE) as working electrode, Ag/AgCl (3MKCl) as a reference electrode, and platinum wire as counter electrode. Supporting electrolyte was $Na_2SO_4$ which is already present in dye effluents from textile industry.

Dye concentration selected for electrolytic experiments was 200 mg/L. This value is included in the range of real dye concentration found in textile effluents. [7] Electrochemical oxidation of dye solution was carried out in electrochemical cell. Anode and cathode were Fisher platinum electrodes. The volume of solution to be treated was 400 mL and the effective electrode area was 25 $cm^2$. The homogeneous nature of the medium during the electrolyses was maintained using magnetic stirring. Applied voltage during electrolysis of 6, 12 and 24V was examined. All the experiments were carried out under galvanostatic conditions with power supply for 6, 12 and 24V (Battery Charger ACCU-

LADDER CBC6). High voltages are applied to the electrochemical cell for the simultaneous oxidation of dye and water, thus maintaining the anode activity. [17] The convenient separation between anode and cathode compartments was achieved with membrane Flemion 0820, AGC Chemicals, Japan.

UVVisible Cintra 6 spectrometer (GBC Scientific Equipment Pty Ltd., Australia) was employed to measure the optical density of dyes solutions before and at different time intervals during electrolysis. The decolorization efficiency was calculated using the relation:

$$\% \text{ decolorization} = (A_0 - A) / A_0 \times 100$$

where $A_0$ is the absorbance of initial dye solution at the maximum absorption wavelength ($\lambda_{max}$) and A is the absorbance at the maximum absorption wavelength of dye solution after the electrochemical oxidation.

Before HPLC analysis samples were concentrated with SPE cartridges from Phenomenex (Strata-X, 33u, 30mg/1ml). The cartridges were conditioned with methanol, equilibrated with distilled water, 1ml of dye samples added and eluted with methanol (with drop of ammonia).

The HPLC analysis was performed using Dionex UltiMate 3000 chromatograph with photodiode array detection (DAD). The chromatograph was fitted with a Hypersil Gold C8 (150mm x 3mm, 3µm) column. Tetrabutylammonium hydrogensulfate (6mM) as component A and acetonitrile as component B were mobile phases. The compounds were eluted at flow rate of 1ml/min, and column was set at $40^0$C. Injection volume was 20µl. Detector was set at 615, 390, 300 and 254 nm.

| | |
|---|---|
| Gradient elution: | 10-50% B in 10min |
| | 50-90% B in 3min |
| | 90-10% B in 13min |

## 3. RESULTS AND DISCUSSION

The structures of reactive dyes are shown in Table 1. Dyes beside azo groups contain sulfonate groups, which increase the water solubility; hydroxyl and amide group, which are responsible for the relative stability of azo groups.

Electrochemical methods use electrons as the main reagent, but may also require the presence of supporting electrolytes. It increases the conductivity of the solution and reduces the electrolysis time. We chose $Na_2SO_4$ as supporting electrolyte because of its presence in wastewaters and because it is an inert electrolyte which does not produce any reactive species during the electrolysis, except under special conditions where it may generate persulfate. [7] NaCl was not used because of suggested formation of toxic organochlorinated by-products persistent to further oxidation. [18]

Our anode was Pt which is so-called “active” anode. [19] The initial reaction corresponds to the oxidation of water molecules leading to the formation of physisorbed hydroxyl radical (M (*OH)):

$$M + H_2O \rightarrow M\,(^*OH) + H^+ + e^-, (1)$$

where M is the electrode.

So-called higher oxide or superoxide (MO) may be formed if higher oxidation states are available for a metal oxide anode, above the standard potential for oxygen evolution ($E_0$ = 1.23 V vs. SHE).

$$M\,(^*OH) \rightarrow MO + H^+ + e^- (2)$$

The redox couple MO/M acts as a mediator in the oxidation of organics (3). It competes with the side reaction of oxygen evolution via chemical decomposition of the higher oxide species (4).

$$MO + R \rightarrow M + RO (3)$$

$$MO \rightarrow M + ½\, O_2 (4)$$

A weaker oxidant like ozone also can be generated from water discharge at the anode ($E_0$ = -1.51 V vs. SHE) [20]:

$$3H_2O \rightarrow O_3 + 6H^+ + 6e^- (5)$$

Reaction of direct oxidation of M (*OH) to $O_2$ (6) competes with reaction of its dimerization to hydrogen peroxide by reaction (7):

$$M\,(^*OH) \rightarrow M + ½\, O_2 + H^+ + e^- (6)$$

$$2\,M\,(^*OH) \rightarrow 2M + H_2O_2 (7)$$

This means that in electrooxidation reactive oxygen species such as *OH radicals, $H_2O_2$ and $O_3$ are generated, although physisorbed *OH is the strongest oxidant of pollutants. [20]

### *3.1 COD study*

COD was measured by standard accredited method (ISO 6060). We tested different voltages of 6, 12 and 24V with and without membrane, on model compound, which was Reactive Blue 52 (200 mg/L). COD values were measured at different time intervals during electrolysis.

**Table 2**. COD values for Reactive Blue 52

| COD values (mg/L $O_2$) | | | | | | |
|---|---|---|---|---|---|---|
| | with membrane | | | without membrane | | |
| | 6V | 12V | 24V | 6V | 12V | 24V |
| start | 139.7 | 138.5 | 140.52 | 137.68 | 141.54 | 136.78 |
| 10min | 128.24 | 72.25 | 106.63 | 121.69 | 91.55 | 105.65 |
| 20min | 111.78 | <30 | 71.39 | 120.34 | 65.26 | 79.32 |
| 30min | 105.46 | <30 | <30 | 115.65 | <30 | 55.64 |
| 60min | 72.93 | <30 | <30 | 84.58 | <30 | <30 |

From Table 2 can be seen the greatest decrease of COD value, which was on voltage of 12V. When compared, COD values on 12V with and without membrane, higher degradation degree was achieved with membrane. COD value for Reactive Blue 52 had fallen below 30 mg/L $O_2$ after just 20 minutes of electrolysis with membrane.

Based on these results for model dye we concluded that the best conditions of anodic oxidation and highest degradation degree were achieved at voltage of 12V. Electrolysis of other dye solutions was done at this voltage.

**Table 3**. COD values for Reactive Black 5

| COD values (mg/L $O_2$) | | |
|---|---|---|
| | with membrane | without membrane |
| | 12V | 12V |
| start | 107.52 | 109.65 |
| 10min | 92.52 | 100.52 |
| 20min | 69.63 | 91.61 |
| 30min | 57.64 | 84.47 |
| 60min | 45.21 | 70.96 |

**Table 4**. COD values for Reactive Green 15

| COD values (mg/L $O_2$) | | |
|---|---|---|
| | with membrane | without membrane |
| | 12V | 12V |
| start | 72.43 | 70.63 |
| 10min | 60.48 | 63.88 |
| 20min | 46.21 | 45.62 |
| 30min | <30 | 37 |
| 60min | <30 | <30 |

As for Reactive Black 5, electrolysis with membrane also gave greater degradation degree (Table 3). COD reduction of 57.95% was achieved after 60 minutes of electrolysis with membrane, and 35.28% without membrane.

After 30 minutes of electrolysis on 12V with membrane, COD value of Reactive Green 15 fell below 30 mg/L $O_2$ (Table 4). Without membrane this value was reached after 60 minutes of electrolysis.

**Table 5**. COD values for Reactive Yellow 125

| COD values (mg/L $O_2$) | | |
|---|---|---|
| | with membrane | without membrane |
| | 12V | 12V |
| start | 49.28 | 51.64 |
| 10min | 42.56 | 46.95 |
| 20min | 34.51 | 37.15 |
| 30min | <30 | <30 |
| 60min | <30 | <30 |

For Reactive Yellow 125 COD value fell below 30 mg/L $O_2$ after 30 minutes of electrolysis on 12V with and without membrane (Table 5).

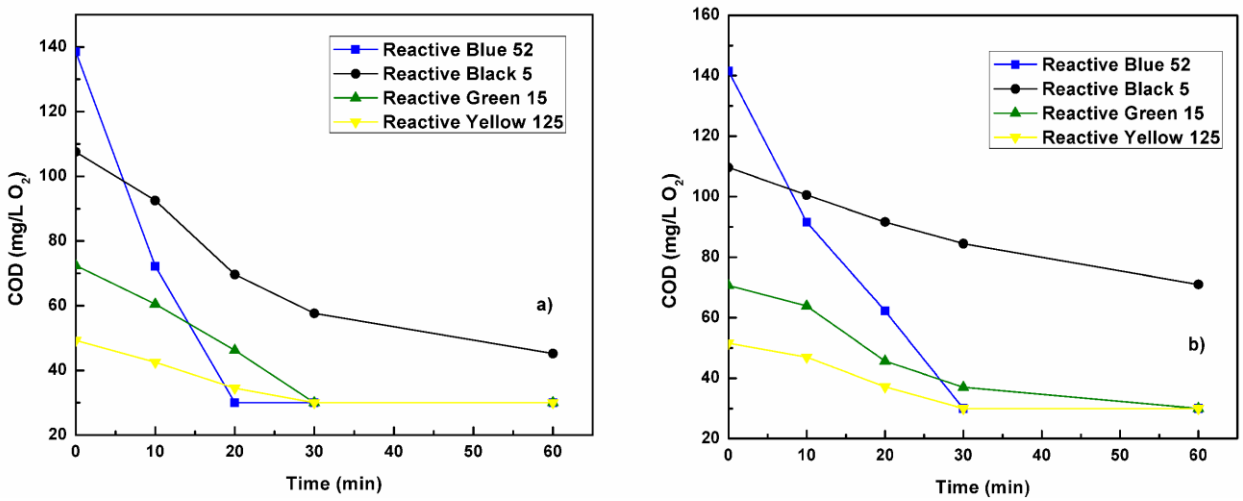



**Figure 1**. The decrease in COD values with time of electrolysis: a) with membrane, b) without membrane

Based on Figure 1 it is clear that higher degradation degree was achieved in shorter time using Flemion membrane.

*3.2 Electric energy consumption*

Electrochemical treatment is undoubtedly an energy-intense process and its efficiency is usually assessed in terms of energy consumption. The electrical power P of the cell can be derived from cell current and voltage:

$$P(W) = I(A) * V(V)$$

where P is power (in W), I is current (in A), V is voltage (in V)

The amount of energy used depends on the power and the time for which it is used:

$$E = P * t$$

where E is electrical energy (in kWh) P is power (in kW) and t is time of electrolysis (in hours).

This value is then divided by the volume of the treated solution (400ml) to get consumption per $m^3$ ($kWh/m^3$).

Energy consumption for different dyes are given in Table 6 below:

**Table 6**. The electric energy consumed during degradation of 200 ppm (w/v) of dyes solutions (native pH):

| | | I (A) | Electrolysis time (min) | Energy consumption ($kWh/m^3$) |
|---|---|---|---|---|
| Reactive Blue 52 | with membrane | 1,6 | 60 | 0.048 |
| | without membrane | 1,8 | 60 | 0.054 |
| Reactive Black 5 | with membrane | 1,6 | 60 | 0.048 |
| | without membrane | 1,8 | 60 | 0.054 |
| Reactive Green 15 | with membrane | 2,4 | 60 | 0.072 |
| | without membrane | 2,4 | 60 | 0.072 |
| Reactive Yellow 125 | with membrane | 2,9 | 60 | 0.087 |
| | without membrane | 3,0 | 60 | 0.090 |

From Table 6 can be seen that lower energy consumption were with membrane. With this energy consumptions we reach almost complete degradation of dyes (COD<30mg/L) after 60 minutes of electrolysis. Using the current average electrical energy price in Serbia of €0.1kWh the cost of energy consumed per $m^3$ of treated water is €0.0048 - €0.009 depending on dye. [27]

*3.3 Cyclic voltammetry*

The extent of dye degradation was monitored with cyclic voltammetry before and after electrolysis. At Figure 2 can be seen signals from initial Reactive Blue 52 (200 mg/L with 0.1M $Na_2SO_4$ and signal after electrochemical degradation (60 minutes of electrolysis on 12V with membrane). Cyclic voltammograms were recorded on METROHM 797 (VA Computrace). The three electrode system consisted of Hanging Mercury Drop Electrode (HMDE) as working electrode, Ag/AgCl (3M KCl) as a reference electrode, and platinum wire as counter electrode. The potential range was selected from -1.7 to +0.0 V. The voltammetric curve shows one anodic peak at -0.94 V ($I_a$) in forward scan, and four cathodic peaks at -1.16 V ($I_c$), -0.68 V ($II_c$), -1.02 V ($III_c$) and at -1.25 V ($IV_c$) in the reverse scan, indicated quasi-reversible electrochemical process. ($I_a/I_c \neq 1$). The redox behavior of copper present in dye appeared as peak I. Similar results Rio et all [7] got for PMX2R dye.

The cathodic and anodic peak currents observed were found to be reduced with electrolysis. From cyclic voltammogram it can be clearly observed that the electrochemical degradation of the dye has been completed. These decrease in peak currents of Reactive Blue 52 attributed to the oxidation of reactive azo group. These data are very much important to assess the feasibility of the electrochemical process for the degradation of azo dyes. [7, 8]

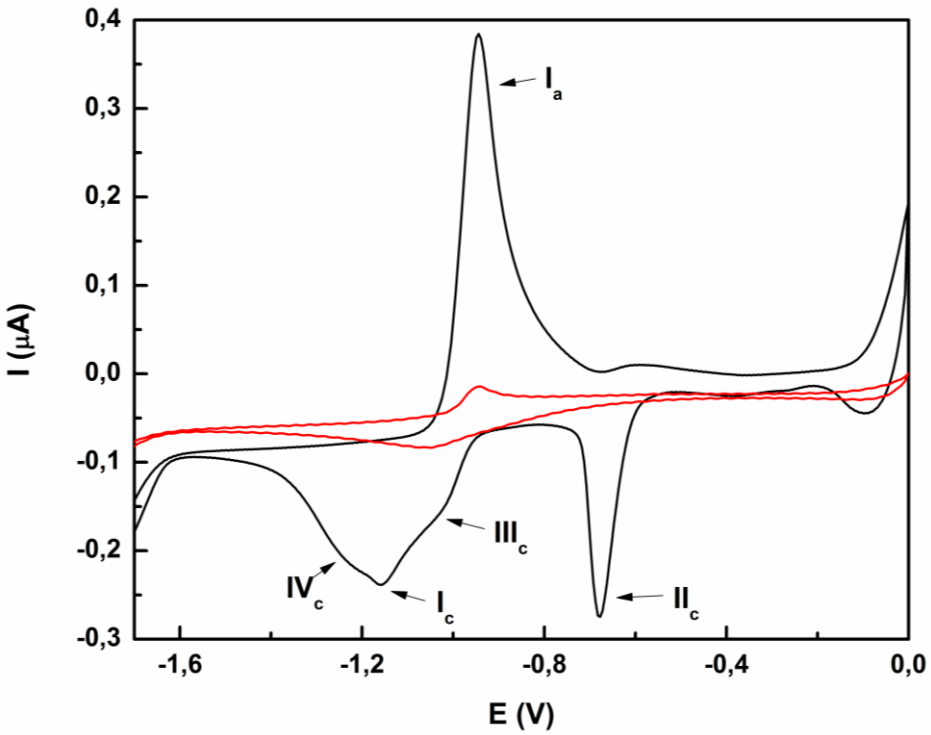



**Figure 2**. Cyclic voltammetry of initial Reactive Blue 52 (200 mg/L) solution (black line) and solution after electrolysis (red line)

*3.4 UV-Vis Study*

Typical UV–visible spectra for untreated and treated dye solutions, after different intervals during electrolysis, have been done and changes in absorbance of dye solutions were investigated. The UV-Vis spectrum of the dye solution was scanned at the $\lambda_{max}$. The decolorization of dye solution was increased with electrolysis time.

The initial spectra showed that the wavelength of maximum absorbance ($\lambda_{max}$) for Reactive Blue 52 (200 mg/L) was at 615 nm in the visible region and corresponds to the azo group. Complete decolorization was achieved at 12V after just 10 minutes of electrolysis with membrane and after 30 minutes of electrolysis without membrane (Figure 3).

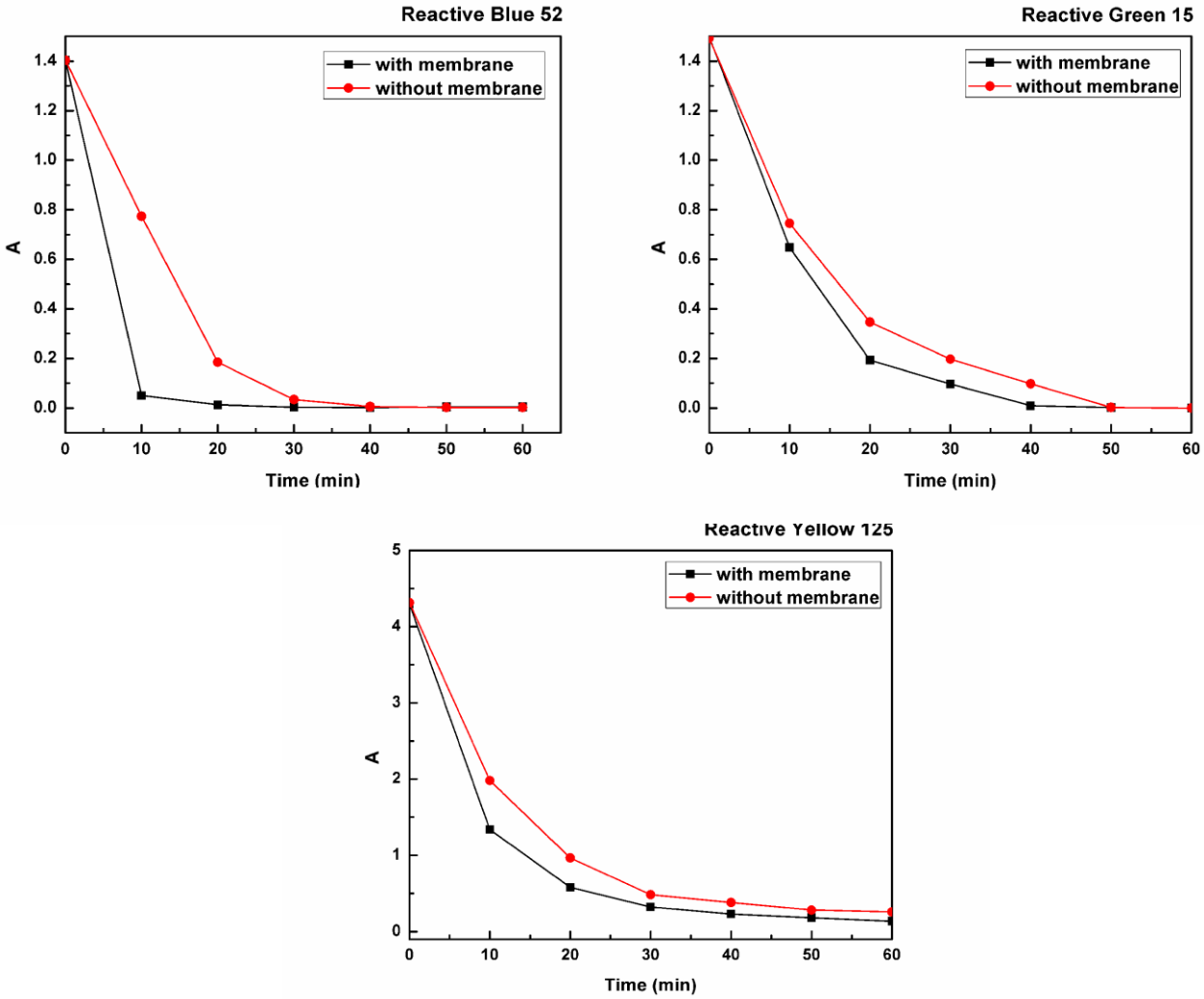



**Figure 3**. Decrease of absorbance with time for Reactive Blue 52 (at $\lambda_{max}$ = 615 nm), Reactive Green 15 (at $\lambda_{max}$ = 620 nm) and Reactive Yellow 125 (at $\lambda_{max}$ = 390 nm), with and without membrane

Wavelength of maximum absorbance for Reactive Black 5 was at 590 nm. Absorbance fell down below 0.2 after 60 minutes of electrolysis with membrane (Figure 4), and below 0.1 after 8h of electrolysis without membrane on 12V. Sakalis [21] studied the electrochemical oxidation of 450 mg/L

Reactive Black 5 over a Ti–Pt anode at about 0.1% salinity and reported decolorization after about 120 min of reaction. Kusvuran [22] reported that the rate of Reactive Black 5 degradation over a Pt anode in the presence of iron ions was strongly dependent on the initial dye concentration; at 100 mg/L dye concentration only about 40% decolorization occurred after 30 min of reaction.

Wavelength of maximum apsorbance for Reactive Green 15 was at 620 nm. Complete decolorization was achieved at 12 V after 40 minutes of electrolysis with membrane and after 50 minutes of electrolysis without membrane (Figure 3).

Wavelength of maximum apsorbance for Reactive Yellow 125 was at 390 nm. Complete decolorization was achieved at 12 V after 50 minutes of electrolysis with membrane and after 60 minutes of electrolysis without membrane (Figure 3).

During electrochemical degradation, the cleavage of —N=N— bonds and aromatic rings has taken place, which results in the decrease of the absorbance band of the dye solutions. Also the absorption band has been shifted from visible to UV region, which indicated the degradation of large dye molecule into smaller fragments. The electro-oxidation showed a considerable degradation of the dye structure which is in accordance with the COD removal percentages observed for this process. Rate of color removal was higher than COD removal due to the faster azo bond degradation.

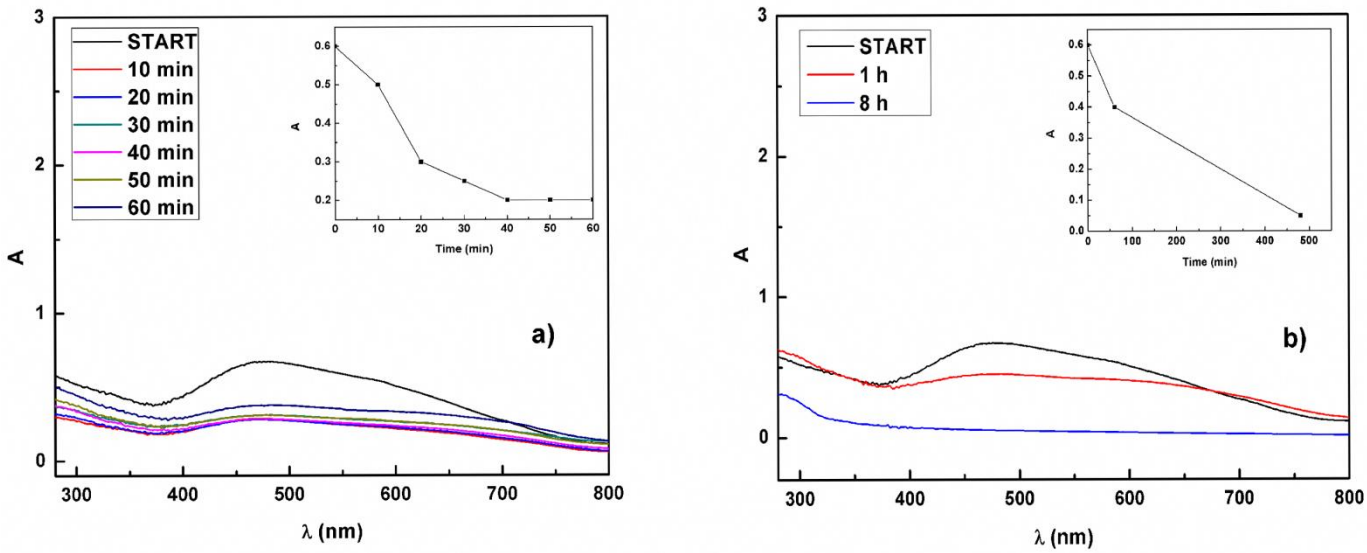



**Figure 4**. Absorption spectra of Reactive Black 5: a) with membrane, b) without membrane, Inset plot: Decrease of absorbance with time at $\lambda_{max}$ = 590 nm

The decrease of absorbance in the visible part of the spectrum indicates the loss of conjugated system in the compounds. This suggests that dyes were oxidized by oxidative species, and then converted into carboxylic intermediates what may finally lead to a complete mineralization of carbon into $CO_2$. Using absorbance measurements it is not possible to determine whether the complete mineralization occurs.

The fact that decolorization occurs at substantially greater rates than COD conversion implies that electrochemical degradation by-products are more resistant to electrooxidation than the original dyes. Similar results regarding the relative rates of electrochemical decolorization and mineralization have also been reported by several other investigators. [23,24,25,26]

### *3.5 HPLC study*

Reversed-phase liquid chromatography was employed to monitor the diminution of model dye, Reactive Blue 52. Since this technique is specifically useful to study the cleavage of the azo group as well as the formation of intermediates, the decolourisation produced during the electrolyses was studied. Chromatograms were obtained during electro-oxidation of 200 ppm Reactive Blue 52 at 12V without membrane, at 615 nm (maximum value of absorbance for RB52) and 254 nm. Chromatograms were obtained for solutions before electrolysis, at 50% of decolorization and 100% of decolorization.

Before HPLC analysis samples were concentrated with SPE cartridges from Phenomenex (Strata-X, 33u, 30mg/1ml). The cartridges were conditioned with methanol, equilibrated with distilled water, 1ml of dye samples added and eluted with methanol (with drop of ammonia).

As it can be seen from Figure 5, the azo group was practically removed when the electro-oxidation process was performed (615 nm). On the other hand, when the detector was set at the wavelength absorbance of the aromatic structures (254 nm), it was detected that main chromatographic peak ($t_R$=11.44 min) decreases, and at 100% of decolorization completely disappear, which is confirmation of UV-Vis study, ie. after 60 minutes of electrolysis complete cleavage of —N=N— bond of Reactive Blue 52 occurs.

At Figure 6 can be seen that, as a consequence of the cleavage of the azo group by electrochemical oxidation, three intermediates were generated in solution ($t_R$= 5,99; $t_R$=8,69 and $t_R$=10,24). This peaks show absorbance at 254 nm. Third peak $t_R$=10,24 disappeared after 60 minutes, we suppose that it is one of intermediate products and is futher degraded.

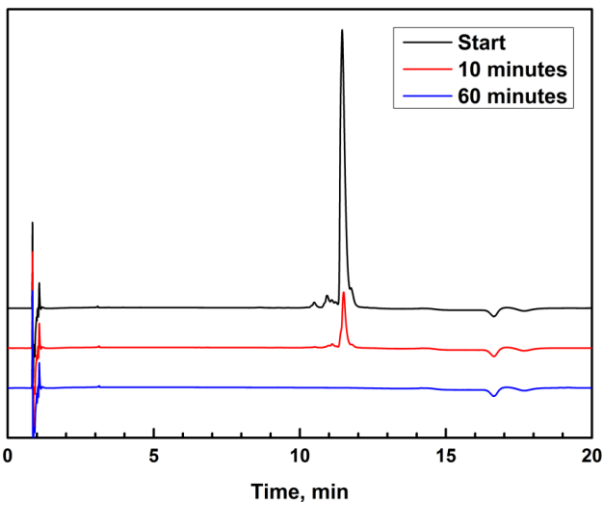



**Figure 5**. Chromatogram obtained by HPLC for electrolysis of Reactive Blue 52, at 615 nm

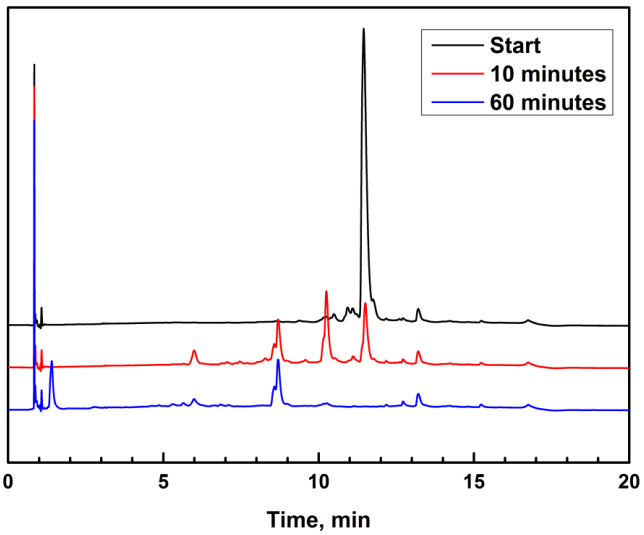



**Figure 6**. Chromatogram obtained by HPLC for electrolysis of Reactive Blue 52, at 254 nm

*3.6 Effect of initial pH*

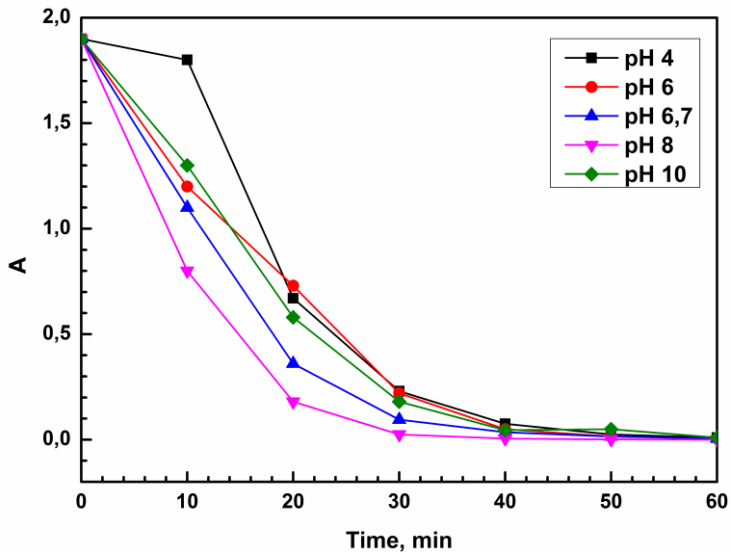



**Figure 7**. Decolorization as function of pH for Reactive Blue 52, 200 ppm solution

Solution pH is one of the important factors that affect the performance of electrochemical process. Hence studies were performed in five different initial pH values to investigate their effects as depicted in Fig. 7. For this experiment we used model dye, Reactive Blue 52, 200 ppm. The electrolysis was carried on 12V, without membrane. Decolorization with membrane was too fast to track differences. The initial pH of the solution were 4; 6; native (6,7); 8 and 10. pH was adjusted using 1M NaOH or $H_2SO_4$.

Fastest decolorization was at pH 8. In a series of repeated experiments, we found the same thing that the fastest decolorization was at pH 8, unlike other authors who have found that the decolorization was the fastest in acidic media or on the native pH. [1, 4, 8]

## 4. CONCLUSIONS

In this study, electrochemical oxidation of reactive textile dyes using platinum anode and $Na_2SO_4$ was realized. Electrochemical degradation was done with sodium sulfate already present in textile effluents, so additional chemical usage was not required and process is more cost effective. After 60 minutes of electrolysis complete degradation of dyes was reached (COD value bellow 30mg/L $O_2$) except Reactive Black 5 which has reached degradation degree of 57.95% with membrane and 35.28% without membrane. Electrochemical oxidation is capable of destroying the chromophore groups, and full decolorization of dyes found in textile effluents can be done at short treatment times. Indirect electrochemical oxidation via hydroxyl radicals is a convenient way for the degradation and mineralization of reactive dyes and offers approach to developing new technology for removal of reactive dyes in real textile industry effluents with low energy consumption.

ACKNOWLEDGEMENTS
This paper is supported by Ministry of Education and Science of the Republic of Serbia, under project number OI 172030.

## References

1. Y. Yavuz and R. Shahbazi, *Sep. Purif. Technol.*, 85 (2011) 130
2. A. J. Méndez-Martínez, M. M. Dávila-Jiménez, O. Ornelas-Dávilab, M. P. Elizalde-González, U. Arroyo-Abadb, I. Sirés and E. Brillas, *Electrochim. Acta*, 59 (2012) 140
3. H. Zollinger, *Color Chemistry: Syntheses, Properties and Applications of Organic Dyes and Pigments*, VCH Publishers, Weinheim, Germany (1991)
4. P. Kariyajjanavar, J. Narayana, Y. A. Nayaka and M. Umanaik, *Portugaliae Electrochimica Acta*, 28 (2010) 265
5. K. T. Chung and S. E. Stevens, *Environ. Toxicol. Chem.*, 12 (1993) 2121
6. P. Carneiro, M. Osugi, C. Fugivara, N. Boralle, M. Furlan and M. V. Zanoni, *Chemosphere*, 59 (2005) 431
7. A. I. del Río, J. Molina, J. Bonastre and F. Cases, *J. Hazard. Mater.*, 172 (2009) 187
8. P. Kariyajjanavar, N. Jogttappaa, and Y. A. Nayakab, *J. Hazard. Mater.*, 190 (2011) 952
9. B. Dojčinović, *Application of the reactor based on dielectric barrier discharge for the decolorization of reactive textile dye*, PhD, Belgrade (2011)
10. M. Rivera, M. Pazos and M. Á. Sanromán, *Desalination*, 274 (2011) 39
11. M. Anbia and S. A. Hariri, *Desalination*, 261 (2010) 61
12. M. A. Sanroman, M. Pazos, M. T. Ricart and C. Cameselle, *Chemosphere*, 57 (2004) 233
13. C. A. Martínez-Huitle and E. Brillas, *Appl. Catal. B-Environ*, 87 (2009) 105
14. K. Juttner, U. Galla and H. Schmieder, *Electrochim. Acta*, 45 (2000) 2575
15. E. Brillas, P. L. Cabot and J. Casado, *Chemical Degradation Methods for Wastes and Pollutants Environmental and Industrial Applications*, Marcel Dekker, New York (2003)
16. A. D. Broadbent, *Basic Principles of Textile Coloration*, Society of Dyers and Colourists, Bradford, England (2001)
17. P. Carneiro, C. Fugivara, R. F. P. Nogueira, N. Boralle and M. V. Zanoni, *Portugaliae Electrochimica Acta*, 21 (2003) 49
18. E. Chatzisymeon, N. P. Xekoukoulotakis, A. Coz, N. Kalogerakis, and D. Mantzavinos, *J. Hazard. Mater. B*, 137 (2006) 998

19. C. Comninellis, *Electrochim. Acta*, 39, (1994) 1857
20. M. Panizza and G. Cerisola, *Electrochim. Acta*, 51 (2005) 191
21. A. Sakalis, K. Mpoulmpasakos, U. Nickel, K. Fytianos and A. Voulgaropoulos, *Chem. Eng. J.*, 111 (2005) 63
22. E. Kusvuran, S. Irmak, H. Ibrahim Yavuz, A. Samil and O. Erbatur, *J. Hazard. Mater. B*, 119 (2005) 109
23. H. S. Awad and N. Abo Galwa, *Chemosphere*, 61 (2005) 1327
24. A. Fernandes, A. Morao, M. Magrinho, A. Lopes and I. Goncalves, *Dyes Pigments*, 61 (2004) 287
25. Z. Shen, W. Wang, J. Jia, J. Ye, X. Feng and A. Peng, *J. Hazard. Mater. B*, 84 (2001) 107
26. J. Naumczyk, L. Szpyrkowicz and F. Zilio-Grandi, *Water. Sci. Technol.*, 34 (1996) 17
27. http://www.energy.eu/

© 2013 by ESG (www.electrochemsci.org)