Toxicity Screening after Electrochemical Degradation of Reactive Textile Dyes

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Abstract

The application of various electrodes for *in situ* degradation of Reactive Yellow 125 (RY125) and Reactive Green 15 (RG15) dyes, as well as ecotoxicity screening test of their degradation products were studied in this paper. The degradation process was performed in a two-electrode cylindrical cell, with Fisher platinum electrode as anode and Pd, Zr, or C electrodes as cathode; in 0.1 M Na_2SO_4 as supporting electrolyte. The optimal conditions (voltage and pH value) for degradation were determined in a platinum-palladium (Pt-Pd) model system for 200 mg/L of both reactive dyes. Then the electrolysis with other electrodes was conducted under the same conditions. Decolorization was monitored spectrofotometrically (UV-Vis) and the degradation efficiency was confirmed by HPLC technique with a DAD detector. Differences in degradation efficiency were observed between these three electrochemical systems (Pt-Pd, Pt-Zr, and Pt-C). The Pt-Pd system was the most efficient for the degradation of both reactive dyes. Achieved decolorization percentage for RG15 and RY125 were 98% and 97%, respectively. The ecotoxicity assessment of degradation products was performed using *Artemia salina*. Toxicity data were compared by Kruskal-Wallis one-way analysis and pairwise group comparisons with Mann-Whitney U tests. Statistically significant differences ($p < 0.05$) in mortality (%) for Pt-Pd and Pt-Zr systems were determined between treated and untreated dye solutions of RG15. System Pt-C had no detectable significance in treatment of solutions of both dyes.

Keywords: electrochemical degradation, azo dyes, ecotoxicity

Introduction

Food, cosmetics, rubber, pharmaceuticals, plastic, paper, leather, textiles, and other products are colored in the modern era. Over 10,000 different textile dyes with an extensive annual production are commercially available worldwide [1, 2]. More than half of them are azo compounds, and they are the most important class of synthetic organic dyes as well as common industrial pollutants [3]. The textile industry discharges into the environment about 2 to 20% of initial amounts of dye [4]. Due to their complex aromatic structure and synthetic origin these textile dyes cannot be degraded easily [5]. Reactive azo dyes are designed to resist fading on exposure to sweat, soap, water, light, oxidizing, reducing agents, and low aerobic biodegradation [6]. If discharged to an aquatic environment these dyes create severe pollution

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problems by releasing toxic and potentially carcinogenic substances [7]. The endocrine, carcinogenic, and mutagenic effects of commercially used azo dyes are well documented [8, 9].

During the last 14 years, the electrochemical techniques with various electrodes have been found to be of special interest for wastewater treatment. Electrochemical processes are easy to operate, commonly conducted at room temperature and atmospheric pressure. No additional chemicals are required – they use the electron as a unique reagent – and there is no secondary pollution problem (sludge). Electrochemical degradation of azo dyes has already been described as efficient, eco-friendly and a cost-effective alternative to classic textile effluent treatments [10].

Nevertheless, products generated during the electrochemical treatment of textile effluents could be significantly more toxic than the parent compound. According to reports of the International Agency of Research and Cancer (IARC), the scission of azo bond generates aromatic amines, which can increase the frequency of mutation in the living organisms [11].

The toxicity test is the way to evaluate the efficiency of a treatment and to quantify the environmental impact of an effluent or individual compound. Effluents from textile industries have high salinity and conductivity [12] and, therefore, the genus *Artemia* was used as a model for rapid preliminary screening of toxicity. *Artemia* is tolerant of a high salinity environment, which makes it proper for a toxity test. Biological tests in combination with chemical analysis are the pillars for strategy of environmental management [13].

There are publications addressing the electrochemical treatment of non-biodegradable reactive yellow dye [14-16], but reactive green dye RG15 is poorly or not at all documented. Also, there is no assessment of environmental impact for many studies of electrochemical treatments used for water purification.

This study aimed to determine optimal conditions for efficient degradation of azo dyes with different electrode systems (Pt-Pd, Pt-Zr, or Pt-C) and to determine the toxicity of dye degradation products after each electrochemical treatment.

Materials and Methods

Chemicals

Two commercial reactive azo dyes Reactive Yellow 125 (RY125, CAS No. 68155-62-4, λ_{max} = 390 nm) and Reactive Green 15 (RG15, CAS No. 61969-07-1, λ_{max}= 620 nm) were both technical grade (Clariant, Switzerland) and they were used without any further purification.

Sodium sulfate (Na_2SO_4, Merck p.a.) was used as a supporting electrolyte. It is actually present in effluents from the textile industry and was identified as a suitable electrolyte for electrochemical treatment of colored effluents [17]. Furthermore, during electrolysis it does not produce any reactive species. Sodium chloride was not used due to

the formation of toxic organochlorinated byproducts persistent for further oxidation [18].

Ammonium acetate and acetonitrile (HPLC grade, Sigma Aldrich) were used for HPLC analysis. Apart from the solutions where HPLC-grade water (Sigma Aldrich) was used, all other solutions were prepared with double distilled water.

The brine shrimp eggs were incubated in artificial sea water (Aqua Medica, Germany). Sodium chloride (NaCl, Sigma Aldrich) was used for osmotic adjustment. The reference substance for all toxicity tests was potassium dichromate ($K_2Cr_2O_7$; analytical grade, Sigma Aldrich).

Instrumentations

An undivided cylindrical electrochemical cell with two-electrodes was used for the electrolysis of each dye. The anode was a Fisher platinum electrode and the cathodes were Pd, Zr, or C. The volume of treated dye solution was 340 mL; the effective cathode area was 1.80 cm^2 and the effective anode area was 25 cm^2. All experiments were carried out under constant potential difference (4.5, 6, and 12 V) with a power supply (adjustable DC power supply PS3010 (0-32VDC, 0-10A) E – HQTM).

A UV-Visible Cintra 10 spectrometer (GBC Scientific Equipment Pty Ltd., Australia) was used to measure absorbance before and during electrolysis (at different time intervals).

The HPLC analysis was carried out with a Dionex UltiMate 3000 chromatograph, with a diode array detector. The applied column was Hypersil Gold C8 (150 mm×3 mm, 3 μm). Ammonium acetate (10 mmol, pH 5) as component A and acetonitrile as component B were mobile phases. The column was set at 40ºC. Injection volume was 20 μl. The detector was set at 615, 390, 254, and 217 nm.

ICP-OES method (Thermo Scientific iCAP 6500 Duo ICP (Thermo Fisher Scientific, Cambridge, UK) was used to check consistency of each cathode.

Analytical Procedure

Aliquots of reaction mixture (2 mL) were taken at regular time intervals (10 min) from the cell during electrochemical treatment and analyzed using UV-Vis spectrophotometry.

The percentage of decolorization was calculated from the change in absorbance according to the following formula:

$$Decolorization\ (\%) = (A_o - A)/A_o \times 100$$

...where: A_o – absorbance of initial dye solution at the maximum absorption wavelength (λ_{max}), and A – absorbance of dye solution after the electrochemical treatment at the maximum absorption wavelength.

The effectiveness of the electrochemical degradation process was monitored with HPLC/DAD at 50% and 100% of decolorization. Compounds were eluted at flow rate of 1 mL/min. Ammonium acetate as component A and acetonitrile as component B were mobile phases. The elution gra-

dient was 5-90% B component during 15 min and 90% for the last 3 min.

To exclude depletion of cathode as the possible influence on toxicity outcome, solutions were also analyzed by ICP-OES. The concentrations of Pd, Zr, or C were found to be under detection limit (data not shown).

Artemia salina – Screening Test

The *Artemia salina* cysts (DAJANA PET, Czech Republic) were hatched in artificial seawater to produce larvae [19]. Incubation temperature was 26±1ºC for 24 hours, pH-range was 7.5 to 8.0, and continuous illumination was provided by a fluorescent 60 W light tube. Using instar II-III larvae, an acute toxicity test was performed in darkness at a temperature of 26±1ºC for 24 h.

Tests were performed in 50 mL borosilicate glasses in the following way: artificial sea water was used as control solution (negative control) and as a diluent for samples. Solutions of various concentrations of untreated and treated azo dyes in control solution were prepared: 3.13%, 6.25%, 12.5%, 25%, 50%, 75%, 100%, (v/v); three replicates per dilution and six per control were made.

Before testing, the pH value of each sample was adjusted to pH 8 (0.1 M NaOH). Volume of the sample was 10 mL per glass and 10 individuals were placed into each glass. Brine shrimps were not fed during the test. Endpoint was the mortality of nauplii. For all experiments solutions with reference substance ($K_2Cr_2O_7$, 100 mg/L, positive control) were prepared in the same way (3.13%, 6.25%, 12.5%, 25%, 50%, 100%, (v/v)); lethal concentrations (LC_{50}; the percentage of the effluent concentration that causes 50% of mortality during 24 h) for reference substance in the case of *Artemia salina* was between 32 to 42 mg/L [20]. LC_{50} values in this study were estimated by regression models: Probit and Spearman-Karber TesTox software [21]. Tests were considered valid if the calculated LC_{50} of reference chemicals was between the values suggested by Melahat Togulga [20] and the mortality in the control did not exceed 10%. Mortality results were expressed as a percentage. A comparison was made between mortality percentages before and after the treatment with each of the different electrodes (Pd, Zr, or C). Since the number of replicates was equal, but low in all treatments, Kruskal-Wallis one-way analysis as a non-parametric alternative to the one-way ANOVA was performed. Pairwise, group comparisons were done with Mann-Whitney U tests using software package IBM SPSS Statistica 20. The toxicity was also presented relative to a dilution ratio. Toxicity assessment was done according to a wastewater toxicology classification scale proposed by Persoone [22], where the results of toxicity tests were calculated as toxicity units acute (TUa). The TUa of an effluent is the inverse of its LC_{50} values: TU = $100/LC_{50}$.

Results and Discussion

Optimization of pH and Voltage

In order to optimize decolorization process the electrolysis was carried out in a Pt-Pd model system at different pH values (native, 3, and 9) and different voltages (4.5, 6, and 12 V). The native values of pH for green dye RG15 and yellow RY125 were 6.06 and 5.68, respectively. The influence of these parameters on decolorization efficiency was defined by changing voltage at constant pH value and then changing pH under constant voltage.

The concentration of dye was 200 mg/L in the volume of 340 mL (0.1 M Na_2SO_4); the temperature was maintained at 25ºC.

Optimal conditions for electrochemical degradation of reactive dyes were found to be pH 9 and power of 12 V in the model system (Pt-Pd). The achieved decolorization percentage of RG15 under these conditions was 98% after 60 min. When power of 4.5 V or 6 V was applied the treatment reached 90% decolorization, but after 90 min. The native pH (6.06) was not chosen for degradation treatment of RG15 as it was less efficient (Fig. 1).

Decolorization percentage of yellow dye RY125 under optimal conditions was 95% after 70 min. Only 80% of decolorization during the treatment with voltages of 4.5V
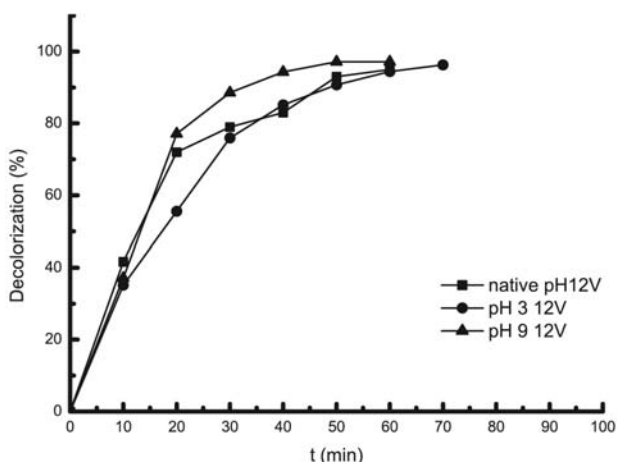

Fig. 1. Model system Pt-Pd, decolorization (%) of Reactive Green 15 (RG15; concentration of 200 mg/L), at 12 V for different pH values (native (6.06), 3, and 9).
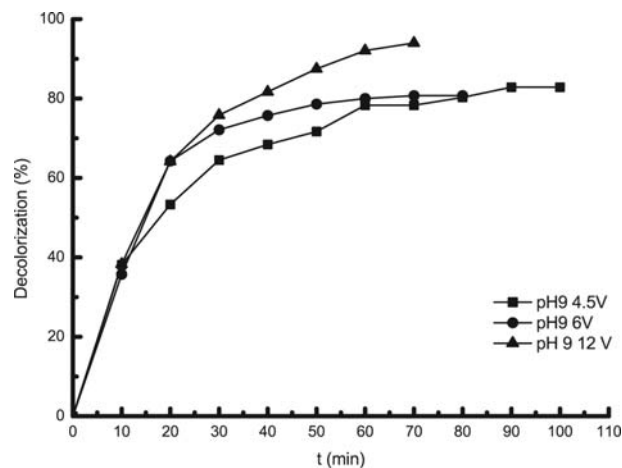

Fig. 2. Model system Pt-Pd, decolorization (%) of Reactive Yellow 125 (RY125; concentration of 200 mg/L) under pH 9 for different voltages (4.5, 6, and 12V).

and 6V was achieved. Furthermore, the treatment lasted longer, and therefore they were less effective (Fig. 2).

In all other experiments where parameters of pH value and voltage were varied the decolorization was less efficient or lasted over 100 min.

The Pt electrode known as "active" anode is characterized by a high percentage of decolorization, but low level of decontamination. It was reported that the application of Pt anode results in a lower yield of hydroxyl radicals. On the surface of the anode there is ongoing adsorption of hydroxyl radicals and reaction with the anode generates higher oxide. Redox couple PtO/PtO_2 is an intermediate in the oxidation of organic compounds. This mechanism was presented in our previous study [23].

After electrolysis, treated solutions had very low pH value (pH 2-3). When Pt was applied as anode some authors reported the presence of aliphatic acids (acetic, oxalic, and maleic) during the electrochemical treatment of textile wastewaters [24].

Having that in mind, after electrolysis the final pH had to be adjusted for toxicity test to pH 8 (0.1M NaOH) in order to prove that pH had no effect on toxicity.

Degradation of Reactive Dyes (RG15, RY125) in High Concentration

When optimal conditions for electrochemical degradation of azo dyes were determined, their initial concentration was increased to 1000 mg/L. Electrolysis was stopped at the maximum decolorization percentage and treated solutions of dye were analyzed with an ecotoxicology screening test. The reason to study such a high concentration was that in some dyehouse effluents (Nigeria), dye concentrations could exceed 600 mg/L [25]. The pH of each dye solution was adjusted to 9, with 0.1 M NaOH.

As expected, the duration of decolorization was prolonged in all systems in comparison with the model system (Pt-Pd) due to very high dye concentrations. The highest percentage of decolorization of RG15 dye (97.77%) was

achieved in a Pt-Pd system after 160 min (Fig. 3a). In two other systems the decolorization percentage after 160 min was: 97.14% in Pt-Zr and 95.12% in Pt-C. After only 80 min of the RG15 treatment in the Pt-Pd system decolorization was 97%. An additional 1% of decolorization was obtained in prolonged treatment. In two other systems (Pt-Zr and Pt-C) the decolorization percentage was under 80% after 80 min.

For yellow RY125 dye the most efficient treatment was also with the Pt-Pd system: 96.67% of decolorization (%) after 180 min, compared to other systems (92.23 % in Pt-Zr and 86.27% in Pt-C, Fig. 3b). Prolonged decolorization of RY125 for all systems was followed up. However, only with the Pt-Zr system was decolorization of 97.10% reached after 300 min.

When comparing decolorization percentages of Pt-Pd treatment for both dyes, higher decolorization percentage was achieved for green dye (RG15) than yellow dye (RY125). Double time (160 min) was needed to reach the same percentage of decolorization for yellow dye.

The forming of the foam was noticed during treatment in all systems (Pt-Pd, Pt-Zr, and Pt-C). According to Zheng [26] the foam originates from the original color molecule. When the amine and methyl groups were detached from the dye molecule, the dye structure changed from polar into nonpolar water insoluble substance. Then during electrolysis the amount of hydrogen bubbles generated from the cathode was increased and they contributed to the rise of the foam [26].

The similarity in decolorization trends for both dyes could be observed between the Pt-Zr and Pt-C electrochemical system, which was also supported for these systems in chromatograms at 50% decolorization (Fig. 4.)

HPLC Analysis

To confirm the degradation of reactive dyes (1000 mg/L) in all systems (Pt-Pd, Pt-Zr, and Pt-C), samples were taken at 50% and maximum decolorization percentage after the electrochemical degradation.
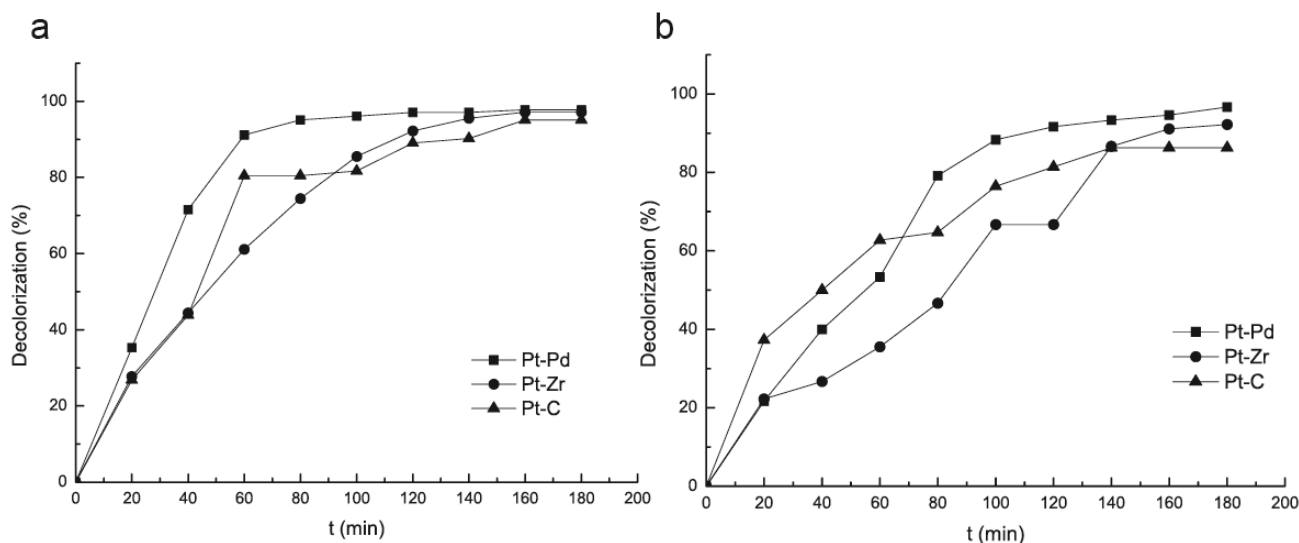

Fig. 3. Decolorization (%) of RG15 (a) and RY125 (b) in the electrochemical process using different electrochemical systems (Pt-Pd, Pt-Zr, or Pt-C) at pH 9 and 12 V.
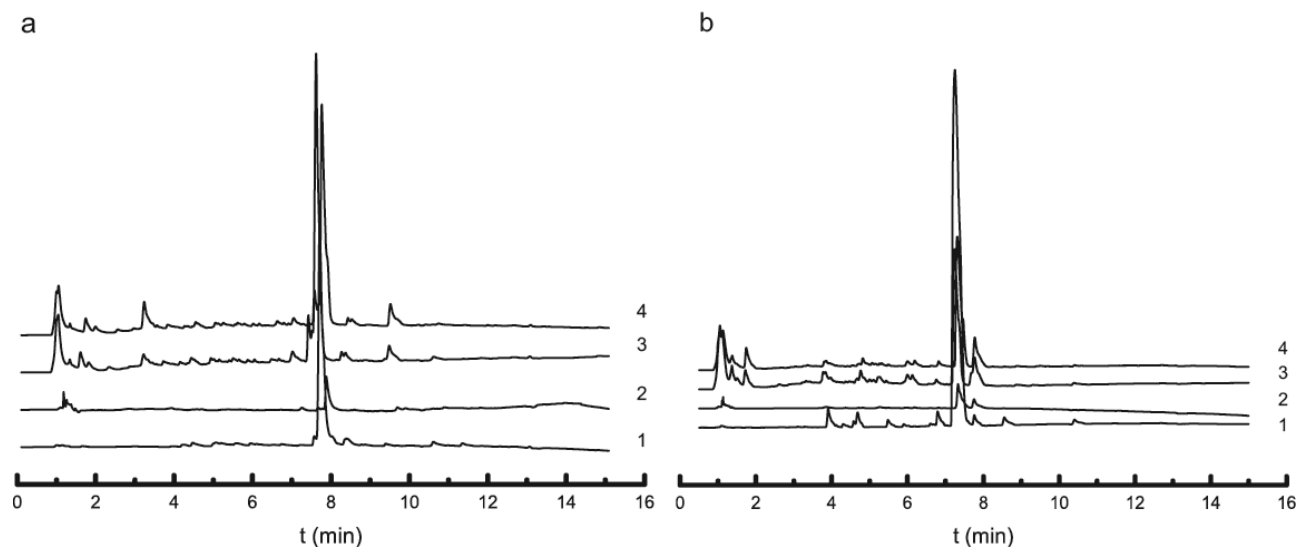
a
b

Fig. 4. Degradation products of RG15 (a) and RY125 (b) dye solution at 50% decolorization, achieved using Pd, Zr, or C as electrode (254 nm). Line 1 is the initial dye solution of RG15 or RY125, line 2 is dye solution after the Pt-Pd treatment, line 3 is dye solution after the Pt-Zr treatment, and line 4 is dye solution after the Pt-C treatment.

The decrease of dye solution absorbance during electrochemical treatment implied that cleavage of –N=N-bond aromatic rings occurs. Good correlation between the degradation of aromatic compounds and decolorization (%) of dyes as a method to assess the efficiency of the degrading process was well supported [27].

The untreated dye solution of RG15 peaks at t_R= 7.66, and afterward the peak intensity decreases due to degradation of chromophora in all three systems (Fig. 4a). The same method was applied for monitoring the degradation efficiency of RY125 dye (t_R= 7.25) in all three systems (Fig. 4b).

This trend was confirmed by analyzing samples of treated dye solution at maximum decolorization percentage (Figs. 5a and b). The detector was set at 254 nm (wavelength absorbance for aromatic structure) and the chromatograms indicated the presence of substances that were not present in the initial solution. A considerable amount of these products was observed in the Pt-Zr and Pt-C system at maximum decolorization percentage for RY125.

On the basis of these chromatograms it could be assumed that the degradation mechanism was the same in every system, but that degradation efficiency of both dyes was the best using the Pt-Pd system. Two other systems (Pt-Zr and Pt-C) were less efficient.

Toxicity Screening Bioassay

Samples were taken at the beginning and at the maximum decolorization percentage in order to test the toxicity of degradation products. There was no mortality recorded
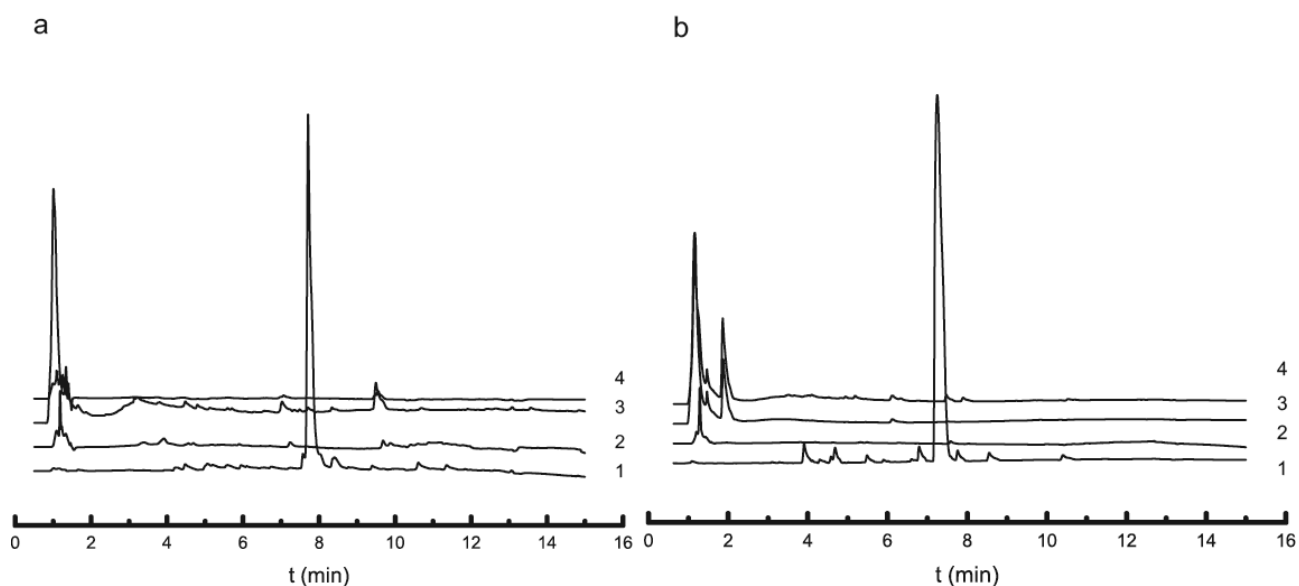
a
b

Fig. 5. Degradation products of RG15 (a) and RY125 (b) azo dyes at maximum decolorization percentage, achieved using Pd, Zr, or C as electrodes (254 nm). Line 1 is the initial dye solution of RG15 or RY125, line 2 is the dye solution after Pt-Pd treatment, line 3 is dye solution after Pt-Zr treatment, and line 4 is dye solution after the Pt-C treatment.

in the control group, so the test acceptability criterion (90% or higher survival rate) was fulfilled. The highest tested concentration (100%, v/v) of untreated dye solutions (RG15 and RY125) had a more toxic effect on nauplii (mortality %) than treated solutions, except in the case of Pt-C treatment for green dye (Figs. 6 and 7). In the Pt-C system the mortality (%) was similar: 30% in treated solution and 27% in untreated dye solution.

Mortality (%) data was arcsin transformed prior to statistical analysis. Concerning RG15 a statistically significant difference in mortality (Fig. 6) was found between all treatments (Kurskal-Wallis test: p<0.05). Pairwise comparison with the use of Mann-Whitney U-test (p < 0.05) showed significant differences between untreated green dye solution (RG15), solutions treated with Pt-Pd (Treatment 1) and Pt-Zr (Treatment 2) system. There was no statistically significant difference in the mortality between untreated RG15 dye solutions and solutions treated with the Pt-C system (Treatment 3).
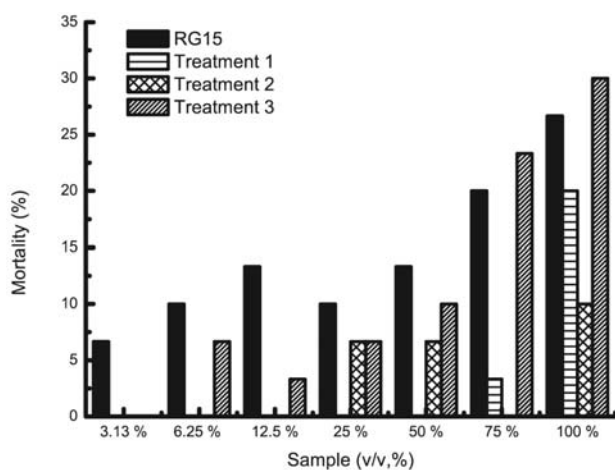

Fig. 6. Toxic Effect (%) of RG15 before and after electrochemical treatment using Pt-Pd (Treatment 1), Pt-Zr (Treatment 2), and Pt-C (Treatment 3) system.
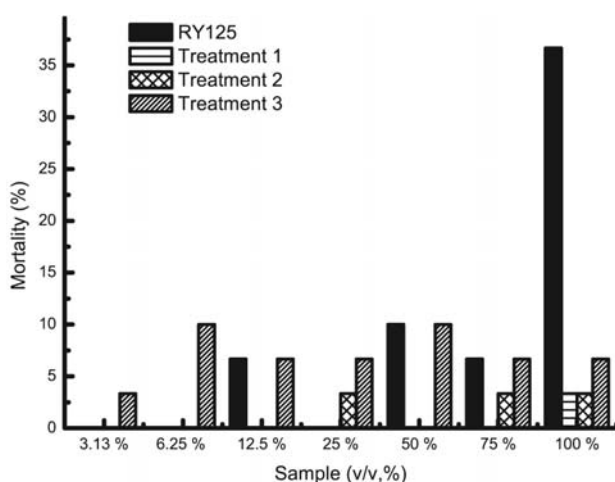

Fig. 7. Toxic Effect (%) of RY125 before and after electrochemical treatment using Pt-Pd (Treatment 1), Pt-Zr (Treatment 2), and Pt-C (Treatment 3) system.

Concerning yellow dye RY125 a statistically significant difference in mortality was found between all treatments (Kurskal-Wallis test: p<0.05). Pairwise comparison with the Mann-Whitney U-test showed no significant difference (p>0.05) between untreated RY125 dye solution and a solution treated with Pt-Pd (Treatment 1), Pt-Zr (Treatment 2), or Pt-C (Treatment 3) systems (Fig. 7).

After the maximum of decolorization percentage of yellow dye the Pt-Pd and Pt-Zr system produced a toxic level lower than acceptability criterion of control group (less than 10%). Toxic effect (mortality, %) for both reactive dyes; for the whole dilution series was the lowest (or not recorded) in the electrochemical treatment with Pt-Pd system.

The 50% mortality was not observed for initial dye solution. Also, it was not observed for tested solution after electrochemical degradation. If mortality is higher than 50% in 100% of effluent (sample), the test is "positive" and effluent has the potential to cause a toxic effect on aquatic life in the receiving water. In our study mortality was less than 50% at 100% of tested samples. Therefore the LC_{50} value could not be determined since it would be higher than 100% of the tested sample, and the TUa <1. Therefore, the treated dye solutions could be considered as "low toxic" to "non toxic."

Conclusion

The electrochemical degradation of two reactive dyes was conducted in an undivided two-electrode cell; Fisher platinum electrode was employed as anode and Pd, Zr, or C electrode as cathodes. For both dyes optimal conditions were achieved at 12V and pH value of 9 in a Pt-Pd model. The efficiency of degradation process in the mixture depended on the applied electrochemical system (Pt-Pd, Pt-Zr, or Pt-C). Degradation efficiency was different compared to the dye solutions after all treatments.

1. In all systems the Pt-Pd treatment was the most efficient for degradation of both reactive dyes. Achieved decolorization percentages for 1,000 mg/L of RG15 and RY125 were 98% and 97%, respectively.

2. The electrochemical system with Pt-Zr and Pt-C treatment could also be considered as a solution for decolorization and degradation of dye molecules.

3. Toxic effects for both reactive dyes were lowest (or not recorded) in the electrochemical system with Pt-Pd treatment. Significant difference (p < 0.05) in mortality (%) was determined between untreated solution of RG15 and the solution treated in Pt-Pd system and Pt-Zr system. There was a non-significant difference (p > 0.05) between untreated dye solution of RY125 and all treated samples.

4. Solutions of reactive dyes that have undergone electrochemical degradation do not exceed toxicity of the parent compound, and according to acute toxicity test the LC_{50} was > 100% (TUa <1) all samples could be considered as "low toxic" to "non toxic."

Chronic tests are planned for further study of electrochemical degradation of RG15 in Pt-Pd or Pt-Zr systems.

Acknowledgements

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