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Colour Degradation of Simulated Textile Effluent by Electrolytic Treatment and Ecotoxicological Evaluation

J. R. Moraes Jr · E. D. Bidoia

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Abstract Since the last century, humanity has sought ways to minimize the impact of the industrial growth in the environment. The textile industry, as one of the major contributors to water pollution, has been dumping coloured effluents which cause great impact in water bodies. The electrolytic process not only degrades the colour of the effluent but also transforms recalcitrant substances by direct or indirect oxidation. The ecotoxicological tests are used nowadays as a way to verify the toxicity degree of water bodies polluted by industrial and farming activities. The ecotoxicological tests consist in exposing determined organisms to the samples with the intention to evaluate their toxicity by observing the organisms' responses. This study had the objective to degrade, by electrolytic process, a simulated textile effluent containing a mixture of Acid Blue 40 and Acid Red 151 dyes and the toxicity evaluation of the treated effluent by ecotoxicological tests. The bioassays used were tests with seeds of *Lactuca sativa* (lettuce), *Eruca sativa* (rocket), and *Cucumis sativus* (cucumber). Tests with the micro crustaceous *Artemia salina* and the yeast *Saccharomyces cerevisiae* were also conducted. The electrolytic treatment degraded the initial colour of the textile effluent, and the ecotoxicological tests indicated low toxicity to the treatment.

J. R. Moraes Jr, · E. D. Bidoia (✉)
Department of Biochemistry and Microbiology, IB, UNESP – Sao Paulo State University, Av. 24 A, 1515 - Bela Vista, 13506-900 Rio Claro, São Paulo, Brazil
e-mail: ederio@rc.unesp.br

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1 Introduction

Water bodies are of great importance to humanity. They are not only the freshwater sources for all life forms, but they are also the final destination of wastewater. Thus, the disorderly discharge of human waste is pushing their capacity to depurate residues to their limits. The textile industry has a huge weight in global economy; however, there is still an opening regarding environmental responsibility. All the dyeing processes have a final operation of running water baths to remove excesses of dyes not fixed on the fibber, which go directly to water bodies. Due to its nature, dyes are highly detectable to the naked eye, even in reduced amounts dumped into water bodies (Guaratini and Zanoni 2000).

The electrolytic process has been studied for use in several sectors of remediation to minimize environmental impacts. Through electrochemical reactions, the electrolytic treatment process can transform recalcitrant substances that compound pollutants. It can also disinfect the effluent through the production of chlorine (Gusmão et al. 2010). In general, the electrolytic process removes organic pollutants from the effluent by direct or indirect oxidative mechanisms (Bahadir and Abdurrahman 2009). The direct oxidative anode process adsorbs pollutants in the anode surface and then destroys them by the anodic reaction of electron transfer.

The indirect oxidative process generates strong oxidants such as chlorine/sodium hypochlorite, ozone, and hydrogen peroxide, which immediately oxidize pollutants in situ (Rajkumar and Palanivelu 2004).

Ecotoxicological studies enables the understanding of how chemical stressors might affect organisms, community, or populations (Hermens et al. 2004). The ecotoxicological tests consist of exposing a determined organism or a group of organisms from the same species to a sample to be evaluated. Alterations observed in the organisms might be physiological, metabolic, or physical. With the acquired observations, the sample quality can be evaluated (Blaise and Kusui 1997).

The aim of this study was to degrade a synthetic textile effluent in order to remove the colour by electrolytic treatment and evaluate its toxicity through ecotoxicological tests with seeds of *Lactuca sativa*, *Eruca sativa*, and *Cucumis sativus*. Ecotoxicological tests were also conducted with brine shrimp (*Artemia salina*) and the yeast *Saccharomyces cerevisiae*.

2 Methods

The simulated effluent was prepared by mixing and heating both dyes, Acid Blue 40 ($C_{22}H_{16}N_3O_6NaS$) and Acid Red 151 ($C_{22}H_{15}N_4O_4S.Na$) from Aldrich®, in deionized water until dilution temperature (65 °C) and adding sodium chloride and sodium carbonate in the mixture (Sousa and Bidoia 2014). The mixture concentration of dyes was 0.10 g L^{-1}, 2.00 g L^{-1} of sodium chloride and 0.26 g L^{-1} of sodium carbonate. The synthetic effluent was acidified with sulphuric acid 0.20 mol L^{-1} to a pH of 3.5 as recommended in Sauer et al. (2002).

The degradation process consisted of passing the synthetic effluent through an electrolytic reactor for 40 min (Sousa and Bidoia 2014). The reactor contained an titanium electrode covered with titanium oxide (70 % TiO_2) and ruthenium oxide (30 % RuO_2). The electric current was adjusted to 5.00 A with an output of 600 L/h. Samples were collected at 0, 3, 5, 15, 30, and 40 min of treatment. All the samples were tested for conductivity, pH, and free residual chlorine. In order to minimize the oxidation properties of the residual chlorine to the ecotoxicological tests, sodium thiosulfate was added to the samples. Spectrophotometric analyses were conduct with each sample to verify the rate of degradation and if it were effective. The wavelength of 525 nm was chosen to calculate the degradation of the colour of the synthetic effluent.

The seeds bioassay was conducted according to Araújo and Monteiro (2005). Petri dishes with filter paper were soaked with 3.00 mL of each sample, and 20 seeds were placed in each one of them. Samples were incubated in a BOD for 72 h at 20 °C. After incubation period, germinated seeds were counted and their roots were measured to calculate de Germination Index according to Eqs. 1, 2, and 3. Distilled water was used as negative control and zinc sulphate ($ZnSO_4$) at 0.05 M as positive control.

$$\text{Relative germination}\ (\%) = \frac{\text{number of germinated seeds in samples}}{\text{number of germinated seed in control}} * 100 \quad (1)$$

$$\text{Relative root elongation}\ (\%) = \frac{\text{average elongation in samples}}{\text{average elongation in control}} * 100 \quad (2)$$

$$\text{Germination Index}\ (\%) = \frac{\text{relative germination}(\%) * \text{relative root elongation}(\%)}{100} \quad (3)$$

The bioassay with *A. salina* (brine shrimp) was conducted according to Veiga and Vital (2002) with some modifications. Synthetic salt water was prepared by diluting marine salt in distilled water in a 3.2 % concentration rate. An aquarium was prepared by covering three sides for light not to pass through them. Inside the aquarium, a net was installed closer to the side not covered. A fluorescent light was put in front of the not covered side of the aquarium. Cysts of *A. salina* were added to the salt water in the aquarium. The *A. salina* nauplii which passed the net for 24 h and were closer to the light were chosen to perform the test. Ten units of 24-h hatched nauplii were added to each sample in test tubes. Samples were incubated at 28 °C for 48 h. After incubation, dead or not swimming units were counted to realize mortality percentage calculation (M %) as Eq. 4. Synthetic salt water was used as negative control and sodium dodecyl sulphate ($NaC_{12}H_{25}SO_4$) at 22 mg L^{-1} as positive control.

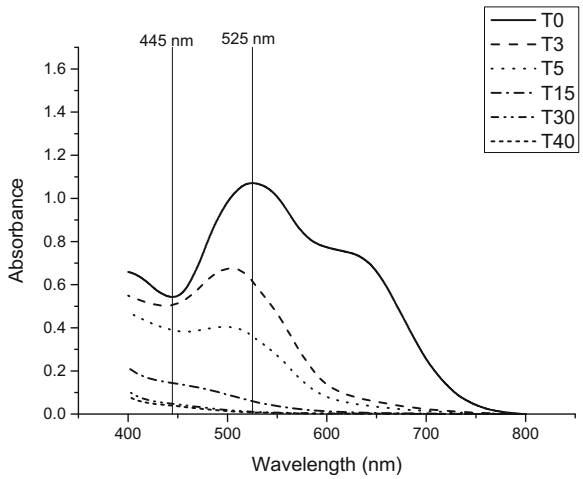

Fig. 1 Light spectrum for the electrolytic treatment of the synthetic effluent

$$M\% = \frac{\text{number of dead organisms} * 100}{\text{number of total organisms in tubes}} \quad (4)$$

The *S. cerevisiae* bioassay was conducted according to Sousa and Bidoia (2014). Tablets of yeast from Fleischmann Royal® were diluted in distilled water. Suspension was centrifuged for 5 min, washed with distilled water, and then resuspended to 150 mL. Samples were prepared by adding 9 mL of each sample in test tubes and 1 mL of *S. cerevisiae* suspension. Test tubes were incubated for 72 h. After incubation period, coloured dead cells with erythrosine were counted using a magnification glass of ×40. A comparison between the samples and control (only distilled water) was realized to verify the percentage of dead cells (Rumlova and Dolezalova 2012).

Table 1 Spectrophotometer analyses and concentration of non-modified dyes

	Absorbance at 525 nm	Concentration of non-modified dyes (g L^{-1})	Relative absorbance
T0	1.071	0.10	1.97
T3	0.6153	0.05	1.22
T5	0.3609	0.02	0.93
T15	0.0598	0.00	0.42
T30	0.0109	0.00	0.23
T40	0.0079	0.00	0.20

All bioassays were conducted in triplicate and they were submitted to statistical non-parametric analyses by Kruskal-Wallis method utilizing the BioEstat 4 software.

3 Results and Discussions

The electrolytic process degraded the colour of the synthetic textile effluent according to Fig. 1. Wavelengths of 525 and 445 nm were used to calculate the relative absorbance due to the variation presented in the non-modified dye curve spectrum (T0).

As presented in Table 1, the electrolytic process degraded all the original colour of the synthetic effluent in 15 min (T15) of treatment. According to Glenn and Gold (1983), the relative absorbance rate remains significantly constant during a treatment process of colour removal when there is no degradation. Thus, the results presented no degradation after 30 min of treatment (T30).

As presented in Table 2, conductivity had not changed significantly during the electrolytic process. The use of sodium chloride (NaCl) and sodium carbonate (Na_2CO_3) had the intention to simulate an actual textile effluent (Sousa et al. 2011) and to raise conductivity. The increase in the solution conductivity results in a decrease in electrical energy consumption due to reduction of cell voltages. The addition of NaCl in order to raise conductivity also presents other advantages in the generation of free chlorine, which could reduce the effects of other anions such as sulfate and bicarbonate (Daneshvar et al. 2006).

According to Table 2, pH values increased during the process. The Brazilian legislation, CONAMA 357 (2005), states pH values for effluent discharges to be

Table 2 Physical and chemical analyses of the electrolytic treatment

	Conductivity (mS cm^{-1})	pH	Free residual chlorine (mg L^{-1})
T0	4.39	3.50	0.00
T3	4.37	3.75	1.77
T5	4.37	3.82	1.77
T15	4.37	3.98	3.55
T30	4.37	4.56	23.04
T40	4.36	6.07	63.81

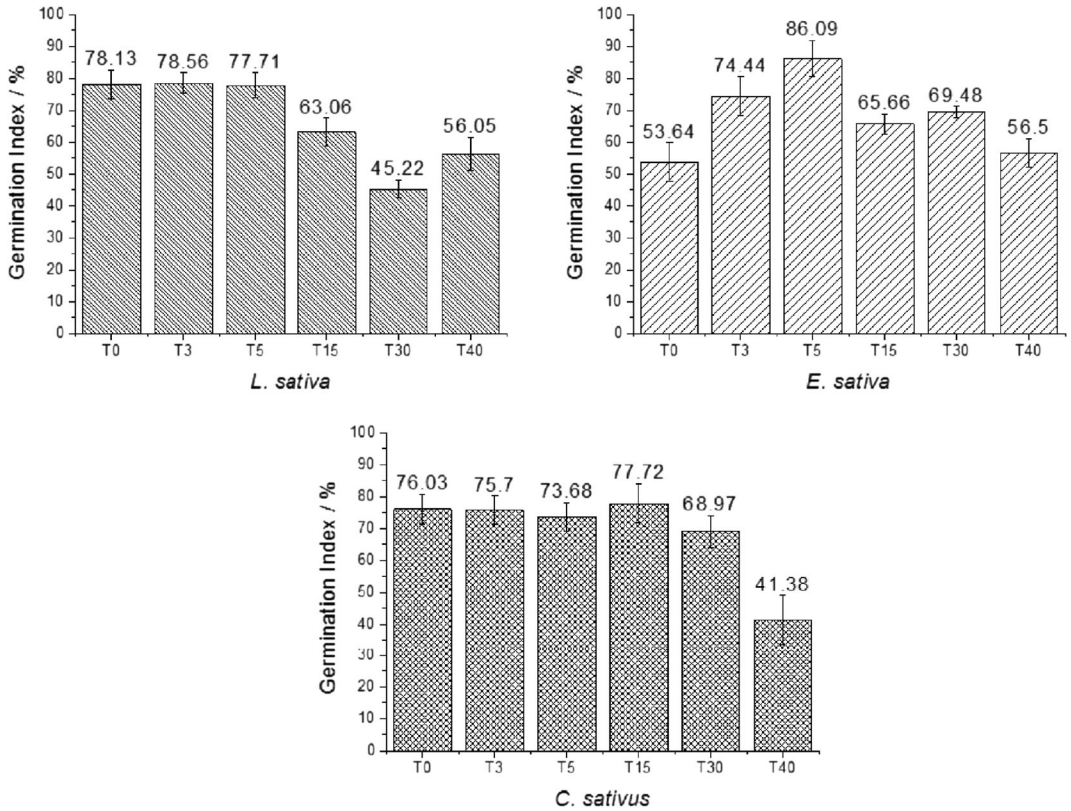

Fig. 2 Seed test results for electrolytic treatment of synthetic textile effluent containing Acid Blue 40 and Acid Red 151

in the range of 5.0 to 9.0. It is recommended to monitor pH values before discharge in water bodies.

Table 3 Statistical analyses by Kruskal-Wallis method (Dunn) for the electrolytic treatment

	L.sativa	*E. sativa*	*C.sativus*	*A.salina*	*S.cerevisiae*
T0–T3	n.s.	n.s.	n.s.	–	n.s.
T0–T5	n.s.	*p* value <0.05	n.s.	–	n.s.
T0–T15	n.s.	n.s.	n.s.	–	n.s.
T0–T30	n.s.	n.s.	n.s.	–	n.s.
T0–T40	n.s.	n.s.	n.s.	–	n.s.
T3–T5	n.s.	n.s.	n.s.	–	n.s.
T3–T15	n.s.	n.s.	n.s.	–	n.s.
T3–T30	n.s.	n.s.	n.s.	–	n.s.
T3–T40	n.s.	n.s.	n.s.	–	n.s.
T5–T15	n.s.	n.s.	n.s.	–	n.s.
T5–T30	n.s.	*p* value <0.05	n.s.	–	n.s.
T5–T40	n.s.	*p* value <0.05	n.s.	–	n.s.
T15–T30	n.s.	n.s.	n.s.	–	n.s.
T15–T40	n.s.	n.s.	n.s.	–	n.s.
T30–T40	n.s.	n.s.	n.s.	–	n.s.

n.s. not significant

The electrolytic process generated free chlorine during the electrolytic treatment (Table 2). The free chlorine not only assists in disinfection, but it is also an important participant of the indirect electrolytic process in degrading the colour of effluent (Rajkumar and

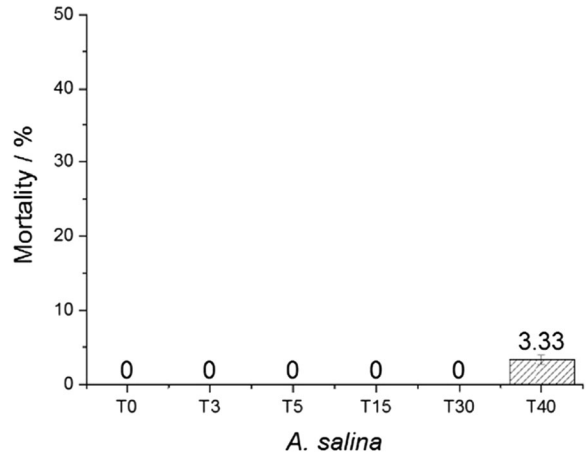

Fig. 3 *A. salina* results for electrolytic treatment of synthetic textile effluent containing Acid Blue 40 and Acid Red 151

Palanivelu 2004). As recommended by USEPA (2002), sodium thiosulfate was added to samples in order to neutralize the oxidative action of the free chlorine before the realization of the ecotoxicological tests.

The electrolytic treatment presented low toxicity for the bioassays with *L. sativa*, according to Fig. 2. The samples collected at 30 and 40 min of treatment (T30 and T40) presented inferior germination index results. According to Table 2, those samples presented higher free chlorine concentrations in which more sodium thiosulfate was added to neutralize its oxidative characteristics. As Bliss et al. (1986) stated, high concentrations of salts in soil are toxic and can inhibit seeds germination. Table 3 presents no significant statistical differences among samples of *L. sativa* ecotoxicological test. The test with *E. sativa* presented better germination index at 5 min of treatment, according to Fig. 2. As observed in Table 3, there was significant statistical difference between T0 and T5. Statistical differences were also observed between 5 to 30 min and 5 to 40 min of treatment, according to Table 3. This indicated that the electrolytic treatment minimized the toxicity of the initial effluent until 15 min of treatment (T15) for this species. The bioassay with *C. sativus* indicated lower germination index for the T40 sample (40 min of treatment), as seen in Fig. 2. In this case, the same situation observed for *L. sativa* happened with *C. sativus*, in which the higher amount of salt (sodium thiosulfate) added restrained the germination. According to Table 3, there were no significant statistical differences among samples of *C. sativus* bioassay.

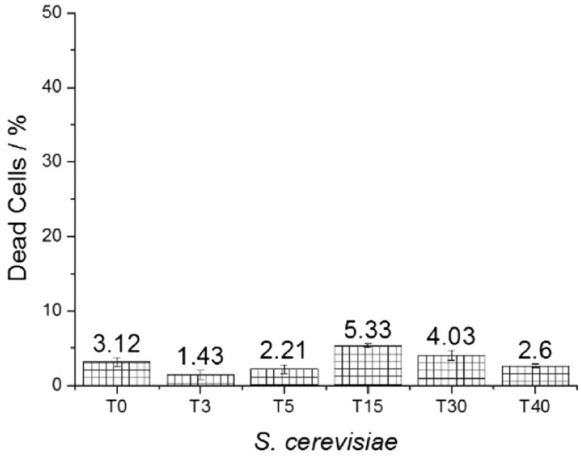

Fig. 4 *S. cerevisiae* results for electrolytic treatment of synthetic textile effluent containing Acid Blue 40 and Acid Red 151

As observed in Fig. 3, the test with *A. salina* presented low toxicity for the electrolytic treatment. Tests with a similar micro crustaceous, *Daphnia magna*, presented a very low tolerance of the organism for free residual chlorine (Oh et al. 2007). Thus, the addition of sodium thiosulfate was effective in minimizing the oxidative nature of the free residual chlorine. It was not possible to analyze statistically the test due to the low toxicity found.

The bioassay with the yeast *S. cerevisiae* presented low toxicity for the electrolytic treatment, according to Fig. 4. Both the electrolytic treatment and the free residual chlorine interaction with sodium thiosulfate were not toxic for the yeast. As presented in Table 3, there were no significant statistical differences for this test.

4 Conclusion

The electrolytic treatment was successful in degrading the colour of the synthetic textile effluent. The final pH value should be addressed for adjustment in compliance with environmental legislation for discharge in water bodies. Seeds of *E. sativa* presented toxicity for the treatment after 15 min of the electrolytic treatment. The ecotoxicological tests in general presented low toxicity for the electrolytic treatment in the conditions tested with the addition of sodium thiosulfate to minimize the chlorine oxidation effects. The study concluded that 15 min of treatment was enough to degrade all the initial colour of the textile effluent and toxicity was low until 15 min.

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