

Electrochemical treatment of textile dyes and dyehouse effluents

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Abstract

The electrochemical oxidation of textile effluents over a titanium–tantalum–platinum–iridium anode was investigated. Batch experiments were conducted in a flow-through electrolytic cell with internal recirculation at current intensities of 5, 10, 14 and 20 A, NaCl concentrations of 0.5, 1, 2 and 4% and recirculation rates of 0.81 and 0.65 L/s using a highly colored, synthetic effluent containing 16 textile dyes at a total concentration of 361 mg/L and chemical oxygen demand (COD) of 281 mg/L. Moreover, an actual dyehouse effluent containing residual dyes as well as various inorganic and organic compounds with a COD of 404 mg/L was tested. In most cases, quantitative effluent decolorization was achieved after 10–15 min of treatment and this required low energy consumption; conversely, the extent of mineralization varied between 30 and 90% after 180 min depending on the operating conditions and the type of effluent. In general, treatment performance improved with increasing current intensity and salinity and decreasing solution pH. However, the use of electrolytes not containing chloride (e.g. FeSO₄ or Na₂SO₄) suppressed degradation. Although the acute toxicity of the actual effluent to marine bacteria *Vibrio fischeri* was weak, it increased sharply following treatment, thus suggesting the formation of persistent toxic by-products.

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1. Introduction

Color is one of the most obvious indicators of water pollution and the discharge of highly colored effluents containing dyes can be damaging to the receiving bodies [1]. Of these, textile effluents typically have strong color due to unfixed dyes, as well as they are biorecalcitrant due to the presence of various auxiliary chemicals such as surfactants, fixation agents, bleaching agents, etc. [2]. The degree of dye fixation to fabrics depends on the fiber, depth of shade and mode of application and, depending on the dye, 2–50% of unfixed dye can enter the waste stream [2]. Reactive dyes are usually found at relatively high concentrations in wastewaters due to their low fixation especially to fibers such as cotton and viscose.

Dye molecules often receive the largest attention due to their color, as well as the toxicity of some of the raw materials used to synthesize dyes (e.g. certain aromatic amines), although dyes are often not the largest contributor to the textile wastewater [3].

Dyes concentration in effluents is usually lower than any other chemical found in these wastewaters, but due to their strong color they are visible even at very low concentrations, thus causing serious aesthetic problems in wastewater disposal [4]. Therefore, methods for decolorization of textile effluents have received considerable attention in recent years. Chemical precipitation, adsorption on activated carbon and natural adsorbents, as well as several advanced oxidation processes have been employed for the treatment of textile effluents. Of the latter, ozonation, photocatalytic oxidation, Fenton and photo-Fenton oxidation, ultraviolet (UV) irradiation and electrochemical oxidation have been reported in the literature as effective means for the treatment of synthetic and actual textile effluents [5,6].

Electrochemical technologies such as electrooxidation, electrocoagulation and electroflotation have been widely used in water and wastewater treatment and several applications have been recently reviewed elsewhere [7]. Electrooxidation over anodes made of graphite, Pt, TiO₂, IrO₂, PbO₂, several Ti-based alloys and, more recently, boron-doped diamond electrodes in the presence of a supporting electrolyte (typically NaCl) has been employed for the decontamination of various industrial effluents.

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Several recent studies report the use of electrooxidation to treat model aqueous solutions containing various dyes. Rajkumar et al. [8] studied the electrochemical degradation of Reactive Blue 19 over a titanium-based dimensionally stable anode regarding the effect of operating conditions (current density, salinity, reaction temperature and initial dye concentration) on treatment performance, while they also identified major reaction intermediates. The effect of various operating conditions on Acid Blue and Basic Brown degradation over a lead/lead oxide anode and on Acid Orange 7 degradation over a boron-doped diamond anode was studied by Awad and Abo Galwa [9] and Fernandes et al. [10], respectively. Basic Yellow 28 and Reactive Black 5 were used as test substances to compare the efficiency of a diamond electrode to that of conventional metallic electrodes (iron, aluminium and copper) [11], while an activated carbon fiber electrode was used to assess the electrochemical degradability of 29 different textile dyes [12]. In further studies [13], several advanced oxidation processes, namely wet oxidation, TiO₂ photocatalysis, electro-Fenton and UV-assisted electro-Fenton were compared concerning their efficiency in treating Reactive Black 5.

Despite the relatively large number of papers dealing with the electrochemical degradation of model aqueous solutions of dyes, appreciably fewer reports regarding the treatment of actual effluents are available. Lin and Peng [14] developed a continuous process comprising coagulation, electrochemical oxidation and activated sludge to treat textile effluents. The effect of changing operating conditions such as coagulant concentration, solution pH, current density, number of electrodes, residence times in electrochemical and biological reactors on treatment efficiency was thoroughly investigated and optimal conditions were established. In further studies, Vlyssides et al. [15] investigated the electrooxidation of textile effluents over a Ti–Pt electrode at different chloride concentrations and reported that electrochemical treatment improved the biotreatability (as assessed by the BOD/COD ratio) of the original effluent. Naumczyk et al. [16] compared the decolorization and mineralization rates of textile effluent electrochemical degradation over three Ti-based electrodes coated with different metals and they also attempted to identify major reaction by-products. In a recent work, Sakalis et al. [17] demonstrated a continuous, pilot-scale cascade electrochemical reactor capable of achieving 90% decolorization of a textile effluent at a residence time of 40 min.

The aim of this work was to investigate the electrochemical treatability of both complex synthetic and actual textile effluents over a Ti–Ta–Pt–Ir anode regarding the effect of varying operating conditions such as current, type and initial concentration of electrolyte and solution pH on decolorization, reduction of COD and energy consumption. The effect of treatment on effluent acute ecotoxicity to marine bacteria *Vibrio fischeri* was also investigated.

2. Materials and methods

2.1. Synthetic effluent

The synthetic effluent (SE) used in this study is a mixture of 16 dyes with a total concentration of 361 mg/L. The contribution

Table 1
Composition of effluents used in this study

Component	Synthetic effluent	Actual effluent
Remazol Black B	159 (44)	nd
Remazol Red RB	37.3 (10.3)	nd
Remazol Golden Yellow RNL	20.3 (5.6)	nd
Cibacron Black WNN	94.2 (26.1)	nd
Cibacron Red FN-R	0.1 (<0.1)	nd
Cibacron Blue FN-G	0.6 (<0.1)	nd
Drimaren Red K-8B	6.7 (1.9)	nd
Drimaren Scarlet K-2G	9.4 (2.6)	nd
Drimaren Yellow K-2R	12.1 (3.3)	nd
Drimaren Navy K-BNN	5.6 (1.6)	nd
Drimaren Yellow K-4G	12 (3.3)	nd
Drimaren Orange X-3LG	0.1 (<0.1)	nd
Drimaren Blue X-3LR	0.05 (<0.1)	nd
Drimaren Violet K-2RL	0.3 (<0.1)	nd
Drimaren Red K-4BL	0.4 (0.1)	nd
Drimaren Blue K-2RL	2.6 (0.7)	nd
Total dye content	360.8 (100)	nd
Organic auxiliary chemicals	0	nd
Na ₂ SO ₄	0	5500
Na ₂ CO ₃	0	440
NaOH	0	110
COD	281	404
Total solids	0	75
pH	7.5	9.5
Absorbance (au)	5.5	0.25
EC ₅₀ (%)	4.1	75

Concentrations are quoted in mg/L. Numbers in brackets show percent dye composition in the synthetic effluent; nd, not determined.

of each dye to the total dye content is shown in Table 1 and this composition was chosen to match exactly the percent composition of the actual dyestuff. All dyes were kindly provided by EPILEKTOS SA, a textile manufacturing industry located in the region of Sterea, Central Greece. The effluent is near-neutral, strongly colored and highly ecotoxic with a COD content of 281 mg/L.

2.2. Actual effluent

The actual effluent (AE) used in this study was provided by EPILEKTOS SA and it was used as received without any pretreatment. The dyeing process through which the effluent was generated is shown in Fig. 1. The cotton fiber is first mercerized and bleached using NaOH, H₂O₂ and other bleaching agents and then rinsed with water prior to dyeing. The dyestuff consists of about 200 kg of 16 dyes (whose percent composition is shown in Table 1) in 30 m³ water to dye 3 tonnes of cotton fibers and is also added large amounts of inorganic salts. Following dyeing, the fiber is washed several times with water and detergents in consecutive baths and finally undergoes fixation and softening. Waste streams from the various baths are collected in an equalization tank where the effluent used in this study was taken from. It consists of residual dyes, NaOH, inorganic salts (Na₂SO₄ and Na₂CO₃) and various organic components such as detergents, softening, dispersing and fixing agents (collectively referred to as organic auxiliary chemicals in Table 1). The effluent is highly alkaline, with a dark

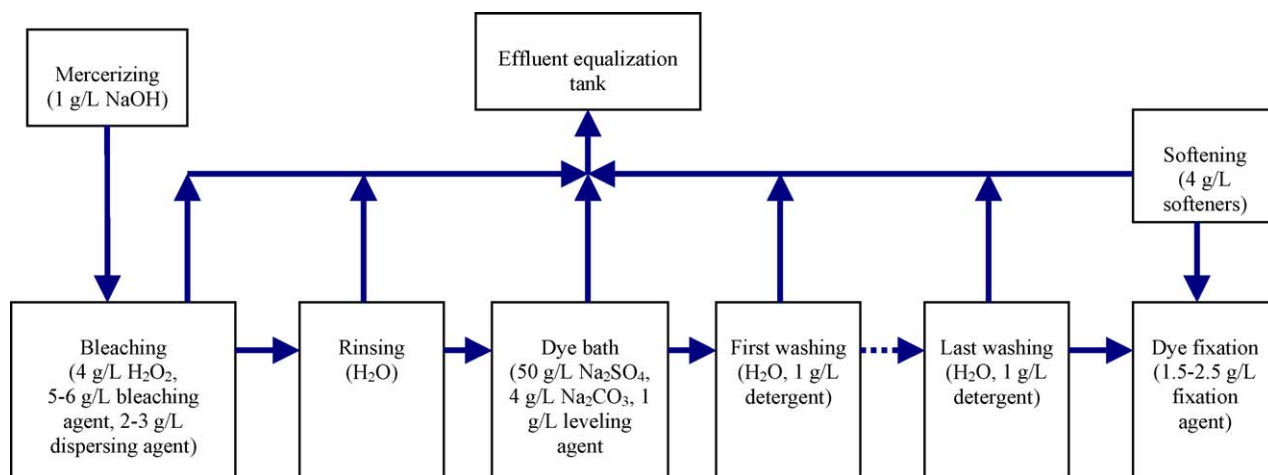


Fig. 1. Flowsheet of the process generating the actual effluent used in this study.

green-blue color and partially ecotoxic with a COD content of 404 mg/L.

2.3. Electrochemical degradation experiments

Experiments were conducted in an electrolytic cell comprising a stainless steel 316L cathode, a titanium (grade II/VII) anode covered by a thin film of tantalum, platinum and iridium alloy and the power supply unit. The cathode was a 5 cm in diameter and 12 cm long hollow cylinder in the center of which was housed the anode which, in turn, was 11 cm long with a diameter of 3 cm. In a typical run, the effluent was mixed with the appropriate amount of NaCl (or other electrolyte), batch loaded in a vessel and continuously pumped in the cell through a pump at a recirculation flowrate of 0.81 L/s (unless otherwise stated), thus maintaining near-perfect mixing; the rate could be adjusted to the desired value through a series of valves. The current intensity was then set to the desired value and the voltage was automatically regulated to match the current value. In all cases, the working volume was 8 L. A spiral coil immersed in the liquid and connected to tap water supply was used to remove the heat liberated from the reaction. All runs were conducted at ambient temperature which remained practically constant throughout the experiment at 26 ± 1 °C. Most of the runs were performed at effluent's ambient pH which was monitored throughout the reaction with a Toledo 225 pH meter. For those experiments where the starting solution pH was adjusted to acidic conditions, the appropriate volume of H₂SO₄ was added in the effluent. A schematic of the experimental configuration is shown in Fig. 2.

2.4. Analytical measurements

The extent of decolorization that had occurred during electrochemical treatment was assessed measuring sample absorbance on a Shimadzu UV 1240 spectrophotometer. For the synthetic and actual effluents, absorbance was measured at $\lambda_{\max} = 595 \pm 5$ nm. Prior to the measurement, the actual effluent was centrifuged for 15 min to remove any particles present in the sample. In those cases where model aqueous solutions

of four major dyes were employed, absorbance was measured at each dye's λ_{\max} ; this was 411, 542, 593 and 597 nm for Remazol Golden Yellow RNL, Remazol Red RB, Cibacron Black WNN and Remazol Black B, respectively.

COD was determined by the dichromate method. The appropriate amount of sample was introduced into commercially available digestion solution containing potassium dichromate, sulfuric acid and mercuric sulfate (Hach Europe, Belgium) and the mixture was then incubated for 120 min at 150 °C in a COD reactor (Model 45600-Hach Company, USA). COD concentration was measured colorimetrically using a DR/2010 spectrophotometer (Hach Company, USA).

2.5. Acute toxicity

The luminescent marine bacteria *V. fischeri* was used to assess the acute ecotoxicity of textile wastewater samples prior to and

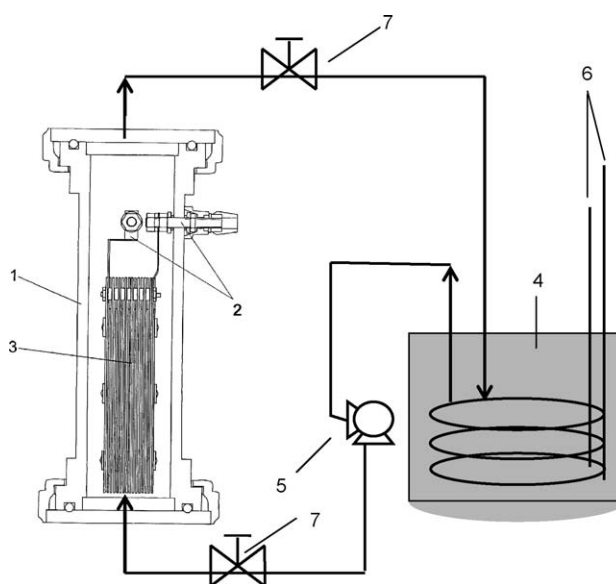


Fig. 2. Schematic of the experimental configuration. (1) Cathode, (2) power supply, (3) anode, (4) OMW feed tank, (5) peristaltic pump, (6) coil for cooling water and (7) valves.

after treatment. The inhibition of bioluminescence of *V. fischeri* exposed to untreated and treated dyehouse wastewater samples for 15 min at 15 °C was measured using a LUMISTox analyzer (Dr. Lange, Germany) and the results were compared to an aqueous control. Toxicity is expressed as EC₅₀, which is the effective concentration of a toxicant causing 50% reduction of light output during the designated time intervals at 15 °C. For each sample, its EC₅₀ value was determined by applying several dilutions.

3. Results and discussion

3.1. Effect of NaCl concentration on COD measurement

The standard COD measurement is known to be affected by a number of inorganic substances which are outlined in the Standard Methods for the Examination of Water and Wastewater [18]. Of these, chloride may have a significant positive effect on the test which is due to its reaction with potassium dichromate as follows:



The commercially available COD digestion solutions used in this study counterbalance chloride interference at chloride concentrations up to 0.2% due to the presence of mercuric sulfate. However, this concentration is usually lower than that used in electrochemical degradation experiments; therefore, it was decided to estimate the effect of salinity on the COD test. This was done by measuring the COD content of effluents at various NaCl concentrations up to 4% as well as without NaCl. It was found that the discrepancy between the measured COD values with and without salt (COD₁ and COD₂, respectively) increased linearly with percent salinity (*S*) as follows:

$$\left(\frac{\text{COD}_1 - \text{COD}_2}{\text{COD}_1} \right) = \begin{cases} 0 & \text{for } S \leq S_{\text{ref}} \\ 0.18S + 0.01 & \text{for } S > S_{\text{ref}} \end{cases} \quad (2)$$

where *S*_{ref} corresponds to the maximum chloride concentration that is compensated due to the presence of mercury sulfate, i.e. 0.2%. Eq. (2) was used to account for the effect of chloride interference on COD measurement. The corrected values were then used to compute process efficiency in terms of specific energy consumption, anode efficiency and current efficiency.

3.2. Effect of operating conditions on treatment

Fig. 3 shows the effect of varying salinity on effluent decolorization as a function of treatment time at 5 A current and ambient solution pH. Increasing salinity from 0.5 to 1–4% increased decolorization from 39 to 50–70%, respectively, after 5 min of reaction with the synthetic effluent. An additional experiment was carried out with the synthetic effluent at 0% salinity; the salt-free solution exhibited no conductivity at the maximum operating output of the power supply (i.e. 25 V). The experiment was then repeated implementing a stepwise addition of 0.05% NaCl every 30 min and the results are also shown in Fig. 3. For instance, the effluent was first added 0.05% salt and left to react for 30 min; although conductivity was very low

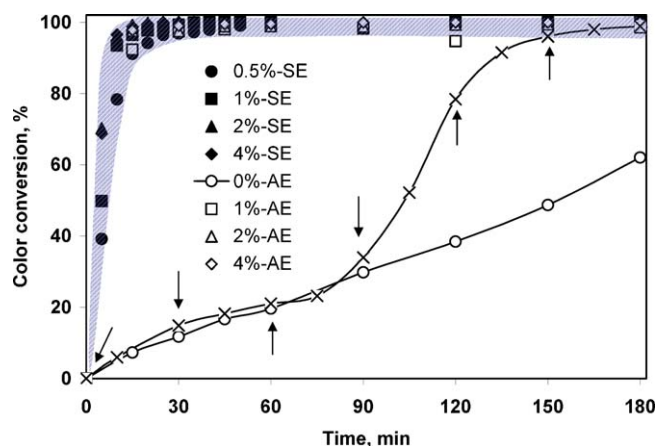


Fig. 3. Effect of salinity on color conversion for synthetic (SE) and actual (AE) effluents at 5 A and ambient solution pH. (X) shows run with SE at reduced salinity varying from 0.05 to 0.3%, with arrows showing periods of NaCl addition.

resulting in 1 A at 25 V, about 15% decolorization occurred at the end of this period. The effluent was then added an extra 0.05% salt and left to react for another 30 min (2 A at 25 V) leading to a total of 21% decolorization after 60 min. This procedure was repeated six times clearly showing the beneficial effect of adding NaCl on effluent decolorization. However and with the exception of the synthetic effluent at salinity values equal to or lower than 0.5% and the actual effluent at 0% salinity, in all other cases color removal became quantitative (e.g. >95%) within 10–15 min of reaction. For the run with the actual effluent in the absence of NaCl, decolorization proceeded slowly reaching a final value of about 60% after 180 min of reaction. Na₂SO₄, Na₂CO₃ and NaOH, all found in the actual effluent at considerable concentrations, serve as the supporting electrolytes to induce electrochemical degradation. However, addition of sodium chloride drastically increased decolorization. Several previous studies have shown the superiority of NaCl over Na₂SO₄ and other electrolytes (e.g. NaOH and H₂SO₄) for the treatment of dye-containing solutions [8–10,17,19].

The effect of changing current on color removal and COD conversion during the electrochemical treatment of synthetic and actual effluents at 0.5 and 4% salinity, respectively, is shown in Fig. 4. Increasing current from 5 to 10–14 A improved decolorization from 39 to 68–87%, respectively, after 5 min with the synthetic effluent. Other than the early stages of the reaction, the applied current, at the conditions employed in this study, does not seem to be critical to decolorization since quantitative removal could be achieved within 10–15 min of reaction; for instance, over 98% color removal occurred after 15 min with the actual effluent regardless the applied current. Conversely, COD conversion appreciably increased with increasing current and this was more pronounced for the run with the synthetic effluent. For instance, the final COD reduction for the synthetic effluent was 55, 65 and 86% at 5, 10 and 14 A, respectively; these values for the actual effluent became 29, 34 and 39% at 5, 10 and 20 A, respectively. The fact that decolorization occurs at substantially greater rates than COD conversion implies that electrochemical degradation by-products are more resistant to

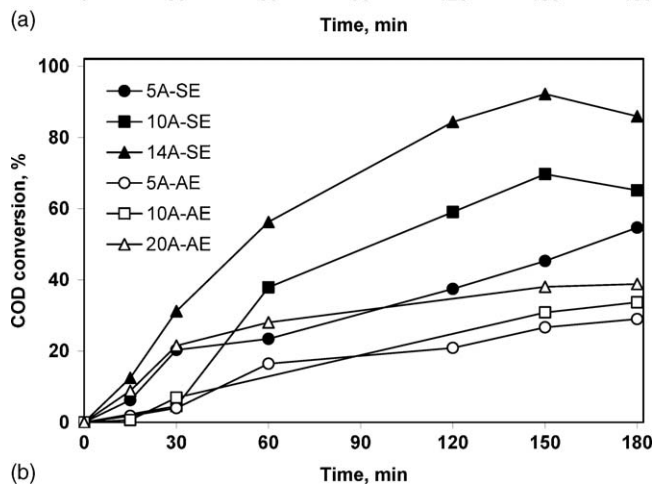
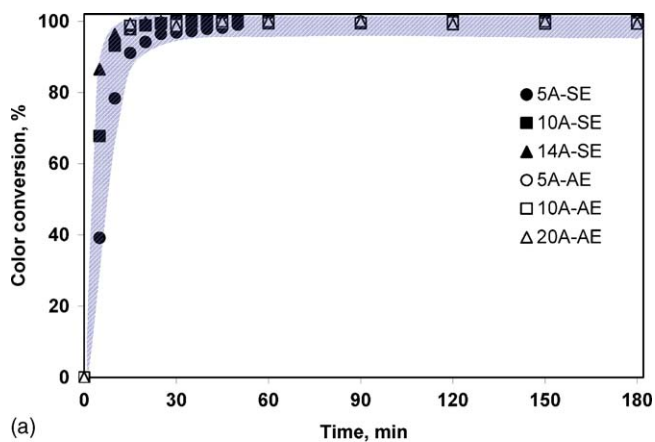


Fig. 4. Effect of current on: (a) color and (b) COD conversion for synthetic (SE) and actual (AE) effluents at 0.5 and 4% salinity, respectively, and ambient solution pH.

electrooxidation than the original dyes; this is readily deduced from the runs with the synthetic effluent whose starting organic content consists exclusively of dyes. Similar results regarding the relative rates of electrochemical decolorization and mineralization have also been reported by several other investigators [9,10,12,16].

It is also interesting to note that the actual effluent is strongly resistant to mineralization and this is possibly due to the presence of persistent organic auxiliary chemicals rather than unoxidized dyes and their degradation by-products. Although the concentration of residual dyes in the actual effluent is not known, a rough estimate can be made based on the absorbance values of the actual and synthetic effluents and the known dye content of the latter. As seen from Table 1, the dye content of the actual effluent should not exceed 15–20 mg/L; consequently, most of the organic content originally present in the actual effluent is due to compounds other than the dyes. The discrepancy between the recorded levels of mineralization becomes even greater bearing in mind that electrochemical oxidation experiments with the actual effluent were conducted at 4% salinity, while those with the synthetic one at 0.5%. However, it should be pointed out that these discrepancies may, to some degree, be due to the different water matrices of the two effluents.

To test the effect of solution pH on treatment, experiments were conducted at pH values of 3 and 6 and the results are shown

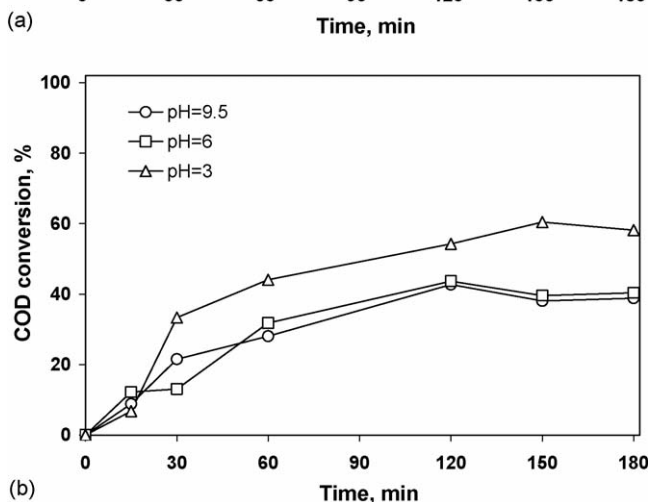
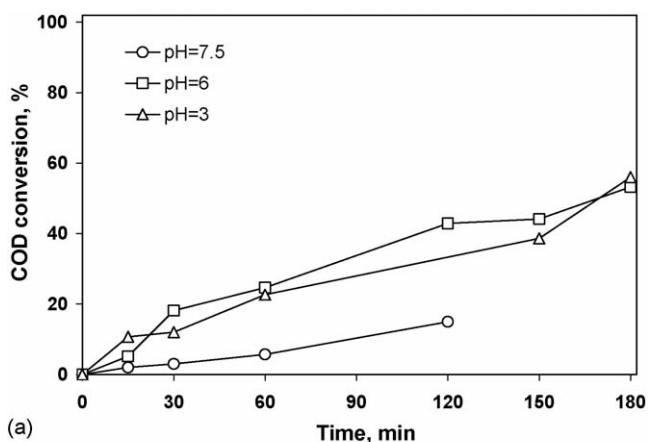


Fig. 5. Effect of pH on COD conversion for: (a) synthetic (5 A and 1% salinity) and (b) actual (20 A and 4% salinity) effluents.

in Fig. 5. As seen, acidic conditions appear to favor COD conversion for both actual and synthetic effluents. On the other hand, color removal was not affected by varying solution pH as, in all cases, complete decolorization was achieved within 10–15 min (data not shown). It should be mentioned here that, since the solutions were not buffered, pH progressively recovered from acidic to alkaline conditions presumably due to the formation of hydroxyl anions in the solution, thus partly masking the effect of pH on degradation. However, it is well-documented [20,21] that pH does not have a significant effect on the electrochemical degradation of organics over titanium anodes in the range 3–10. Ceron-Rivera et al. [11] reported that the rate of electrochemical degradation of Reactive Black 5 over an iron anode at pH 5.5 was as much as four times faster than that at pH 7.5, while Awad and Abo Galwa [9] found that the electrochemical oxidation of Acid Blue and Basic Brown over a lead/lead oxide anode was favored at pH 2–3 but strongly suppressed at pH 12. Lin and Peng [14] reported that treatment performance (in terms of COD decrease) of an actual textile effluent over an iron anode was maximized at neutral conditions but it deteriorated at alkaline conditions.

In further experiments, the effect of two iron-containing electrolytes, namely ferric chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) and ferrous sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) on treatment efficiency was investigated. The rationale behind the use of these electrolytes is that iron can serve as an effective homogeneous catalyst to degrade organic

Table 2

Percent color conversion during the electrochemical treatment of model solutions of four dyes at 5 A and 0.5% salinity

Treatment time (min)	Remazol Black B	Remazol Red RB	Remazol Golden Yellow RNL	Cibacron Black WNN
0	0 (4.5)	0 (9.5)	0 (2)	0 (6)
5	84.7	53	55.9	81.2
10	96.7	96.8	75.5	92.6
15	98.8	99.4	84.5	96
30	99.7 (0.6)	99.8 (0.4)	90.2 (1)	99.7 (1)

Initial dye concentration: 160 mg/L. Numbers in brackets show EC₅₀ values (%) for each dye.

compounds as well as reduce hydrogen peroxide to hydroxyl radicals, thus simulating Fenton-type reactions. The synthetic effluent was treated at 5 A in the presence of 0.77% FeCl₃; this corresponds to chloride concentration in the reaction mixture equal to that of 0.5% NaCl. Treatment performance with ferric chloride, in terms of color and COD removal, was similar to that with NaCl at a common chloride concentration. Complete decolorization occurred within 15–30 min and this was accompanied by a final (i.e. after 180 min) COD reduction of about 50–60%. An additional experiment was performed with 0.79% FeSO₄; this corresponds to iron concentration equal to that of 0.77% FeCl₃. Degradation was slow yielding only about 26 and 85% color removal after 30 and 180 min of reaction with the final COD removal being only 10%, thus highlighting the beneficial role of chloride as an oxidizing agent. It should be mentioned that addition of FeCl₃ or FeSO₄ in the effluent resulted in partial iron precipitation and this was accompanied by a substantial pH decrease from 7.5 to 2–3; this value remained practically constant throughout the experiment.

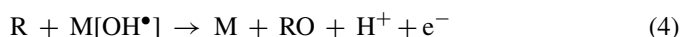
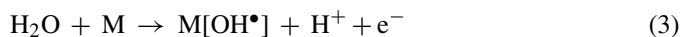
To assess the effect of flowrate on treatment, experiments with the synthetic and actual effluents were performed at 0.5% NaCl and 10 A and 4% NaCl and 20 A, respectively, and a reduced recirculation rate of 0.65 L/s. Decreasing recirculation had practically no impact on color removal which was quantitative within 10–15 min in either case; however, the final extent of COD conversion mildly decreased by about 10%. This can be explained by the combined effect of: (a) decreased production of oxidants and (b) the fact that a smaller number of organics flow through the cell in a single pass, both of which occur at reduced flow-through velocities [22,23].

In a final set of experiments, the four dominant, in terms of concentration, dyes found in the effluent were separately oxidized electrochemically at an initial concentration of 160 mg/L. As seen in Table 2, all but Remazol Golden Yellow RNL were completely decolorized within 10–15 min. The chemical formulae of the major dyes are shown in Fig. 6; Remazol Black B (also referred to as Reactive Black 5) is a diazo dye with two vinyl sulfone reactive groups, while Golden Yellow RNL (also referred to as Reactive Orange 107) is a vinyl sulfone-based monoazo dye. On the other hand, Remazol Red RB (also referred to as Reactive Red 198) is a heterobifunctional monoazo dye with both a vinyl sulfone and a monochlorotriazine reactive group, while Black WNN (not shown in Fig. 6) is a proprietary mixture of several azo dyes. The initial rate of Remazol Black 5 decolorization seems to be greater than that of Remazol Red RB and Golden Yellow RNL possibly due to the existence of two chromophore N=N bonds. Sakalis et al. [17] studied the

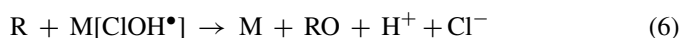
electrochemical oxidation of 450 mg/L Reactive Black 5 over a Ti–Pt anode at about 0.1% salinity and reported quantitative decolorization after about 120 min of reaction. Kusvuran et al. [13] reported that the rate of Reactive Black 5 degradation over a Pt anode in the presence of iron ions was strongly dependent on the initial dye concentration; at 100 mg/L dye concentration and 20 mg/L iron concentration, only about 40% decolorization occurred after 30 min of reaction.

3.3. Electrochemical degradation mechanisms

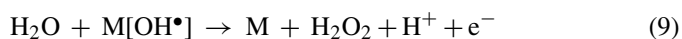
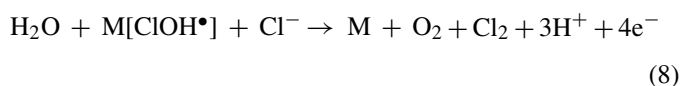
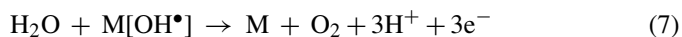
Two mechanisms are thought to be responsible for organic matter (R) electrochemical degradation, namely: (a) direct anodic oxidation where the pollutants are adsorbed on the anode surface (M) and destroyed by the anodic electron transfer reaction and (b) indirect oxidation in the liquid bulk which is mediated by the oxidants that are formed electrochemically; such oxidants include chlorine, hypochlorite, hydroxyl radicals, ozone and hydrogen peroxide. Anodic water discharge results in the formation of hydroxyl radicals that are adsorbed on the anode surface and can then oxidize the organic matter [22,24]:



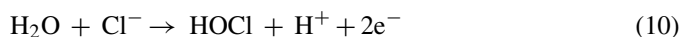
In the presence of NaCl, chlorohydroxyl radicals are also formed on the anode surface and then oxidize the organic matter:



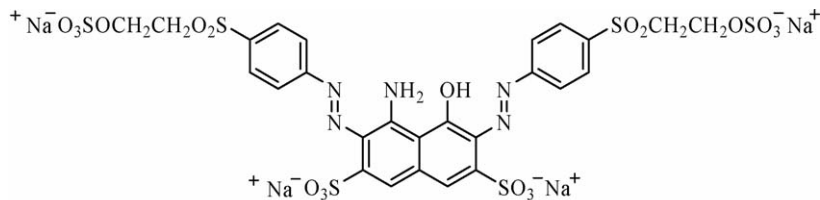
Reactions between water and radicals near the anode can yield molecular oxygen, free chlorine and hydrogen peroxide:



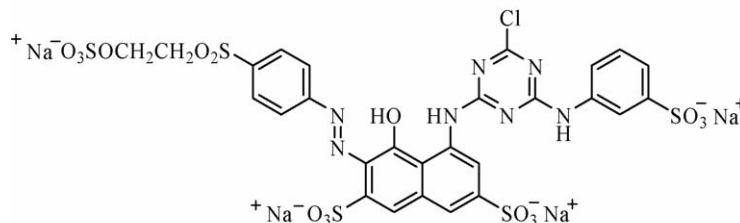
Furthermore, hypochlorite can be formed as follows:



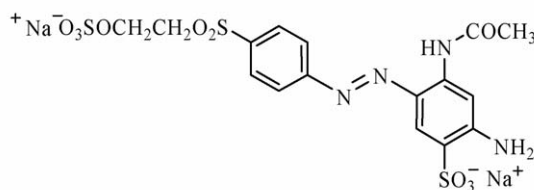
Therefore, direct anodic oxidation through reactions (4) and (6) results in reduced COD as well as the formation of primary oxidants such as oxygen, chlorine, hypochlorite and hydrogen peroxide. Free chlorine and oxygen can further react on the



Remazol Black B, C.I. Reactive Black 5



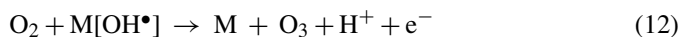
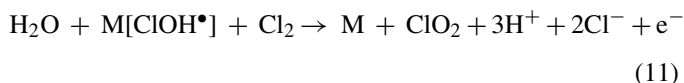
Remazol Red RB, C.I. Reactive Red 198



Remazol Golden Yellow RNL, C.I. Reactive Orange 107

Fig. 6. Chemical formulae of the major dyes used in this study.

anode yielding secondary oxidants such as chlorine dioxide and ozone, respectively:



The presence of Na_2SO_4 and other sulfate-containing electrolytes in the reaction mixture leads to the formation of SO_2 (especially in acidic media) which is a moderate reductant [17]. Primary and secondary oxidants are quite stable and migrate in the solution bulk where they indirectly oxidize the effluent. The efficiency of direct oxidation depends on the anode activity, the diffusion rate of organics on the anode surface and the applied current density. On the other hand, the efficiency of indirect oxidation depends on the diffusion rate of oxidants in the solution and the pH value [24]. At acidic conditions, free chlorine is the dominant oxidizing agent, while at slightly alkaline conditions hypochlorite, chloride ions and hydroxyl radicals are all important. Most of the experiments in this study were performed at ambient pH which was alkaline for both effluents; given that pH typically varied throughout the course of the reaction between 7.5 and 8.5 for the runs with the synthetic effluent and 9 and 9.5 for the runs with the actual one implies that indirect oxidation might have proceeded through various oxidants.

3.4. Energy consumption

Electrochemical treatment is undoubtedly an energy-intense process and its efficiency is usually assessed in terms of specific energy consumption (SEC). This is defined as the amount of energy consumed per unit mass of organic load (e.g. dye or COD) removed. Alternatively, treatment performance may be expressed in terms of anode efficiency, i.e. the mass of organic load removed divided by the electrode area, the applied current and the treatment time. Representative temporal profiles of cumulative SEC and anode efficiency with respect to dye removal during the electrochemical treatment of synthetic and actual effluents are shown in Fig. 7. Anode efficiency reached a maximum within 10–15 min of reaction and then sharply decreased presumably due to the rapid decolorization of both effluents.

Current efficiency (CE) is defined as the percentage of applied current utilized to reduce COD:

$$\text{CE} = \left(\frac{\text{COD}_0 - \text{COD}_t}{8It} \right) FV \quad (13)$$

where COD_0 and COD_t , respectively, refer to the starting and final COD values, I the applied current, F the Faraday constant, V the liquid volume and t is the treatment time.

Table 3 summarizes SEC values with respect to dye and COD removal as well as CE values for various runs with synthetic and actual effluents. Values of SEC with respect to dye degradation

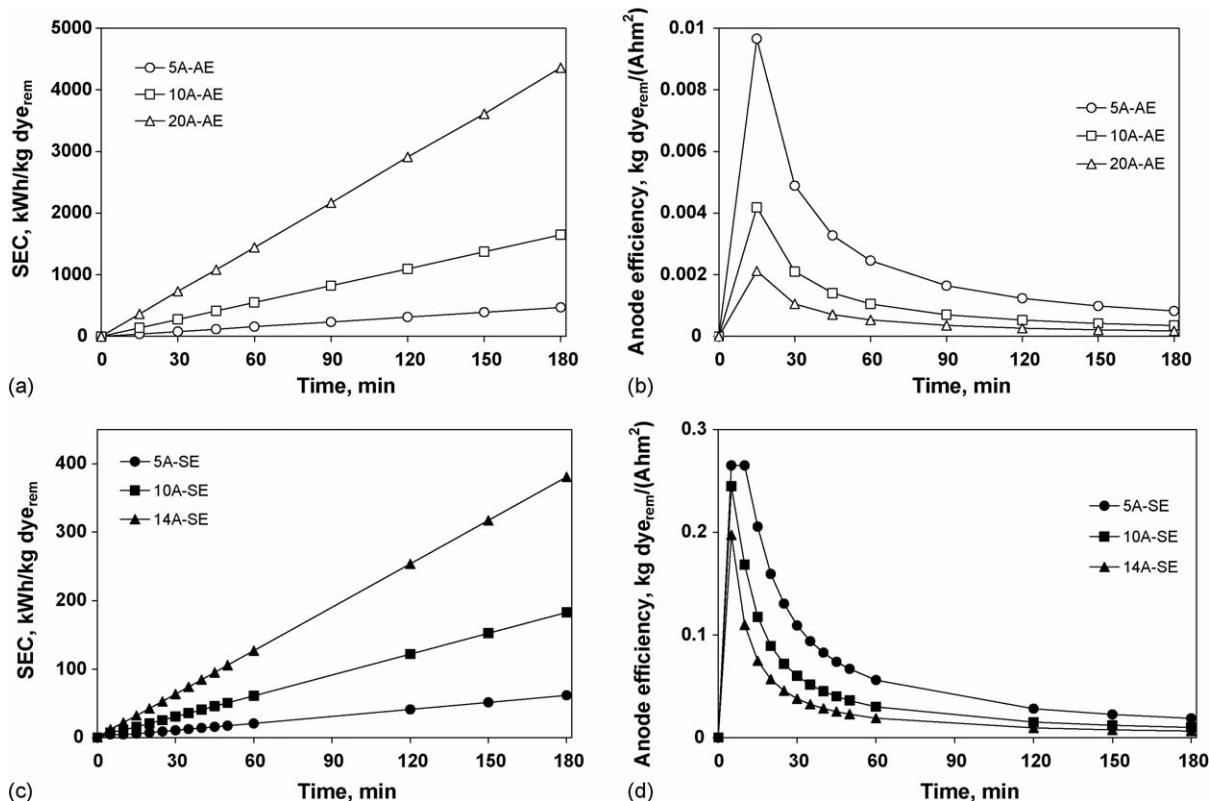


Fig. 7. Specific energy consumption (a and c) and anode efficiency (b and d) during the electrochemical treatment of synthetic (SE) and actual (AE) effluents at 0.5 and 4% salinity, respectively, and ambient solution pH.

were computed after 15 min of reaction given the fast effluent decolorization at the conditions employed in this study; conversely, SEC values for COD removal were computed after 180 min given the relatively low mineralization rates recorded. Likewise, CE values were computed after relatively long treatment times, i.e. 60 and 180 min. With the exception of run 10, dye degradation occurred readily and this is reflected to the relatively

low energy requirement for decolorization; for instance, electrochemical oxidation at 5 A would cost no more than €0.5/kg of dye removed for the complete decolorization of the synthetic effluent (based on €0.1/kWh). SEC for the decolorization of the actual effluent is far greater than that for the synthetic one (e.g. compare runs 2–4 with runs 11–13) since the latter is far more colored than the former. Nonetheless, the absolute energy

Table 3

Specific energy consumption (SEC), current efficiency (CE) and final toxicity (EC_{50}) during the electrochemical treatment of synthetic (runs 1–9) and actual (runs 10–16) effluents at various conditions

Run	Current (A)	Voltage (V)	Salinity (%)	pH	SEC _{15 min} (kWh/kg dye _{rem})	SEC _{180 min} (kWh/kg COD _{rem})	CE _{60 min} (%)	CE _{180 min} (%)	EC _{50–180 min} (%)
1	5	12	0.5	7.5	5.6	128	36.2	31.4	3.6
2	5	8	1	7.5	3.5	nd	nd	nd	nd
3	5	6	2	7.5	2.6	nd	nd	nd	nd
4	5	5	4	7.5	2.2	nd	nd	nd	nd
5	10	19	0.5	7.5	15.7	367.6	30.2	17.4	1
6	14	25	0.5	7.5	32.3	529.4	31.1	15.8	1.1
7	5	8	1	6	3.4	90.5	41.2	29.6	0.5
8	5	8	1	3	3	77.3	36.9	30.3	0.5
9	10	19	0.5	7.5	15.5	468	26.6	13	5.2
10	5	15	0	9.5	2651	nd	nd	nd	nd
11	5	6	1	9.5	61.4	nd	nd	nd	nd
12	5	5	2	9.5	48.1	nd	nd	nd	3
13	5	4	4	9.5	39.9	94.6	24.1	13.1	1
14	10	6	4	9.5	138.3	119	nd	16.9	1
15	20	8	4	9.5	363.7	488.5	11.9	5.5	0.3
16	20	8	4	9.5	434	594.5	8.3	4.5	0.2

Runs 9 and 16 were performed at a recirculation rate of 0.65 L/s, while the rest at 0.81 L/s; nd, not determined.

consumption for the actual effluent is lower than that for the synthetic one by about 25% since the former contains extra electrolytes in addition to NaCl. Increasing current intensity at constant salinity increased SEC for both dye and COD removal and for both effluents. For instance, increasing current from 5 to 14 A at 0.5% salinity (runs 1 and 6) nearly quadrupled SEC for COD removal, thus showing that an increase in COD conversion with current intensity (as shown in Fig. 4b) is accompanied by a proportionately greater increase in energy consumption. The cumulative energy consumption after 180 min of treatment was 0.18, 0.57 and 1.05 kWh at 5, 10 and 14, respectively, while the respective amount of COD removed was 1.4, 1.55 and 2 g. This is due to the fact that degradation by-products appear to be persistent to further electrochemical oxidation and possibly to the fact that some energy is wasted for the competing water electrolysis reaction that becomes dominant at higher current densities and relatively low organic concentrations [25]. Current efficiency was found to decrease with increasing treatment time, thus indicating energy waste to side reactions other than those contributing to COD decrease.

3.5. Effluent ecotoxicity

Several samples collected at the end of electrochemical treatment at various conditions were tested with respect to their acute ecotoxicity to *V. fischeri* and representative results are given in Tables 2 and 3. The original synthetic effluent is strongly toxic and this is obviously due to its high dye content; as seen in Table 2, Remazol Black B at a concentration equal to that found in the synthetic effluent has an EC₅₀ value as low as 4.5% and this is also the case with the other three major dyes. The toxicity of Reactive Black 5 to *V. fischeri* has also been demonstrated elsewhere [26]. On the other hand, the original actual effluent is only weakly toxic although it contains several organic and inorganic species that are not present in the synthetic effluent.

Although NaCl mediated electrochemical treatment was capable of degrading completely the dyes as well as reducing the total organic load, the final effluent was always very toxic and this is believed to be due to the formation of organochlorinated compounds as well as secondary residual oxidants that remained in the reaction mixture even after prolonged electrochemical oxidation. Toxicity remained high even after 180 min of synthetic effluent treatment at 14 A and 0.5% salinity, conditions that yielded nearly 90% COD removal (i.e. run 6 in Table 3 and Fig. 4b). Naumczyk et al. [16] reported that 80% of the 22 identified (by means of GC/MS analysis) organic compounds originally present in a textile effluent could be removed electrochemically over various Ti-based anodes (including a Ti–Pt–Ir one); however, this gave rise to the formation of 20 organochlorinated compounds most of which remained in the final effluent.

Increased toxicity was also recorded (data not shown) following treatment with FeCl₃ or FeSO₄ as the conducting electrolyte, implying that the presence of iron and/or other non-chlorinated organic by-products may also contribute to effluent toxicity. Kusvuran et al. [13] who studied the effect of electro-Fenton treatment of Reactive Black 5 on the growth of *Pseudomonas putida* reported that oxidation for 15 min increased sharply the

toxicity of the original solution which remained quite high even after 45 min of reaction.

4. Conclusions

The main conclusions drawn from this study can be summarized as follows:

- (1) Electrochemical oxidation is capable of destroying the chromophore groups of dyes found in textile effluents at short treatment times and low energy consumption. However, this is accompanied by a moderate degree of mineralization. Treatment efficiency, in terms of both conversion and specific energy consumption, is affected by the operating conditions employed, i.e. applied current, type and concentration of electrolyte and effluent pH. Moreover, the water matrix may also affect treatment since actual effluents usually contain large concentrations of several organic and inorganic species whose interference is not taken into account when synthetic model solutions of dyes are used instead of actual effluents.
- (2) Although the ecotoxicity of the untreated actual effluent to *V. fischeri* is weak, it sharply increases after electrochemical oxidation and this is ascribed to the formation of organochlorinated and other toxic by-products that are persistent to further oxidation.

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