

Chapter 31

Electrochemical Oxidation of Synthetic Dyes in Simulated Wastewaters

Electrochemical Oxidation of Dyes in Wastewaters

G. Gallios, X. Violintzis, I. Voinovskii, and A. Voulgaropoulos

Abstract An electrochemical oxidation method for the degradation of synthetic reactive azodyes found in textile wastewaters is discussed. Four commercial synthetic dyes (black, blue, red and yellow) commonly used in dyeing operations were studied in single, binary and ternary mixtures. Low (100 mg/L) and high (500, 1,000 and 2,000 mg/L) initial dye concentrations were studied. The effect of various sodium chloride concentrations (as supporting electrolyte) on the effectiveness of electrochemical oxidation was examined. The effect of current intensity (1.5, 2.5 and 3.0 A) and pH (values 3, 5, 7 and 10) was studied as well. The kinetics of the electrochemical oxidation for each dye were studied and compared. The conditions for effective dye degradation even from 2,000 mg/L initial concentration were established. The method was proved very effective even with binary and ternary mixtures of basic synthetic dyes. The Chemical Oxygen Demand (COD) and the Total Organic Carbon (TOC) were reduced by 60% and 25% respectively, meaning that the treated solutions were friendlier to the environment.

Keywords Synthetic dyes • Oxidation • Electrochemical • Removal • Wastewater

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31.1 Introduction

Textile industries produce large quantities of wastewater from the dyeing and finishing processes that cause severe pollution problem. Textile wastewater is strongly colored and has high values of pH, temperature and COD, while it shows low biodegradability. The release of colored effluents into the environment is undesirable because of their color, and because many dyes from wastewater and their breakdown products exhibit toxic, even mutagenic or carcinogenic properties, affecting the aquatic ecological system [1–5].

Today nearly one million metric tones of dyes is annually produced in the world; azo dyes ($R_1-N=N-R_2$) represent about 70% on weight basis of this amount. Recent estimates indicate that 12% of the synthetic dyes used yearly are lost to wastewater streams. Approximately 20% of these enter the environment through effluents from wastewater treatment plants [6].

Increased color intensity is the most serious problem from textile industry wastewater. Additionally, azodyes can produce hazardous aromatic amines and highly toxic by-products that occur from metabolic processes in plants and animals after disposal in lakes, rivers, or seas. The low biodegradability of the synthetic azodyes is due to the lack of natural biodegradation paths, and to stereochemical interferences concerning the accession of the reductant or oxidant molecule to the azo-group [1].

Textile industry wastewaters are treated by conventional methods such as adsorption, chemical oxidation or reduction, and biological degradation. Adsorption shifts the pollution problem into solid waste disposal, while chemical treatment produces final wastewaters contaminated with significant amounts of chemical reagents. Biological treatment, the most commonly used procedure, causes sludge formation and cannot degrade the pollutants completely given that huge polyaromatic organic molecules are hard to biodegrade because of stereochemical interferences [2, 3].

Because textile wastewater composition varies widely, traditional treatment methods are becoming less effective; however, newly developed electrochemical treatment of textile wastewaters is proving very effective because of its versatility, energy efficiency, automation, and cost effectiveness. Electrochemical treatment methods remove color with little or no consumption of chemicals; and degradation of recalcitrant pollutants can be achieved [7, 8]. This study demonstrates the effectiveness of electrochemical degradation of four synthetic reactive azodyes widely used in the textile industry at both low and high initial dye concentrations.

31.2 Materials and Methods

Four (4) commercial synthetic reactive dyes (Kahafix Reactive Black XL, CI Direct Red 239, CI Reactive Blue CI 19 and CI Reactive Yellow 176) were used for creating the simulated solutions. Kahafix Reactive Black XL is a mixture of 75% Reactive Black 5% and 25% Reactive Orange, and is widely used for cotton dyeing. The other colors used were single colors. The electrochemical cell used in the

experiments was constructed from Plexiglas, with a working volume of 500 mL and electrode placements at 1 cm distance. One anode placed between two cathodes in the center of the cell was used as electrodes. The anode was made of niobe/synthetic diamond doped with boron (Nd/D) and the cathodes from stainless steel (SS). Initial solutions were prepared by dissolving appropriate amounts of the respective dye in deionized water. The examined concentrations were 100, 500, 1,000, 2,000 mg/L. Sodium chloride (NaCl) was used as supporting electrolyte.

All experiments were carried out at room temperature. For each experiment a model dye solution was prepared of a certain concentration. The pH was adjusted to the desirable value ($3-10 \pm 0.2$) by the addition of NaOH or HNO_3 solutions. A certain volume of the dye solution (500 mL) was transferred to the electrochemical cell, a small amount of supporting electrolyte (4–20 mL NaCl 1 mol/L) was added and potential was applied with a galvanostat. The current intensity was kept constant (at 1.6, 2.5 A or 3 A) during the experiment. An air pump supplied air at the base of the cell. Samples of 10 mL were taken at various time intervals. The concentration of the dye was determined by measuring the absorbance peaks, at wavelengths corresponding to each azodyes using a Hitachi 2000 UV-Vis spectrophotometer. COD was measured with cuvette test LCK 114 and LCK 314 and TOC using a Shimadzu TOC-V CSH, Total Organic Carbon Analyzer.

31.3 Results and Discussion

31.3.1 Kinetics of Dye Degradation

The physical methods used to remove azodyes from the wastewaters of textile industries, such as sorption procedures and membrane ultrafiltration, produce azodye concentrates that are disposed off as toxic wastes. The best solution is to degrade them to smaller biodegradable compounds before disposal. Our previous work showed that electrochemical oxidation is effective in degrading synthetic dyes from low initial dye concentrations (5–100 mg/L). This work examined higher initial dye concentrations (500, 1,000 and 2,000 mg/L) that are not usually found in textile wastewaters (due to the dilution from washing operations), but are produced from other treatment methods. For example, concentrates of reactive dyes produced by flotation of synthetic dye solutions were degraded effectively by power ultrasounds [9].

The kinetics of the commercial black dye degradation is given in Fig. 31.1a, b. This dye is a mixture with black and orange components both were measured at the respective wavelengths (602 nm for black and 489 nm for orange). The treatment conditions were current intensity 2.5 A, pH 10.0 and 12 mL of 1M NaCl added as electrolyte. A fast decoloration was observed for all the examined solutions. The time needed for the degradation of the dye increased proportionally with the initial dye concentration. Almost complete decoloration was achieved for all concentrations in about 30 min, showing the effectiveness of the method. This is considered a great achievement since

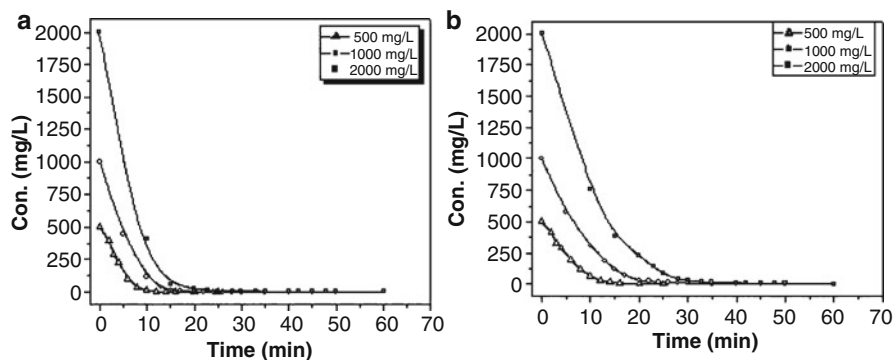


Fig. 31.1 (a) Black dye degradation (measured at 602 nm) as a function of time. (b) Orange dye degradation (measured at 489 nm) as a function of time

Table 31.1 Half-lives for various initial dye concentrations

Initial dye conc. (mg/L)	500	1,000X	2,000
$t_{1/2}$ (Reactive Black) (min)	3.5	4.6	5.2
$t_{1/2}$ (Reactive Orange) (min)	4.9	6.5	7.2

other advanced oxidation methods need more than 60 min to achieve similar results with lower initial dye concentrations. Very little published work demonstrates high concentrations reduced to less than the current limit (of 1 mg/L) for pure dyes in such a short amount of time. With 500 mg/L initial concentration, the black component was completely removed in 10 min (Fig. 31.1a) while 15 min were needed for the orange color component (Fig. 31.1b). For initial concentrations 1,000 mg/L and 2,000 mg/L, more time was needed for complete decoloration (20 min for black and 30 min for orange component). However, both were completely decolorized at the end of the respective time treatments. As expected, higher initial dye concentrations needed more time for complete decoloration. However, after 30 min treatments, complete decoloration of all dye solutions was obtained (even that of 2,000 mg/L initial dye concentration). Final concentrations were below the limit and no further treatment was needed for color removal. The results showed that the black color component had faster kinetics than the orange component at all studied concentrations.

The corresponding half-lives of black and orange components are given in Table 31.1. The optimized oxidation conditions used here of 7.2 min are enough to reduce dye concentration to half even from 2,000 mg/L.

Real textile wastewaters contain other components that may adsorb at different wavelengths. Sometimes when a dye is oxidized, components that adsorb at different wavelengths may be formed. To examine this effect, the full visible spectra of the studied dyes were recorded at different treatment times with results given in Fig. 31.2. The initial values were clipped at three units of Absorbance (meaning that the original absorbance was more). The initial dye has a high absorbance at the whole range of the visible spectra (400–700 nm).

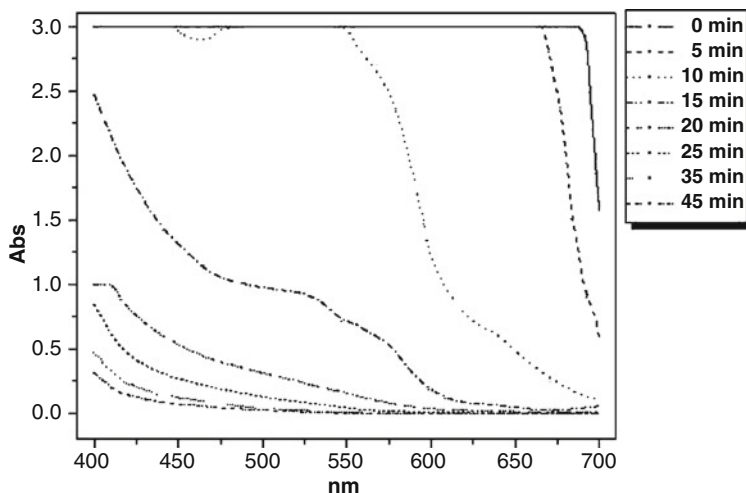


Fig. 31.2 The UV-Vis spectra of the black azodye during the electrochemical treatment. Initial dye conc. 1,000 mg/L, current intensity 2.5 A, 16 mL NaCl 1M and pH 10.0

With a 5 min treatment, the black component was reduced by 50% (Table 31.1, 1,000 mg/L) but the absorbance is still very high. After 10 min of treatment, a visible effect in the black region is observed. At 20 min, the absorbance is decreased significantly at the whole visible range. After 30–35 min treatment, the decoloration is almost complete. A very small absorbance is observed after 45 min of treatment. Under these conditions, the rate of dye degradation is controlled by mass transfer limitations. The dye molecules diffuse to the electrodes' surfaces, react there, and the reaction products diffuse from the electrodes' surface to the bulk of the solution. As the concentration increases, the reaction rate becomes diffusion controlled, since the rate of the electron transfer is much faster than the diffusion rate, rendering the degradation rate proportional to the bulk concentration of the dye [8].

31.3.2 Effect of Electrolyte Concentration

In electrochemical processes, the type and concentration of the supporting electrolyte is very important. Typical textile wastewaters contain significant quantities of NaCl for improving the dye efficiency, thus our study used NaCl as the supporting electrolyte. The results are presented in Fig. 31.3a (black) and 31.3b (orange). Clearly, NaCl significantly affects the kinetics of dye decoloration. With increased quantities of NaCl (4, 8 and 12 mL), the decoloration rate increases significantly. However, further addition of an electrolyte (12, 16 and 20 mL) had minimal effect on the decoloration rate.

The drastic effect of chlorides on the dye's degradation rate can be explained, if the electrolysis of NaCl is considered. The electrolysis of NaCl results in some very

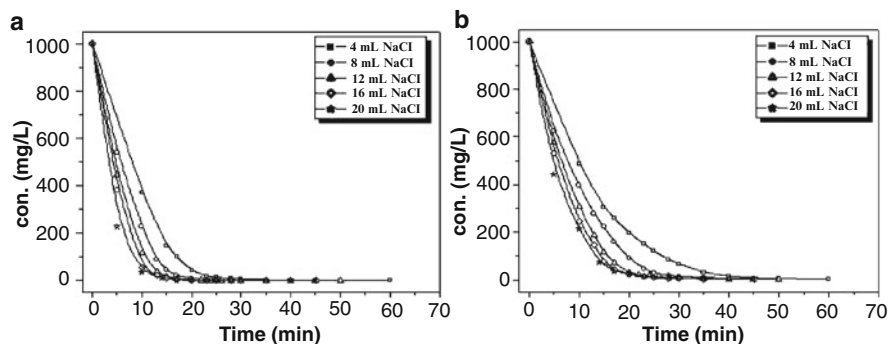


Fig. 31.3 (a) Effect of 1M NaCl quantity on black dye component removal (measured at 602 nm). Dye conc. 1,000 mg/L, current intensity 2.5 A and pH 10.0. (b) Effect of 1M NaCl quantity on orange dye component removal (measured at 489 nm). Dye conc. 1,000 mg/L, current intensity 2.5 A and pH 10.0

strong oxidants, such as free chlorine (Cl_2), at the anode, with subsequent formation of hypochlorite anions (ClO^-). The whole decoloration proceeds via direct oxidation reactions on the electrodes, enhanced by indirect oxidation reactions by the produced oxidants. Stronger oxidants achieve better enhancement. Consequently, dye molecules can effectively be degraded in aquatic media containing chloride anions (Cl^-) [2]. Concentrations of chloride ions above certain value cannot improve the decoloration rate. So, the best results are taken by the addition of 12 mL of 1M NaCl, which achieves a satisfactory degradation process with minimum production of environmentally unfriendly chemical compounds. Note that chloride ions are present in significant quantities in textile industry wastewater and adequate decoloration should occur with no further addition of electrolyte.

31.3.3 Effect of pH

In all wastewater treatment operations, the pH of solution is an important parameter to be tested. However, as total concentrations increase, the effect of pH becomes less important. We studied the effect of pH on dye decoloration under optimized oxidation conditions for 1,000 mg/L initial dye concentration. The results are shown in Fig. 31.4a for black and 31.4b for orange dye component. Four different pH values (3, 5, 7 and 10) common to pH values of wastewaters were used. A small effect of pH is observed on dye decoloration and is the same for both black and orange components. At acidic pH values, the degradation process is initially faster, achieving a higher degree of decoloration than at higher pH values. However, after 20 min for black and 25 min for orange, the final decoloration is similar at all pH values studied. Acidic-neutral pH is the optimal range for the production of some very important oxidants, such as (Cl_2) and (ClO^-) anions, which enhance the decoloration process.

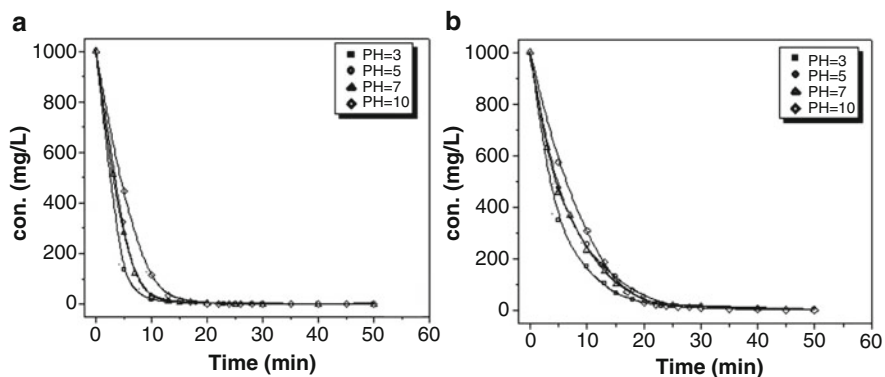


Fig. 31.4 Effect of pH on (a) black dye component removal (at 602 nm). Dye conc. 1,000 mg/L, $I=2.5$ A and 12 mL NaCl 1M. (b) orange dye component removal (at 489 nm). Dye conc. 1,000 mg/L, $I=2.5$ A and 12 mL NaCl 1M

In alkaline pH, the formation of the above-mentioned important agents is restrained. However, our results show that the pH does not play an important role for the complete treatment at 30 min.

31.3.4 Effect of Current Intensity

The amount and the type of the supporting electrolyte are strictly coupled with the applied voltage for the same current intensity. A high concentration of electrolyte needs low voltage to attain the current intensity, while a low concentration requires higher voltage for the same result. In any case, the lowest possible potential value should be applied to achieve a satisfactory level of decoloration. Higher values lead to energy loss, high temperatures and faster electrode damage. As the voltage varies during the process, the current intensity was chosen as the parameter to keep constant through the experiments. The current intensity directly affects the flow of electrons, and consequently the whole oxidation process. However, once enough electrons are present for all redox processes, further increases should not affect the whole process. In previous work with smaller current intensities (0.5–1.5 A), the increase of current intensity increased the kinetics of the process. We chose 2.5 A as a value for effective and fast treatment of dye solutions with initial concentrations up to 2,000 mg/L. However, to test if a further increase in current intensity would affect the kinetics, 3.0 A was also tested and the results were compared with those for 2.5 A current intensity. The results are presented in Fig. 31.5a for the black and 31.5b for the orange component of the dye. A small difference is observed at the initial decoloration steps but the final result is the same for both current intensities; thus 2.5 A was chosen for our work.

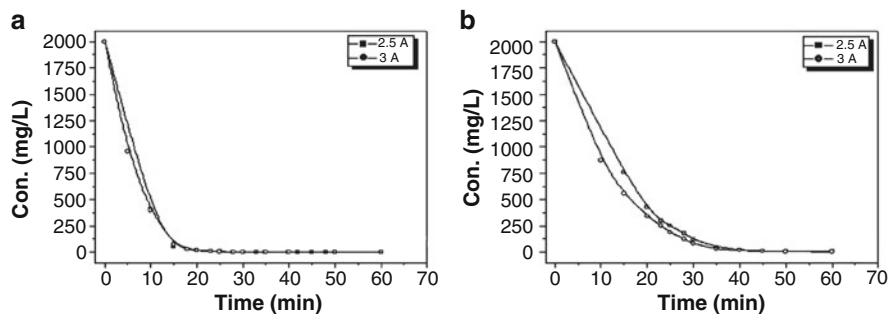


Fig. 31.5 Effect of applied current intensity on (a) black dye component removal (at 602 nm). Dye conc. 2,000 mg/L, 12 mL NaCl 1M and pH 10.0. (b) on orange dye component removal (at 489 nm). Dye conc. 2,000 mg/L, 8 mL NaCl 1M and pH 10.0

31.3.5 Decoloration of Artificial Mixtures

The real wastewaters of textile dyeing operations contain mixtures of dyes and many other components. Basic dyes such as blue, red, yellow, and black are usually found with varying concentrations. Therefore, a good treatment method to be applied in existing installations should be able to effectively treat various mixtures of dyes. For this reason, we studied the electrochemical oxidation of basic synthetic reactive dyes of Blue (CI 19), Red (CI 239) and Yellow (CI 176) in single, binary and ternary mixture solutions. The results are presented in Fig. 31.6a for single solutions and in Fig. 31.6b for mixtures of the basic dyes. The applied current intensity was 1.6 A and 4 mL of NaCl 1M was added as an electrolyte. Results showed that in single solutions, the blue color is degraded faster than the other two (Fig. 31.6a), and red is degraded faster than yellow. At around 30 min, all colors are degraded satisfactory. With single solutions, it is easy to determine the final concentration of each color; but with mixtures of colors, it is much more difficult. The American Dye Manufacturers Institute recommends the ADMI units method that determines all visible wavelengths, so even colors produced from treatment are accounted for. The limit for safe discharge is 300 ADMI units. The ADMI units' method was used for presenting the results from electrochemical oxidation of binary and ternary mixtures shown in Fig. 31.6b. The horizontal line represents the discharge limit of 300 ADMI units. Results showed that the yellow and blue mixture is degraded in 12 min which is much faster than the degradation of the yellow and red mixture of approximately 30 min. The ternary mixture containing all three colors degraded slowly but completely after 55 min of treatment (Fig. 31.6b). The decoloration curves show some hysteresis at the beginning which might be due to the partial reactions taking place between the intermediate products from the oxidation of dyes.

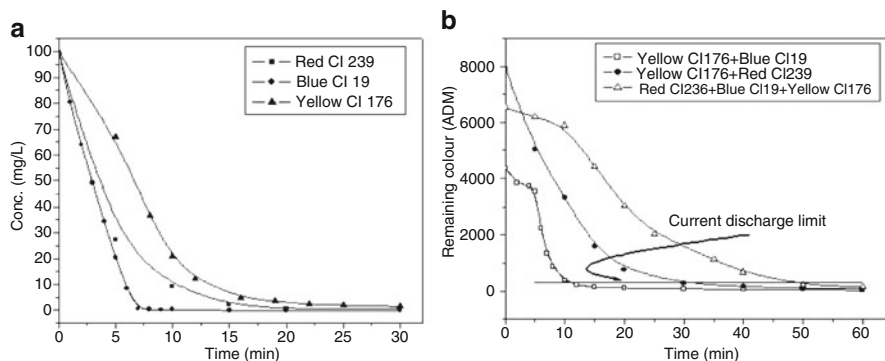


Fig. 31.6 (a) Decoloration of (a) individual dyes – Initial conc. 100 mg/L, $I = 1.6$ A, 4 mL NaCl 1M and pH 10.0. (b) mixtures of dyes. Initial conc. 100 mg/L, $I = 1.6$ A, 4 mL NaCl 1M and pH 10.0

Comparing the yellow-blue and yellow-red mixtures (Fig. 31.6b) with the yellow degradation curve (Fig. 31.6a); it seems that the presence of the blue color causes the yellow to degrade faster. This might be due to interactions between partial oxidation products of the basic dyes, but further study with analysis of intermediate products is needed. The final conclusion is that electrochemical oxidation is effective in treating mixtures of basic dyes to values below the discharge limit of 300 ADMI units.

31.3.6 Total Organic Carbon (TOC) and Chemical Oxygen Demand (COD)

A significant decrease of COD (63% from 1,000 mg/L, 55% from 2,000 mg/L) and TOC (22% for 1,000 mg/L and 28% for 2,000 mg/L) values is observed after the electrochemical oxidation. This shows that around 25% of organic carbon has been oxidised to harmless inorganic compounds and the final wastewater is friendlier to environment. As the colour completely disappeared, the recalcitrant non-biodegradable polyaromatic compounds were broken into smaller more biodegradable compounds which could be easily eliminated by existing biological treatment methods. Similar TOC reduction was observed for the other colours. Figure 31.6a results show that the blue colour degrades most quickly meaning that the break of the azo bonds is fast, but as the TOC decrease is only 6%, the oxidation does not proceed to carbon mineralization. The yellow colour degrades most slowly, but carbon mineralization is obtained by 21%, indicating that the final products from yellow colour are friendlier to the environment than ones coming from the blue colour.

31.4 Conclusions

Electrochemical oxidation is an effective method for decoloration of commonly used commercial synthetic reactive azodyes from solutions of single dyes and binary and ternary mixtures of blue, red and yellow dyes. It effectively treats high initial concentrations of a commonly used commercial black dye. Chloride anions play a very important role in decreasing the decoloration time. Since this electrolyte exists in the textile wastewater as a remaining dye-bath additive, experiments with real samples should run without further addition of any chemical reagent. The process is effective in a wide range of pH between 3.0 and 10.0 when high initial concentrations of dyes and appropriate current intensity are used. This wide optimal pH range renders the method rather versatile. The final treated wastewaters are friendlier for the environment as the TOC is reduced by 25% and the COD by 60%.

Acknowledgements The dye and relevant information on their use were supplied by KYKE Hellas.

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