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Lidia Szpyrkowicz[a]; Marta Radaelli[a]
[a] Department of Environmental Sciences, University of Venice, Italy

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Electrochemical Single-Cell Reactor for Treatment of Industrial Wastewater Composed of a Spent Textile Bath

Lidia Szpyrkowicz
Department of Environmental Sciences, University of Venice, Venice
Italy

Marta Radaelli
Department of Environmental Sciences, University of Venice, Venice,
Italy

Abstract: In the paper the electro-oxidation of a spent dyeing bath, mediated by the Cl^-/Cl_2 redox couple, was studied and proposed for the treatment of textile wastewater as a technology alternative to hypochlorite oxidation. The work focused on the optimization of the electrochemical reactor. Particular attention was paid to the dependence of transport mechanisms and reaction rates on temperature, applied current, and hydrodynamic conditions in the reactor. The simultaneous production of H_2O_2 from the cathodic reduction of O_2, which could also react with the dye, was also assessed. The regime which controlled the reaction was determined from the Hatta number.

Keywords: Cl^-/Cl_2 redox mediator, Electro-oxidation, Hatta numbers, Textile wastewater

INTRODUCTION

The wastewater deriving from the process of dyeing consists of a mixture of various dyes and additives, many of which are toxic and/or have a low

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Address correspondence to Lidia Szpyrkowicz, Department of Environmental Sciences, University of Venice, Dorsoduro 2137, 30123 Venice Italy. E-mail: lidia@unive.it

biodegradability. This constitutes an important environmental problem. In addition to the unreacted dyeing compounds, the pollution load may also include surfactants, salts and organics washed out from the material undergoing dyeing. The wastewater is generally characterised by high COD, the pH varying from 2 to 12 and high color (1, 2, 3); this last parameter is often the one most difficult to deal with. Conventional treatment of dye polluted wastewater usually involves biochemical oxidative destruction, which often produces a final effluent that is still coloured. Various processes have been studied for the pre-treatment of dye-bearing wastewater, mainly with the aim of removing its color, including chemical oxidation with different reagents such as ozone, ozone + UV, hydrogen peroxide, hydrogen peroxide + UV, hydrogen peroxide + ferrous ions (Fenton's reagent) (4, 5, 6, 7, 8). Oxidation of dyes by hypochlorite was found to produce excellent results at the costs lower than the previously cited methods, but it introduces additional salinity to the treated effluents.

In the recent years, it has been shown that direct oxidation on boron-doped diamond anodes (9) and redox-couple mediated electro-oxidation can be competitive technologies for the treatment of textile wastewater (10, 11, 12, 13, 14). Electrochemical oxidation mediated by the Cl^-/Cl_2 redox couple is the most viable option due to the presence of chlorides in this type of wastewater. However, despite proven efficiency and cost effectiveness, optimization of the electrochemical reactor for this kind of application is still needed before the process can be implemented at an industrial scale.

The Cl_2/Cl^- mediated electro-oxidation is complex, involving consecutive and parallel reactions, such as anodic generation of the mediator, cathodic loss reactions and bulk solution reactions. The rates of these reactions, the reactor zones where they occur, and transport mechanisms in the reactor depend, in principle, on the temperature, the applied current and the hydrodynamic conditions in the reactor. In view of the above, the objective of this study was to investigate the performance of the reactor for decolorization of the spent textile bath by varying the operating conditions. In particular, the possibility that oxygen dissolved in the electrolyte can be reduced at the cathode to form H_2O_2, which like Cl_2, can react with the pollutant and influence the overall conversion, was also assessed.

METHODS

The dyeing bath used in this study had the following composition: 0.6 g/L reactive dye Red Procion X-EXGL (Dystar), 16.25 g/L NaCl, 2.5 g/L Na_2CO_3 and 0.25 g/L NaOH.

Experimental runs were carried out in a batch 0.6 L single-cell reactor equipped with a $10 \times 10\ cm^2$ plate Ti/Pt-Ir anode and a stainless steel plate cathode of the same dimensions. The details of this set-up are given in (15).

The hydrodynamic conditions were imposed by varying the pump speed of a peristaltic pump (Watson Marlow 313 F/D), circulating the solution at flow rates of 54 and 108 ml/min. The other means of agitation was by air bubbles, introduced at the flow rate of $5.58 \cdot 10^{-2}$ Nm^3/min, through porous frit placed at the bottom of the reactor.

The reactor was operated using a galvanostatic control. The anode potential was measured against a home made satured calomel reference electrode (SCE 0.045V vs Ag/AgCl) in a Luggin capillary probe, using an impedance voltmeter (Keithley 169 Multimeter). A DC stabilized power source with voltage monitoring and control range of between 1 and 10 V was used.

The experiments were performed under isothermal conditions, using a thermostatic bath (Haake DC 130). Pervious studies (15), in which the temperature was varied between 10 to 40°C, showed that the higher the temperature, the better the reactor performance. In the present study, the temperature range was further extended from 40° to 80°C.

The color of the wastewater was determined by measuring the absorbance at a fixed wavelength (535 nm) using a Hach DR 2000 single beam spectrophotometer after sample dilution (1:25). The active chlorine concentration was determined using the reaction with N,N diethyl-p-phenylenediamine (16). The pH (Orion GLP 21) and TOC (Shimadzu 5050A) was also measured.

Previous cyclic voltammetric measurements, carried out using a standard three-electrode cell at various dye concentrations in the chloride and sulphate media showed that there is no direct discharge of the dye on the electrodes and that the removal of color can be attributed solely to the homogeneous phase reactions with the redox mediators (17).

RESULTS AND DISCUSSION

The Chemistry of the System

As described in the previous papers (11, 15, 17) chloride ions in the solution can be oxidized at the anode to Cl_2, through the following overall reaction:

$$2Cl^- \leftrightharpoons Cl_2 + 2e \qquad (1)$$

Chlorine formed at the anode dissolves and diffuses into the bulk solution, and depending on the solution pH, may disproportionate to form either OCl^- or HClO. These active chlorine species ["Cl_2"] can react with the dye molecule, leading in the first instance to the rupture of the chromophore and liberation of chloride ions, which can enter again into the cycle of chlorine generation:

$$[\text{``}Cl_2\text{''}] + [R] \longrightarrow [R]_{OX} + Cl^- \qquad (2)$$

where [R] and $[R]_{ox}$ represent, respectively, the reduced and oxidized dye molecule.

More details of the chlorine-water system have been given in (18).

Influence of Operating Conditions on the Process Rates

Influence of Temperature

In Fig. 1 the dependence of the performance of the reactor on temperature is shown. The experiments were conducted at the current density of 260 A/m^2. For comparison the trends obtained in previous studies over the temperature range 10°–40°C (15) are also shown. It can be observed that the positive effect of temperature increase continued at temperature above 40°C, previously established as the optimal, till the temperature of 70°C was reached. A further increase of the temperature till 80°C did not result in any additional improvement in decolorization. An explanation of this is the fact that chlorine concentration equal to its solubility at a given temperature (19) was reached and any further generation of chlorine did not result in the increase of its concentration due to desorption.

Influence of Stirring

Figure 2 depicts the rate of decolorization under stagnant conditions and when the hydrodynamics of the system was varied by pumping. These experiments were performed using the following current densities of 200, 400, 600 and 800 A/m^2, operating under isothermal conditions at 30° ± 1°C.

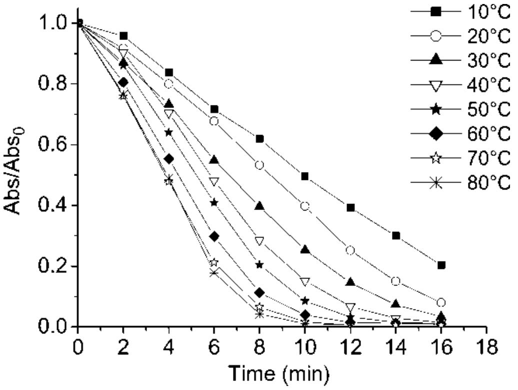

Figure 1. Color removal for different temperatures (current density 260 A/m^2; stagnant conditions).

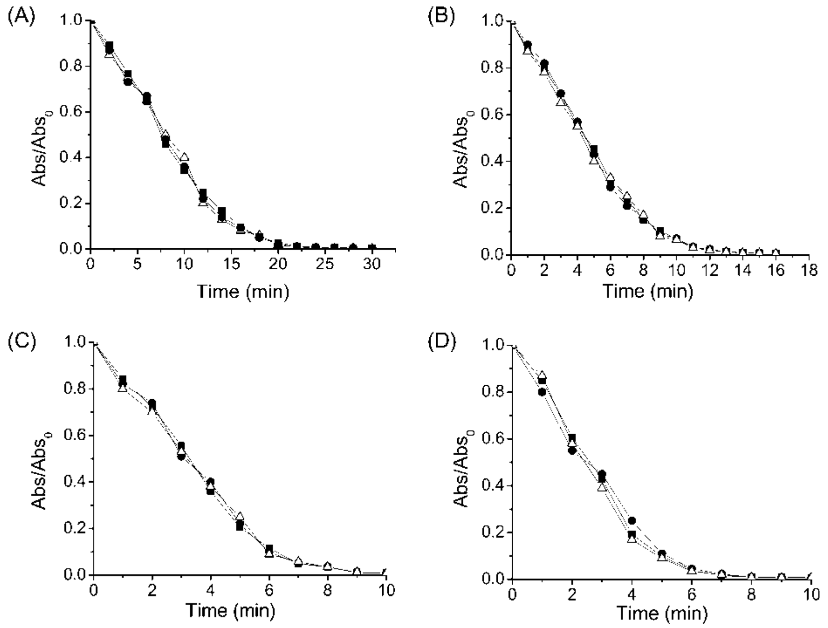

Figure 2. Performance of decolorization under different hydrodynamic conditions: ■ stagnant conditions; stirring by pumping at: ● 54 ml/min; Δ 108 ml/min; current densities: A - 200 A/m^2; B - 400 A/m^2; C - 600 A/m^2; D - 800 A/m^2.

Figure 2 shows that there were no differences in the performance of the reactor when the hydrodynamic conditions were changed by pumping. This can be explained by higher rates of the loss reactions of Cl_2 mediator both at the cathode:

$$OCl^- + H_2O + 2e^- \rightleftharpoons Cl^- + 2OH^- \tag{3}$$

and at the anode:

$$6HOCl + 3H_2O \longrightarrow 2ClO_3^- + 4Cl^- + 1.5O_2 + 12H^+ + 6e^- \tag{4}$$

Since the above reactions are mass transfer controlled, while from one side higher flow rates may have increased the mass transfer rates of chloride to the electrode and thus the rate of chlorine evolution, from the other they produced also an increase in the rates of loss reactions. As a results, the net concentration of the mediator in the bulk of the solution remained unaffected by the stirring rate.

On the contrary, the way of agitating the solution did influence the performance of the reactor.

Figure 3 compares the time trends of decolorization at 200 A/m^2 current density, when the reactor was stirred by air bubbling and by pumping, respectively. During mixing with air, the solution was oversaturated with oxygen. It is

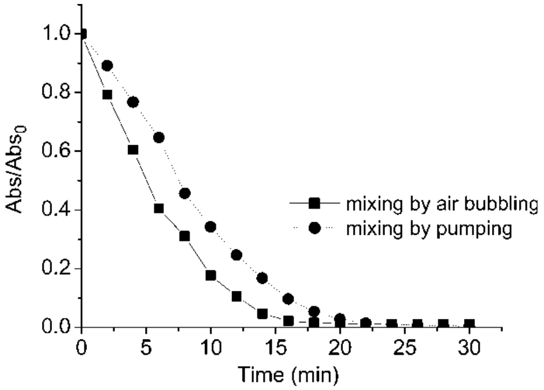

Figure 3. The influence of mixing mode on color removal (current density 200 A/m^2).

possible to observe that the decolorization obtained when the solution was enriched with O_2 was more rapid. A possible explanation of this behavior can be the presence of H_2O_2, which derived from the cathodic reduction of O_2. This oxidant can react with the dye and the following sequence of reactions can occur:

$$O_2 + H_2O + 2e \longrightarrow HO_2^- + OH^- \tag{5}$$

$$HO_2^- + H_2O + 2e \longrightarrow 3OH^- \tag{6}$$

$$HO_2^- + H_2O \longrightarrow H_2O_2 + OH^- \tag{7}$$

$$[H_2O_2] + [R] \longrightarrow [R]_{ox} \tag{8}$$

A hypothesis regarding the generation of H_2O_2 at a stainless steel cathode during mixing by air bubbling was checked by performing additional experiments using N_2 as a bubbling gas (current density $200 A/m^2$). The performance of the reactor followed the same trend as the one shown in Fig. 3 for the experiment with mixing by pumping. Apart of this investigation another experiment was carried out, using a Ti/Pt cathode instead of stainless steel and agitating the solution by air bubbling. Also, in this case there was no change in the trend of color of the electrolyzed solution. This last behavior is explained by the electrocatalytic properties of Pt to reduce HO_2^- to OH^-, which would preclude generation and accumulation of H_2O_2 in the bulk of the solution. The above results indirectly support the hypothesis of H_2O_2 generation due to O_2 reduction and its participation in the reaction with the dye.

Influence of Current Density

In Fig. 4 the dependence of the performance of the reactor on the applied current density is shown. Considering that better results were obtained when the solution was bubbled with air, these experiments were performed using such

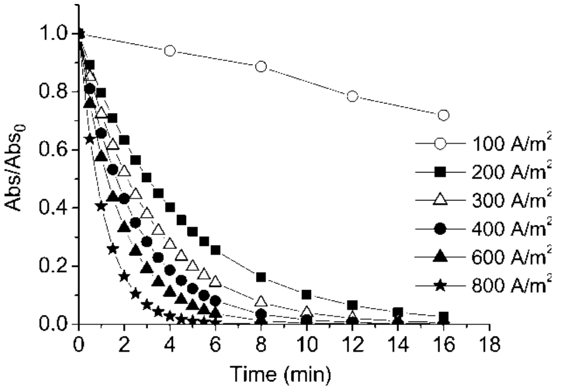

Figure 4. Color removal at different current densities in the presence of air bubbling (temp. 30°C ± 1°C).

mixing. As can be seen, the higher the density of the current, the reaction of decolorization proceeded faster, as the rise in current density corresponded to the increase in the concentration of the redox mediators produced at the electrodes. Assuming that at the anode the main reaction was the evolution of Cl_2, as given by reaction (1), it can be expected that the performance of the reactor could continue to improve till the limiting current density (j_L) for this reaction was achieved. The value of the limiting current density for chlorine evolution was estimated from:

$$j_L = k_m n C_{Cl^-} F \tag{9}$$

where k_m is the mass transfer coefficient (m/s), C_{Cl^-} is the concentration of chlorides (mol/m^3), n is the number of electrons participating in the reaction (n = 1), F is the Faraday constant (F = 96500 C/e$^-$). For stagnant conditions in the reactor and the value of k_m estimated as $2.20 \cdot 10^{-5}$ m/s (15), the limiting current for chlorine evolution was calculated as 590 A/m^2. Despite that the limiting current density for Cl_2 evolution was apparently already reached when the reactor operated at 600 A/m^2, the reactor still improved its performance when the current density was risen to 800 A/m^2. This can be explained by considering that simultaneously to the anodic evolution of Cl_2, the reaction of H_2O_2 generation occurred on the cathode (oxygen for this reaction was supplied continuously by air bubbling). Thus there was the presence in the reactor of H_2O_2, another oxidising species, which further contributed to the decolorization of the dyes.

The positive effect of dissolved oxygen and the use of compressed air to stir the solution were further investigated at different current densities. By comparing the decolorization results with and without bubbling the solution with air, shown in Figs. 4 and 5, respectively, significant differences can be observed. In particular, it is interesting to note that the electrolysis carried out

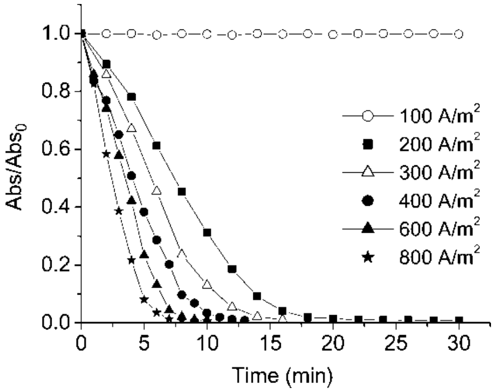

Figure 5. Color removal at different current densities in the absence of air bubbling (temperature 30°C ± 1°C).

at the current density equal to 100 A/m^2 did lead to the disappearance of the color when the solution contained dissolved oxygen, while this effect was not observed for the experiment conducted at the same current density, but without the use of the compressed air. In this last case, in fact, no active chlorine could be generated as the anode potential was lower that the chlorine evolution potential. It is probable that, under the conditions when active chlorine was produced, the dissolved oxygen behaved as an electron scavenger reducing in this manner the loss reaction of OCl^- on the cathode. In a single-cell reactor the two positive effects of introducing air/oxygen (viz. H_2O_2 generation and limitation of OCl^- loss reaction on the cathode) overlap.

Evaluation of the Kinetic Regime

For all the experiments in which the solution was not bubbled with compressed air, the decolorization kinetics was second order:

$$\frac{d(Abs)}{dt} = -k(Abs)C_{Cl_2} \tag{10}$$

where k is the second order rate constant (L/mol s), Abs is the measured absorbency, C_{Cl2} is the concentration of dissolved chlorine (mol/L).

Integration of Equation (10) and substituting for calculated chlorine concentration in time yields the following equation:

$$ln\frac{(Abs)_t}{(Abs)_o} = -\frac{k\Phi IAt^2}{4nFV} = -k't^2 \tag{11}$$

where I is the current density (A/m^2), Φ is the Faradic efficiency for chlorine evolution reaction, n is the number of electrons, A is the surface area of the anode (m^2), t is the time (s), F is the Faraday constant ($F = 96500\ C/e^-$) and V is the volume of the dye bath (m^3).

The values of k' were derived for different temperatures from the slopes of the ln (Abs_t/Abs_0) vs the $t^2$and were used to calculate the second order rate constant k.

Table 1 shows the values obtained under different operating conditions adopted in this study and the corresponding correlation coefficient.

The data obtained for the experiments in which air was bubbled through the solution were better interpreted by pseudo-first order kinetics:

$$\frac{d(Abs)}{dt} = -k(Abs) \tag{12}$$

The slopes of the plots of $\ln(Abs/Abs_0)$ vs t were used to obtain the pseudo-first order kinetic rate constants and are given in Table 2.

Information about the spatial distribution of the reactions and their position relative to the electrode surface may be obtained from the Ha number, by analogy to fluid/fluid reactions. The Ha number is defined from the ratio of the maximum possible conversion in the film and the maximum diffusional transport through the film. It has been found that (20) for the Ha numbers >2 the reactions occur in the liquid film adjacent to the interface of the gas (or a solid phase in the case of the gas evolving electrode) and the liquid. For small values of the Ha number ($Ha < 0.02$) the reactions can

Table 1. The kinetic rate constants of decolorization of dye molecules by Cl_2/Cl^- mediator

Operating conditions	Kinetic rate constant[a] (L/mol · s)	R^2
Current density (A/m^2)		
200	0.366 ± 0,014	0.99
400	0.543 ± 0,008	0.99
600	0.726 ± 0,008	0.99
800	0.888 ± 0,048	0.99
Temperature (°C)		
10	0.186	0.99
20	0.297	0.99
30	0.399	0.99
40	0.523	0.99
50	0.677	0.99
60	0.916	0.99
70	1.259	0.99
80	1.432	0.99

[a] The kinetic rate constants for different current densities are the mean values of the constants calculated from the time trends of decolorization at different hydrodynamic conditions at a given current density.

Table 2. The kinetic rate constants of decolorization of dye molecules by $Cl_2/Cl^-$and H_2O_2

Operating conditions	Kinetic rate constant k × 10^3 (s^{-1})	R^2
Current density (A/m^2)		
100	0.35	0.98
200	3.80	1
300	5.40	1
400	7.00	1
600	9.20	1
800	15.00	1

be considered infinitely slow with respect to the mass transport and they occur in the bulk of the solution. Thus the Hatta number (Ha) provides information about the solution zone (or kinetic regimes) in which the color removal reactions occur.

The Ha number was defined (20) from the equation:

$$\mathrm{Ha} = (k[R]D_{Cl2})^{1/2}/k_m \tag{13}$$

where k is the reaction rate constant (m^3/mol s), $[R]$ is the initial concentration of the dye (mol/m^3), k_m is the mass transfer coefficient (m/s), D_{Cl2} is the diffusivity

Table 3. The values of the Hatta number for decolorization of dye molecules by Cl_2/Cl^- under different operating conditions

	Ha number		
Operating conditions	Stagnant conditions	Pumping rate 54 ml/min	Pumping rate 108 ml/min
Current density (A/m^2) (30°C)			
200	0.025	0.024	0.022
400	0.030	0.029	0.027
600	0.035	0.033	0.031
800	0.039	0.037	0.035
Temperature (°C) (260 A/m^2)			
10	0.014		
20	0.019		
30	0.026		
40	0.034		
50	0.044		
60	0.061		
70	0.080		
80	0.093		

of [OCl$^-$] at a given temperature (m^2/s). For the flow rates of 54 and 108 ml/min, the value of k_m is equal to $2.30 \cdot 10^{-5}$ and $2.45 \cdot 10^{-5}$ m/s, respectively (15).

The values of the Hatta number are shown in Table 3 for different reactor operating conditions. The Ha values are less then 0.02 for stagnant conditions, current density of 260 A/m^2 and temperature of 10 and 20°C. This indicates that the reaction between the dye and the chlorine-containing mediator under these conditions is slow relative to the mass transport of active chlorine from the electrode. It can be concluded that the reaction occurs in the bulk of the solution at temperature lower than 30°C and in both the bulk solution and the reaction zone near the anode when the temperatures are higher than 30°C ($0.02 < \mathrm{Ha} < 0.2$). This explains why the increase in mixing due to higher pump flow rate does not have any positive impact on the reaction rate: under such conditions the reaction that occurs in the reaction zone near the anode is not significant. The increase in the chlorine concentration and oxidative reactions at the anode, obtained when the mass transport is enhanced by the higher pump speed, is counterbalanced by a decrease in the oxidative reaction in the bulk solution. The latter is due to a drop in the mediator concentration as a result of increased transport to the cathode due to the higher pump speed, and subsequent reduction at the cathode to form non-oxidative species.

CONCLUSIONS

The results of the present study show that reaction temperature, current density, and mode of mixing impact remarkably on the rate of decolorization. By careful selection of the operating conditions, the reaction rates can be increased by the factor of 4 or more, thus reducing the time required for treatment of the wastewater. In particular, elevated temperature (up to 70°C), high current density and the use of air bubbling to agitate the solution are the optimal conditions for the removal of dye pollutants in wastewater using redox-couple mediated electro-oxidation.

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