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Photoassisted Electrochemical Treatment of Azo and Phtalocyanine Reactive Dyes in the Presence of Surfactants

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Abstract: An electrochemical treatment (EC) was applied at different intensities to degrade the chromophoric groups of dyes C.I. Reactive Black 5 (RB5) and C.I. Reactive Blue 7 (Rb7) until uncolored species were obtained. Decolorization rate constants of the azo dye RB5 were higher than the phtalocyanine Rb7 ones. In addition, the EC treatment was more efficient at higher intensities, but these conditions significantly increased the generation of undesirable by-products such as chloroform. The combination of EC with UV irradiation (UVEC) drastically minimized the generation of chloroform. The photo-assisted electrochemical treatment was also able to achieve decolorization values of 99%. Finally, mixtures of dyes and surfactants were treated by EC and UVEC. In the presence of surfactants, the decolorization kinetic of dyes was slowed due to the competitive reactions of surfactants degradation. Both methods achieved total decolorization and in both cases, the generation of haloforms was negligible.

Keywords: textile washing effluents; reactive dyes; azo dyes; phtalocyanine dyes; surfactants; decolorization; electrochemical treatment; photo-assisted electrochemical treatment

1. Introduction

In the textile industry, several rinsing and soaping steps are carried out after dyeing processes in order to remove residual dyes from finished articles. Therefore, huge amounts of wastewater containing a mixture of dyes and surfactants are produced, the main characteristics of which are high coloration and foam content.

Among textile dyes, the reactive ones represent about 20%–30% of the total market [1,2]. Due to their fastness properties and brilliant colors, they are widely used in the cotton dyeing industry. However, remarkable rate of unfixed dyes (up to 30%) remain in the residual baths, which increases the environmental and aesthetic problems caused by both dyeing and washing effluents [3]. According to the structure of their chromophore, azo dyes are the most widely used dye class, accounting for more than 60% of the total dye production [4]. These dyes can be fragmented by reductive cleavage of the azo group to generate aromatic amines [5]. The aromatic amines can be harmful and some of them have been classified as carcinogenic and genotoxic by the International Agency for Research on Cancer [6]. Another important chromophore group is the phtalocyanine, based on metallic complexes, mainly Cu, to produce blue and green shades. They are potentially mutagenic and also toxic due to the heavy metal content [7].

Azo and phthalocyanine dyes are both highly water soluble and resistant to biological degradation under aerobic conditions. Therefore, biological treatments are generally insufficient to remove these dyes.

In addition, surfactants can cause operational difficulties in biological plants due to their foam [8]. The increasing consumption of surfactants results in a serious environmental problem because most surfactants are toxic to aquatic organisms due to their surface activity. Toxicity of surfactants is mainly attributed to their persistent adherence on the biological membranes of organisms. They also produce adverse effects in rivers because they do not allow the correct oxygen exchange through the water surface [9].

Consequently, to comply with current regulations, the use of tertiary treatments to remove color and foam is required. On the other hand, the presence of surfactants in dyeing and washing effluents can interfere with the dye removal treatment.

Whereas foam is easy to remove, several physico-chemical methods are currently used for the wastewater color removal but they produce a new waste that requires an additional treatment to be destroyed [10,11]. Moreover, additional drawback should be considered, such as the regeneration in the case of active carbon adsorption [12,13] and the cleaning treatments for the membrane filtration [14,15]. On the other hand, advanced oxidation methods (ozonation [16,17], Fenton and Photo-Fenton reactions [18,19] or heterogeneous photocatalysis [20] could be expensive and involve some operational difficulties. Enzymatic degradation is limited by inhibitory effects caused by some dyebath auxiliary products, such as salts and surfactants [21,22]. Currently, electrochemical technology has been proposed as a clear alternative for color removal. It has good versatility, operates under smooth conditions and is easy to automatize [23,24]. It is also a clean technology: the electron is the only reagent and no chemicals are required [25,26].

In the presence of chloride ions, chlorinated compounds, mainly haloforms, can be generated as byproducts. For this reason, the electrochemical treatment coupled to UV irradiation has been recently reported as a good alternative to minimize the generation of haloforms in decolorization treatments [2,27]. The combination of both technologies has been demonstrated to be more efficient from the ecological and energetic points of view, especially taking into account that UV irradiation can be substituted by solar light [28].

In contrast with the number of studies on color removal, little attention has been paid to the possibility of applying electrochemical technologies to the degradation of surfactants. An interesting study on the electrochemical degradation of sodium dodecylbenzene sulfonate was published by Kong, *et al.* [29]. In addition, Yüksel, *et al.* applied an electrocoagulation method to degrade the same family of anionic surfactants [30]. However, as far as we know, the treatment of effluents containing mixtures of dyes and surfactants has not been reported.

The current work aims to approach the treatment of dyeing and washing textile effluents. It is focused on the application of electrochemical techniques for the removal of color in the presence of a surfactant. Initially, the electrochemical treatment (EC) was applied to dye samples at two different intensities (2 A and 10 A) to evaluate color removal and generation of halogenated compounds. Afterwards, the electrochemical treatment was coupled to UV irradiation (UVEC) to avoid the generation of undesirable byproducts. Finally, the EC and UVEC treatments were applied to mixtures of dyes and surfactants to study the influence of these compounds on the degradation of dyes and the generation of haloforms.

2. Materials and Methods

2.1. Dyes and Reagents

In this work, two reactive dyes and one commercial detergent were selected:

- Color Index Reactive Black 5 (RB5)
- Color Index Reactive Blue 7 (Rb7)

- COTEMOLL TLTR, hereinafter referred as S

Dyes were supplied by DyStar Hispania (L'Hospitalet de Llobregat, Spain). Their structures are shown in Figure 1. As can be seen, RB5 is constituted by a diazo chromophore group and a double sulfatoethylsulfone reactive group, whereas Rb7 contains a phthalocyanine chromophore and triazine reactive group.

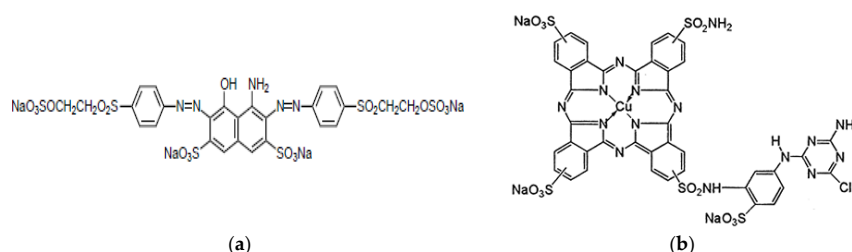


Figure 1. Chemical structure of (a) RB5 (C.I. Reactive Black 5); and (b) Rb7 (C.I. Reactive Blue 7).

The detergent, supplied by Color Center (Terrassa, Spain), has an anionic-non ionic character and contains a mixture of unidentified surfactants and polymers in water and iso-propanol solution (90:10).

Simulated effluents were prepared using analytical grade NaOH, Na₂SO₄, and/or NaCl, supplied by Merck (Mollet del Vallès, Spain).

2.2. Preparation of Synthetic Effluents

Four simulated effluents were prepared; two of them with the hydrolyzed dye (RB5 and Rb7) and two other solutions with the mixture of dye and detergent (RB5 + S and Rb7 + S).

According to the constitution of industrial textile effluents (see Appendix A and Appendix B), the dye concentration was fixed at 0.18 g/L and the surfactant (S) at 0.5 g/L.

All effluents contained 35 g/L Na₂SO₄ to simulate the residual dyeing electrolyte. Further, due to the influence of chloride ions in the electrochemical reactions, 0.3 g/L NaCl was added to each effluent in order to simulate the decalcified tap water used in the industrial dyeing process.

Reactive dyes are always hydrolyzed in industrial wastewater. To prepare the simulated effluents, dyes solutions were previously hydrolyzed by the addition of NaOH until pH 12 and they were heated to 80 °C for 2 h. After cooling at room temperature, pH was adjusted to 9 with H₂SO₄. Finally, the rest of salts and the detergent were added.

2.3. Electrolytic Cell

Synthetic effluents were treated at 2 A and 10 A in a 2-L undividable electrolytic cell (Figure 2) under galvanostatic conditions (power supply source Grelco GVD310 0–30 Vcc/0–10 A, Grelco, Cornellà, Spain). The cathode was made of stainless steel and the anode was a Ti/Pt electrode, both cylindrical with 59.32 cm² of active surface.



Figure 2. Electrolytic cell with the UV source.

The results refer both to the intensity and the specific applied charge (Q) as it is a normalized parameter expressed in $A \cdot h \cdot L^{-1}$.

The photo-assisted electrochemical treatment (UVEC) was carried out in the same cell with simultaneous UV irradiation by means of a lamp placed in the cell in a quartz cylinder (Philips TUV, PL-S, UV-C at 254 nm and 9 watts, Roosendaal, The Netherlands).

2.4. Decolorization on TOC Measurements: Kinetic Evaluation

Decolorization was calculated from the initial dye concentration and dye concentration at time t (C_0 and C_t , respectively) by measuring the absorbance at the visible maximum absorption wavelength (583 nm for RB5 and 617 nm for Rb7). Decolorization (D) was reported in %:

$$D(\%) = (C_0 - C_t) \times 100 / C_0 \quad (1)$$

Absorbance measurements were carried out with a UV-vis spectrophotometer (Shimadzu UV-2401 PC, Kyoto, Japan). In the working range, the dye absorbance (Abs) has a linear behavior *versus* the dye concentration (conc), according to the Equations (2) and (3):

$$RB5 : Abs = 31.618 \times conc + 0.0088 \quad (R^2 = 0.9999) \quad (2)$$

$$Rb7 : Abs = 17.308 \times conc + 0.0254 \quad (R^2 = 0.9991) \quad (3)$$

The total organic carbon (TOC) was determined with a Shimadzu TOC5050A analyzer (Kyoto, Japan). The % degradation was calculated according to Equation (4).

$$TOC \text{ removal } (\%) = (TOC_0 - TOC_t) \times 100 / TOC_0 \quad (4)$$

where TOC_0 corresponds to the initial value and TOC_t is the value at time t .

In accordance with our previous studies [28], the dye degradation follows a first-order reaction with an electrochemical treatment. The discoloration rate constants (k_D) were calculated from the slope of the semilogarithmic plot of absorbance *versus* treatment time (t) following the kinetic Equation (5).

$$\ln(Abs_t / Abs_0) = k_D \times t \quad (5)$$

The mineralization rate constants (k_M) were calculated from the slope of the semilogarithmic plot of TOC *versus* treatment time (t), in accordance with Equation (6).

$$\ln(TOC_t / TOC_0) = k_M \times t \quad (6)$$

2.5. GCMS Analysis

The generation of volatile halogenated compounds was evaluated by means of Gas Chromatography- Mass Spectroscopy (GCMS) analyses (Shimadzu QP 2010, Kyoto, Japan). The analysis of 23 halogenated compounds was carried out using a 0.2 mg/mL standard solution comprised of a mixture of 22 compounds and p-bromofluorobenzene as an internal standard (IS). These compounds were selected according to the EPA-624 method. All standards and IS were purchased from AccuStandard (New Haven, CT, USA).

The sample injection was carried out by mean of a headspace technique: 15 mL of the sample was placed in a 20-mL vial and sealed with silicone/PFTE (polytetrafluoroethylene) septum; the vial was heated to 80 °C for 45 min and 1 mL of the head space gas was injected into the GCMS equipment. The injection temperature was 200 °C. The chromatography program started at 35 °C for 10 min; the gradient rate was increased at a rate of 4 °C/min until 150 °C; this temperature was maintained for 10 min. The column used was TRB-624 (30 m, 0.25 mm of internal diameter and 1.4 μ m package). The carrier gas was helium at a flow rate of 0.95 mL/min.

The identification of halogenated compounds was performed using Nist 147, Nist 27 and Wiley 229 as reference libraries. Their chromatographic parameters are listed in Table 1.

Table 1. Halogenated compounds: detection limits (D.L.) and retention times.

Compound	CAS Number	D.L. ($\mu\text{g/L}$)	Retention Time (min)
Bromomethane	74-83-9	10	2.50
Chloroethane	75-00-3	1.0	2.65
Trichlorofluoromethane	75-69-4	2.5	3.00
1,1-Dichloroethene	75-35-4	2.5	3.86
Dichloromethane	75-09-2	1.0	4.90
1,1-Dichloroethane	75-34-3	2.5	6.55
Trichloromethane	67-66-3	1.0	9.69
1,1,1-Trichloroethane	71-55-6	2.5	10.07
Tetrachloromethane	56-23-5	2.5	10.63
Benzene	71-43-2	2.5	11.67
1,2-Dichloroethane	107-06-2	10	12.02
Trichloroethene	79-01-6	1.0	14.29
Bromodichloromethane	75-27-4	5	16.52
c-1,3-Dichloropropene	10061-01-5	10	18.22
Tetrachloroethene	127-18-4	1.0	21.03
Dibromochloromethane	124-48-1	10	22.32
Chlorobenzene	108-90-7	1.0	24.32
Ethylbenzene	100-41-4	1.0	24.82
Tribromomethane	75-25-2	10	27.45
1-bromo,3-fluorobenzene	1073-06-9	2.5	28.61
1,3-Dichlorobenzene	541-73-1	1.0	32.48
1,4-Dichlorobenzene	106-46-7	0.5	32.85
1,2-Dichlorobenzene	95-50-1	0.5	34.17

The quantitative analysis was carried out by means of the Equation (7):

$$\text{Concentration}_c = (\text{Area}_c \times \text{Concentration}_{\text{IS}}) / (\text{Area}_{\text{IS}} \times R_f) \quad (7)$$

where R_f is the response factor, which is specific for each compound. It corresponds to the area and concentration rates for the analyzed compound *versus* the IS.

3. Results and Discussion

3.1. Electrochemical Treatment (EC) of Dyes

The decolorization rates of RB5 and Rb7 were evaluated at two different intensities (2 A and 10 A). The influence of this parameter is shown in Figure 3.

In all cases, more than 90% color removal was achieved (Figure 3a,c). First order kinetics were obtained for all the decolorization reactions (Figure 3b,d).

As expected, the decolorization rate constants (slopes of curves in Figure 3b,d) depend on the intensity: the lower the intensity, the longer the treatment time. However, the rate k_D /intensity is not the same for both dyes: the decolorization constant of RB5 increases dramatically at higher intensity, whereas the ratio is much lower in the case of Rb7. For that reason, in Table 2, all these results referred to the specific applied charge (Q) that is a normalized parameter. Decolorization values from 93% to 99% were achieved.

The electrochemical treatment was demonstrated to be effective for the color removal of both dyes. According to the Q results, the treatment at 10 A was the most efficient: it required a lower specific applied charge to achieve the same degradation. This can be attributed to the higher rate of oxidants generation, which enhanced the dye discoloration.

The total organic carbon (TOC) removal was also evaluated to calculate the mineralization rate constants; results are included in Table 2. In this work, only a partial mineralization of organic matter was considered because, according to our previous studies [28], the full mineralization requires intensive electrochemical treatment that implies prohibitive power consumption.

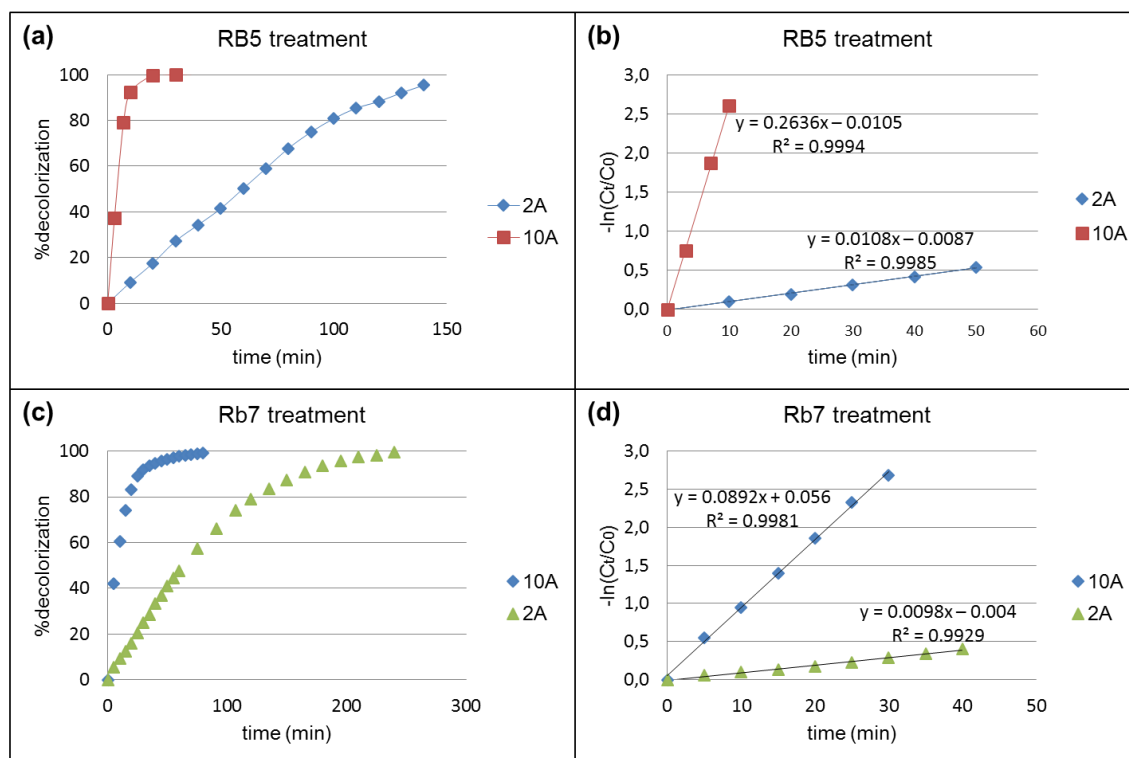


Figure 3. Evolution of dye degradation by electrochemical treatment at 2 A and 10 A. (a) and (c) % decolorization; (b) and (d) kinetic rate of decolorization.

Table 2. Results of the electrochemical treatment (EC) of dyes performed at 2 A and 10 A.

Sample	Intensity (A)	Q (A·h/L)	Decolorization (%)	k_D (min^{-1})	TOC Removal (%)	k_M (min^{-1})
RB5	2	2.1	95	0.0108	6.7	0.0004
	10	0.8	99	0.2636	28	0.0059
Rb7	2	2.8	93	0.0098	5.4	0.0003
	10	2.5	99	0.0892	19	0.0027

As expected, in all cases k_D was higher than k_M because the decolorization corresponds only to the degradation of chromophore group whereas the mineralization includes the degradation of the total organic matter. Previous literature also reported that in the presence of chlorides, the electrochemical process produces a mixture of chlorine oxidants with high selectivity toward the chromophore group, thus accelerating the color removal rate prior to mineralization [31,32].

In the case of electrochemical treatments, the dye degradation behavior is similar to that obtained with other advanced oxidation processes. Thus, Zuorro and Lavecchia [33] applied UV radiation and hydrogen peroxide to oxidize a diazo dye. They inferred that the decolorization process followed pseudo-first-order kinetics. The full decolorization was also achieved in a short treatment time, whereas the mineralization process was significantly slower.

3.2. Determination of Haloforms by GCMS

In our previous studies [2,27], we noted that some halogenated volatile compounds were generated, mainly haloforms, during the electrochemical treatment in the presence of chloride ions. For this reason, in this work, the generation of haloforms in the EC treatment of RB5 and Rb7 was evaluated after each treatment. The collected samples were analyzed by GCMS with HS injection. Figure 4 shows, as an example, the chromatogram obtained for RB5 at 2 A and 10 A. Similar chromatograms were obtained for the other effluents.

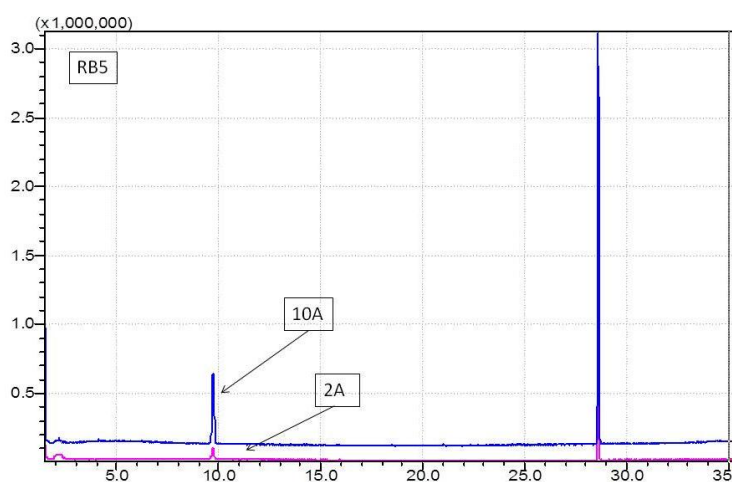


Figure 4. Gas chromatogram for RB5 dye samples treated at 2 A and 10 A.

In general, chromatograms exhibited two peaks. The first one (at 9.69 min) corresponded to chloroform (trichloromethane), identified with 94% similarity (library Wiley 229). The second peak (at 28.61 min) corresponded to the p-bromofluorobenzene, the Internal Standard added for the quantification.

The amount of chloroform generated in each experiment was calculated from Equation (7) (Section 2.5), with 1 ppm of Internal Standard and 0.9594 as R_f . Results are plotted in Figure 5.

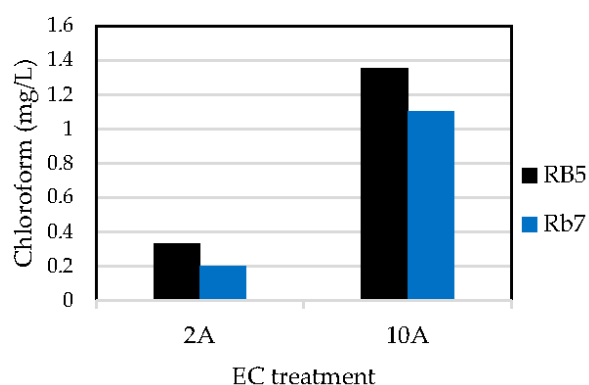


Figure 5. Chloroform generation in the electrochemical treatment (EC) carried out at 2 A and 10 A.

As can be seen, the treatment carried out at 10 A generated more chloroform (1.35–1.11 mg/L) than the treatment at 2 A (0.33–0.20 mg/L). When increasing the intensity 5 times, the amount of chloroform is increased 4–5.5 times, which indicates that working at lower intensities is more favorable to reduce haloform emissions.

3.3. Photo-Assisted Electrochemical (UVEC) Treatment Of Dyes

Recent studies [2,27] have shown that the combination of electrochemistry with UV radiation can improve the degradation of dyes and simultaneously, decrease the generation of haloforms. In this section, the efficiency of the electrochemical photoassisted treatment was evaluated at 10 A, the intensity with more efficient results but higher environmental concern.

The EC and UVEC treatments were performed until 99% color removal. At this point, the mineralization values were 28% and 26% for RB5 with EC and UVEC, respectively, whereas 19% and 18% were obtained for Rb7 (Table 3).

Table 3. Results of EC and UVEC treatments of dyes.

Sample	Treatment	Decolorization (%)	k_D (min^{-1})	TOC Removal (%)	Chloroform (mg/L)
RB5	EC	99	0.2636	28	1.35
	UVEC	99	0.1325	26	0.13
Rb7	EC	99	0.0892	19	1.11
	UVEC	99	0.0423	18	0.12

The decolorization rate constants and the chloroform generation showed marked differences with both treatments (Table 3). According to these results, the decolorization kinetic constants are approximately halved with the photoassisted treatment, probably due to the action of UV on the oxidant species generated during the electrolysis [2].

In contrast, the generation of chloroform is reduced about ten times with the UVEC treatment, which makes this technology very attractive.

3.4. Influence of Surfactants on the EC and UVEC Treatments Of Dyes

In order to simulate the real conditions of industrial textile effluents, the EC and UVEC treatments were applied to two mixtures of dyes and surfactants: RB5 + S and Rb7 + S (Table 4). All experiments achieved 99% decolorization. In this sense, the presence of surfactants did not prevent reaching full decolorization for both treatments. At this point, 16%–17% TOC removal was obtained.

Table 4. Results of EC and UVEC treatments of dyes in the presence of surfactants.

Sample	Treatment	Decolorization (%)	k_D (min^{-1})	TOC Removal (%)	Chloroform (mg/L)
RB5 + S	EC	99	0.0461	17	0.16
	UVEC	99	0.0471	17	0.14
Rb7 + S	EC	99	0.0282	16	0.13
	UVEC	99	0.0276	16	0.11

The decolorization rate constants and the chloroform generated showed similar results (Table 4) with both treatments (EC and UVEC). In mixtures of dyes and surfactants, the application of UVEC treatment is not necessary to obtain low values of chloroform generation.

Figure 6 shows a comparison of the decolorization rate constants and chloroform generation obtained in the treatments of dyes with respect to the treatments of dye/surfactant mixtures. The aim of this comparison was to show the effect of the presence of surfactant in the treatment efficiency. All the treatments were conducted until 99% decolorization.

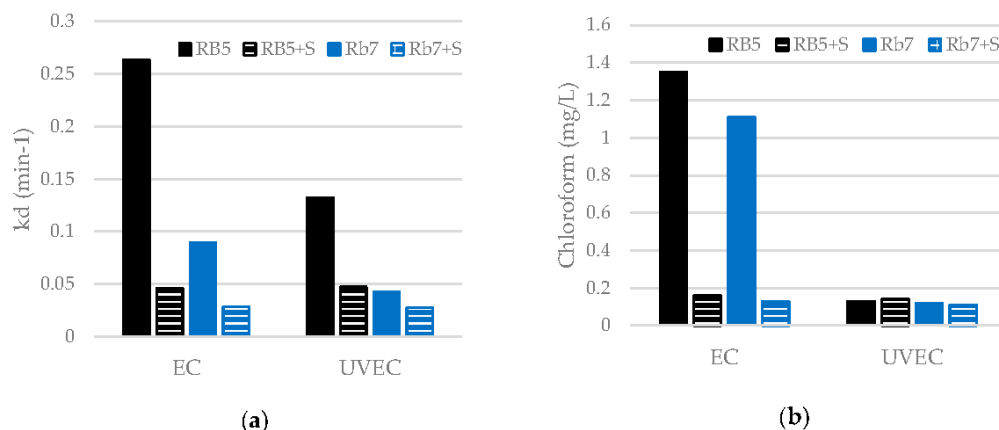


Figure 6. Comparison of the results obtained in the treatments of dyes with respect to the treatments of dye/surfactant mixtures: (a) decolorization rate constants; (b) chloroform generation.

The decolorization kinetic constants for mixtures are significantly lower than for dyes (Figure 6a), in both the EC and UVEC treatments. In the trials with mixtures, the surfactant compete with the dye in the reaction with the oxidant species generated during the electrolysis.

The chloroform generation for mixtures is much lower than for dyes in the EC treatments (Figure 6b). In fact, chloroform generation in mixtures is very low in all cases, independent of the treatment (EC or UVEC).

In general, the presence of surfactants involves a slower reaction of oxidant species, which implies lower decolorization rate constants and lower chloroform generation as a by-product. Besides the competitive reaction of surfactant with dye in the electrochemical oxidation, this behavior could also be attributed to a decrease of the electrode surface due to the bubbles produced by the surfactant. As the contact of chloride ions with the anodic surface is lower, the formation of chloride oxidant species is also diminished. Although the lower concentration of oxidant species results in a lower decolorization rate, it is favorable to reduce the generation of chloroform.

4. Conclusions

In the treatment of hydrolyzed reactive dye solutions, the electrochemical (EC) treatment achieved decolorization values higher than 90%. The azo group of RB5 was easier to degrade than the phthalocyanine group of Rb7.

Higher kinetic rates and TOC removal values were obtained at 10 A. Considering the specific charge applied, the treatment at 10 A was also more efficient. However, the GCMS analysis showed that the higher the intensity applied during the EC treatment, the higher the generation of halogenated volatile compounds. This problem can be solved with the coupled electrochemical and UV treatment (UVEC). The photo-assisted electrochemical treatment drastically decreased the generation of haloforms.

Both EC and UVEC were effective to remove color in the case of the dye and surfactant mixtures. In addition, the generation of haloforms was negligible in both cases. However, the decolorization kinetic rate was reduced due to the competitive reaction of the surfactant with the oxidant species generated during the electrolysis.

As a general conclusion, the UVEC method is recommended to treat exhausted dye baths that only contain dyes in order to prevent chloroform generation. On the contrary, the EC method is recommended to treat washing baths that contain mixtures of dyes and surfactants, since both methods achieved similar results and the EC method requires lower energy consumption (the UV irradiation is not applied).

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Conflicts of Interest: The authors declare no conflict of interest.

Appendix A: Dyeing and Washing Process for Effluent Characterization

Cotton knitted fabric (Pique), scoured and prepared for dyeing, was kindly supplied by Tipsa S.A. (Tordera, Spain). It was dyed in batch at a liquor ratio 1/10 ((L/R: fiber weight/ water volume) by mean of a Linitest laboratory dyeing machine (Original Hanau Ltd., Hanau, Germany), using 250 mL stainless steel drums. All dyeings were carried out in triplicate. The two dyes selected in this study (RB5 and Rb7) were kindly supplied by DyStar Hispania (L'Hospitalet de Llobregat, Spain). RB5 corresponds to C.I. Reactive Black 5 and Rb7 corresponds to C.I. Reactive Blue 7.

All dyeings were performed at 3% dye o.w.f (of weight fabric) and 1/10 LR (liquor ratio), which is equivalent to a solution of 3 g dye/L. Na_2SO_4 (80 g/L) was used as dyeing electrolyte and pH 12 was adjusted with NaOH.

The dyeing method was “all in” which implies that the dye and the total amount of electrolyte were added into the solution at the beginning of the process. According to procedure indicated by the dye manufacturer, the dyeing started at 50 °C for 15 min; then the temperature was raised to 80 °C at a gradient of 1.4 °C/min. After 30 min at 80 °C, the alkali was added. Then, this temperature was maintained until the end of the dyeing (60 additional minutes). Once the dyeing was finished, the exhausted residual bath was collected and characterized to prepare the simulated dyeing effluent.

The fabric samples were washed to remove the unfixed dye, following a six steps washing procedure. Samples were washed two times with water at 70 °C during 10 min, followed by a soaping step at 100 °C with 2 g/L Cotemoll TLTR. Finally two successive rinsing baths at 70 °C and an additional one at 50 °C were applied to remove the soap. All these rinsing and soaping baths were also collected and characterized to prepare the simulated effluents.

Appendix B: Characterization of Dyeing and Washing Effluents

A sample of the exhausted dye bath and each one of the six washing baths were collected and characterized separately, as can be seen in Table B1.

Table B1. Characterization of the dyeing and washing effluents obtained with the two dyes studied.

Bath	RB5			Rb7		
	Dye Conc. (g/L)	Cond. ¹ (ms/cm)	Na_2SO_4 Conc. (g/L)	Dye Conc. (g/L)	Cond. ¹ (ms/cm)	Na_2SO_4 Conc. (g/L)
Dyeing	0.35	80.3	109.3	0.50	76.4	107.2
1st washing	0.22	22.6	20.9	0.23	20.9	20.7
2nd washing	0.045	6.1	5.9	0.052	5.1	4.8
soaping *	0.017	2.3	1.8	0.026	2.3	1.7
4th washing	0.009	0.9	0.7	0.012	1.1	0.8
5th washing	0.006	0.7	0.5	0.008	0.9	0.6
6th washing	0.002	0.6	0.4	0.003	0.7	0.5

* the 3th washing is a soaping performed with 2 g/L Soap. ¹ Cond. corresponds to Conductivity.

As can be seen in Table B1, the 4th, 5th and 6th washing baths have a very low coloration and also low conductivity. They can be discharged directly to be treated in a biological waste water treatment plant and consequently, they are not considered in this work to carry out the electrochemical treatment.

The dyeing effluent, the residuals washings 1–2 and soaping bath (3th washing) should be submitted to the electrochemical treatment previous to the biological plant because their coloration and conductivity are higher.

The mixture of the dyeing bath and 1–3th residual washings will produce an average effluent with the following concentrations:

- Residual baths of RB dyeing : dye 0.16 g/L and Na₂SO₄ 34.5 g/L;
- Residual baths of CT dyeing: dye 0.20 g/L and Na₂SO₄ 33.6 g/L.

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