Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2013.769714

51 (2013) 4593–4602
June

Taylor & Francis
Taylor & Francis Group

Continuous reuse of water and electrolyte from decolorized reactive dyebaths

Víctor López-Grimau[a,*], Carmen Gutiérrez-Bouzán[b], José Valldeperas[b], Martí Crespi[b]

[a]*Department of Projects Engineering, ETSEIAT, Universitat Politècnica de Catalunya, Terrassa 08222, Spain*
Tel. +34 937397316; Fax: +34 937398272; email: victor.lopez-grimau@upc.edu
[b]*INTEXTER, Institute of Textile Research. Universitat Politècnica de Catalunya, Terrassa 08222, Spain*

Received 14 February 2012; Accepted 16 November 2012

ABSTRACT

In this work, the feasibility of reusing water and salt from reactive dyebaths after electrochemical decolourization was evaluated. Dyeing series of ten reuses with three reactive dyes (Navy Blue Procion H-EXL, Crimson Procion H-EXL and Yellow Procion H-EXL) were carried out (individually and in a trichromie) and color differences and total organic carbon values were measured to study how the successive reuses affect the quality dyeing. The first reuse produced dyeings with low colour differences with respect to a standard dyeing. In the subsequent reuses, colour differences increased until they reached a constant value at the 4th or 5th reuse, following a similar behavior to the organic matter content. At this point, it is determined the percentage of dye increase that allows for continuous dyeing of acceptable quality for the textile industry. To obtain dyeings with acceptable color differences ($DE^*_{CMC\,(2:1)} \leqslant 1$) independent of the number of consecutive reuses, a 30% increase in blue dyestuff and 10% for red dyestuff must be added, whereas in the case of yellow dyeing, it was not necessary to increase the dye amount after subsequent reuses. In each dyeing, this process allowed savings of 70% of water and an average of 60% for salt.

Keywords: Electrochemical treatment; Reactive dyebaths; Continuous reuse; Salt recovery; Color differences

---

1. Introduction

Reactive dyes are widely used in dyeing cellulosic fibers since they offer high washing fastness and brilliant colors. During the dyeing process with reactive dyes, the addition of high concentrations of electrolyte is necessary to obtain a better fixation and exhaustion. Generally, an amount of 50–80 $g\,L^{-1}$ of a salt [1] is added as electrolyte depending on the dyeing procedure and the dyeing conditions (type of dye, dye concentration, shade), being NaCl or Na_2SO_4 the most common. This salt does not have affinity to the fiber and it is completely discharged with the wastewater. The salinity of the industrial effluents is controlled by environmental regulations as it supposes a severe environmental problem in Mediterranean areas where the hydric resources are scarce. In Spain, the concentration limits for chlorides and sulfates in wastewater discharged into watercourses are fixed in 2 $g\,L^{-1}$ [2]. The presence of high concentrations of salt is very harmful for the aquatic ecosystems and it causes operational problems to the biological

---

*Corresponding author.

wastewater treatment plants. Moreover, its elimination is only possible through applying costly treatments as inverse osmosis [3,4] or electrodialysis [5].

These problems make especially interesting the possibility of reusing the water and the salt of the residual dyebath, once discolored, for new dyeing processes with reactive dyes. This reuse entails a significant saving of water and electrolyte. However, previously, the effect of the residual non-colored dye fragments and organic matter coming from the fiber in the dyeing quality has to be studied. The reactive dyes have a low degree of exhaustion and fixation, from 70 to 90% [1]. The unfixed dye becomes hydrolyzed and it is not able to form covalent bonds with the cellulose; consequently, it cannot be reused. In return, the hydrolyzed dye has to be degraded since it can stain the textile fiber and/or it can interfere in the reaction of the new reactive dye, reducing their exhaustion or increasing their hydrolysis; in both cases, this increases the difficulty in reproducing the color of the dyeings.

There are different techniques to remove color, being the most used: activated carbon adsorption [6,7], sorption on low-cost sorbents [8], coagulation–flocculation processes [9,10], membrane filtration [11,12] and advanced oxidation processes (AOP) [13–17]. Among the different AOP, electrochemical decolorization provides great advantages in the treatment of high colored textile wastewater, such as the recovery of the dyeing salt as electrolyte of the electrochemical reaction, the non-addition of chemical compounds (organic or inorganic) to the water and the non-generation of sludge [18].

The dye oxidation can occur directly on the electrode surface but it mostly takes place through the reaction of molecules formed in the anode, known as indirect oxidation. In this sense, reactive oxygen species such as hydroxyl radical ($^{\cdot}$OH), atomic oxygen ($^{\cdot}$O), hydrogen peroxide and ozone can be generated from water by discharge at the anode [19]. In addition, the presence of chloride as dyeing electrolyte in reactive dyebaths has an important role in improving the efficiency of electrochemical treatment by the generation of chlorine oxidants (Cl_2, OCl^- and chlorine radicals) [20].

In this work, electrochemical treatment was carried out in a reactor with Ti/Pt oxides electrodes initially designed for disinfection treatments. The aim of the study was to propose a simple commercial cell that is easy to apply at industrial level. The electrochemical decolourization process with this type of cells has been largely studied by the authors and has already been published in previous studies on reactive dyeing wastewater [20–23]. A low current density was selected in order to minimize electrical consumption. In addition, color removal was improved by irradiation of UV light. The UV light induces the homolytic breakage of chlorine bonds formed during electrochemical treatment to generate new $^{\cdot}$Cl radicals which continue the dye oxidation. In addition, $^{\cdot}$Cl radicals in alkaline media can oxidize water molecules, producing hydroxyl radicals ($^{\cdot}$OH) and being reduced to chloride ions (Cl^-).

In a preliminary work, high-quality dyeing is obtained in the first reuse of the decolored dye baths [24]. These promising results led our considering the proposal of a cyclical reuse method with continuous processes of treatment and dyeing with the aim to study its feasibility in the textile industry. In the following work, dyeing series of ten successive reuses with three bifunctional monochlorotriazine reactive dyes Procion H-EXL (Navy Blue, Crimson and Yellow) are performed (individually and in trichromie). Color differences were calculated to study its evolution with respect to the number of reuses in order to evaluate the industrial application of the continuous reuse process. The effect of the number of reuses on the quality dyeing evolution was studied, because the organic matter content of water should increase at each reuse (dye fragments and organic matter coming from the fiber). A higher presence of organic matter could interfere in the fixation of the new reactive dyeing.

2. Materials and methods

2.1. Dyeing procedure

Batch dyeings of cotton knitted fabrics were carried out at a liquor ratio (LR) 1/10 (fibre weight/water volume) in a Linitest laboratory dyeing machine (Original Hanau Ltd, Germany) in a stainless steel drum of 6.5 L in capacity. All dyeings were carried out in duplicate. The drum was substituted by a routable support that allowed the use of up to 12 dyeing stations of 250 mL when simultaneous dyeings were carried out at different dye concentrations. Cotton knitted fabric (Pique), scoured and prepared for dyeing, was kindly supplied by Tipsa S.A. (Spain).

Three reactive dyes were selected according to the three primary colors (commercial grade, kindly supplied by DyStar Inc., Spain): Procion Crimson H-EXL (C.I. Reactive Red 231) Procion Yellow H-EXL (C.I. Reactive Yellow 138: 1) and Procion Navy Blue H-EXL (C.I. not available). These dyes are bifunctional with two monochlorotriazine reactive groups.

Individual dyeings were performed with each dye at a 3% concentration o.w.f (of weight fabric), the equivalent of 2/1 SD (Standard Depth) ($3\,\mathrm{g\,L^{-1}}$ at a LR of 1/10). In the case of trichromies (dyeings with the combination of three dyes which correspond to primary colors), the concentration of each dye was 1% o.w.f ($1\,\mathrm{g\,L^{-1}}$ for each dye, LR 1/10). As dyeing electrolyte, $80\,\mathrm{g\,L^{-1}}$ of NaCl was selected. A mixture of $5\,\mathrm{g\,L^{-1}}$ Na_2CO_3 and $0.5\,\mathrm{g\,L^{-1}}$ NaOH was used as dyeing alkali.

A temperature time profile similar to an "all in" dyeing method was selected according to the recommendations given by DyStar: the dye and the total amount of electrolyte were added into the solution at the beginning of the process, the dyeing started at 50℃ for 15 min, then the temperature was raised to 80℃ at a gradient of 1.4℃/min. The alkali was added after 30 min at 80℃ and finally, the dyeing lasted for 60 min more.

Once the dyeing was done, the exhausted residual baths were collected and the cotton fabric samples were washed to remove the unfixed dye. A standard washing procedure was followed, as proposed by the manufacturer [25]. Samples were washed three times with water at 70℃ during 10 min. Later a soaping bath was performed at 100℃ with $2\,\mathrm{g\,L^{-1}}$ of a detergent–dispersant with anionic non-ionic character (Cotemoll TLTR, kindly supplied by Color Center S. A., Spain). Finally, the samples were rinsed two times (at 70 and 50℃) to eliminate the soap.

2.2. Electrochemical decolorization

The treatment of the exhausted dyebaths was conducted in an undivided electrolytic cell. It was supplied by Elchem Inc. (Germany) with the commercial name of ECO 75 Cell. The cathodes were constituted by titanium and the anodes were made of titanium covered by platinum oxides. The total surface area of each electrode was $486\,\mathrm{cm^2}$ and the volume of the vessel was 1 L.

A pump to feed the cell and a tank to store the treated wastewater completed the experimental plant. This plant operated continuously at a flow rate of $20\,\mathrm{L\,h^{-1}}$. The treatment was carried out under galvanostatic conditions with a power supply (Grelco GVD310 0–30 V cc/0–10 A). The current density was fixed at $6\,\mathrm{mA\,cm^{-2}}$ according to our previous studies focussed on the optimization of the electrical consumption [26]. At this current density, the electrical consumption was $6.9\,\mathrm{Wh\,L^{-1}}$. A color removal higher than 80% was reached at the exit of the electrolytic cell for all the samples. Then, the effluents were stored for 1 h in a tank exposed to UV light in order to achieve complete decolourization according to the optimization of the decolorization treatment carried out in our previous studies [21,22]. The UV light source was one 40 W fluorescent tube (Philips TL 40 W/08) which emitted at a wavelength of 254 nm. Decoloration was calculated using Eq. (1) by measuring the absorbance of treated and untreated samples at the wavelength of maximum absorbance of each dye (605 nm for Procion Navy Blue H-EXL, 522 nm for Procion Crimson H-EXL and 413 nm for Procion Yellow H-EXL). The absorbance measurements were carried out with a UV–visible spectrophotometer (Shimadzu UV-240 SP 1750 model, Germany) with cuvettes of an optical path length of 10 mm.

$$\text{Decolouration}\,(\%) = \frac{\text{Abs}_u - \text{Abs}_t}{\text{Abs}_u} \times 100 \tag{1}$$

where Abs_u and Abs_t are the absorbance of the dye for untreated and treated samples, respectively.

2.3. Water preparation for reuse

The percentage of discolored water recovered from the initial dyebath was fixed at 70%. The water volume lost during dyeing by adsorption into the fiber and by evaporation (30%), which is therefore not recovered, was restored with decalcified water.

Before the water reuse, the excess oxidant compounds generated during electrochemical treatment, mainly Cl_2 and ClO^-, had to be eliminated because of the high sensitivity of reactive dyes to chemical oxidation. Their concentration was determined by a colorimetric test CHEMets Kit Chlorine K-2505D (range of analysis: 5–150 ppm of oxidants, expressed as Cl_2 concentration) and they were removed by adding the stoichiometric amount of sodium bisulphite: $NaHSO_3$ (which produced Na_2SO_4), followed by aeration.

The dyeing effluents showed an alkaline pH that was adjusted to pH 7 by adding HCl 0.1 M. pH was measured with a pH-meter Crison GLP21 model. The final chloride content was analyzed by titration with $AgNO_3$ [27] and the required amount of NaCl was added in order to reach a concentration of $80\,\mathrm{g\,L^{-1}}$, according to the dyeing method. NaCl is needed in the dyeing process to promote the diffusion and fixation of the dye from the solution into the fabric. All dyeings were performed at the same NaCl concentration. The amount of unrecovered NaCl (lost in the previous dyeing) must be added to perform a new dyeing.

2.4. Parameters studied in the reuse

In order to study the feasibility of reusing the discolored residual dyebath, 10 successive reuses with each dye and the trichromie were carried out. Each series of reuse started with a standard dyeing with decalcified tap water. In each reused bath, the organic matter content and the percentage of recovered salt were calculated. Combustion-Infrared Method [28] measured the organic matter content as total organic carbon (TOC) with a TOC analyzer (Shimadzu TOC-5050A, Germany). In the dyed fabrics, color reproducibility was studied from color differences (DE*) calculated with respect to the standard dyeing. DE* of each dyeing was obtained with a Colorimeter (Elrephomat Carl Zeiss, Inc., Germany) by evaluating chromatic coordinates. The measurements of DE* with respect to the standard dyeing were performed in triplicate, taking three points of the dyed fabric. Results which caused a coefficient of variation higher than 5% were discarded.

Chromatic coordinates are defined by three parameters: L*, C* and H*, which represents lightness, chroma and hue, respectively. DL*, DC* and DH* are the differences of each parameter versus the reference. These values allowed the calculation of CMC(2:1) color differences ($\mathrm{DE}^*_{\mathrm{CMC(2:1)}}$) according to UNE-EN ISO 105-J03: 1997 [29] (Eq. (2)):

$$\mathrm{DE}^*_{\mathrm{CMC(2:1)}} = [(\mathrm{DL}^*/2S_\mathrm{L})^2 + (\mathrm{DC}^*/S_\mathrm{C})^2 + (\mathrm{DH}^*/S_\mathrm{H})^2]^{1/2} \tag{2}$$

where S_L, S_C and S_H are calculated from the chromatic coordinates of the standard dyeings (L_R, C_R and h_R) as follows:

$$S_\mathrm{L} = 0.040975L_\mathrm{R}/(1 + 0.01765L_\mathrm{R})$$

$$\text{If } L_\mathrm{R} < 16S_\mathrm{L} = 0.511$$

$$S_\mathrm{C} = [0.0638C_\mathrm{R}/(1 + 0.0131C_\mathrm{R})] + 0.638$$

$$S_\mathrm{H} = S_\mathrm{C}(\mathrm{Tf} + 1 - f)$$

$$f = (\mathrm{C}_\mathrm{R})^4/[(\mathrm{C}_\mathrm{R})^4 + 1{,}900]^{1/2}$$

$$T = 0.36 + [0.4 \cdot \cos(35 + h_\mathrm{R})] \quad \text{if } h_\mathrm{R} \geq 345^\circ \text{ or } h_\mathrm{R} \leq 164^\circ$$

$$T = 0.56 + [0.2 \cdot \cos(168 + h_\mathrm{R})] \text{ if } 164^\circ < h_\mathrm{R} < 345^\circ$$

In general, in the textile industry, the acceptance limit for color differences is one unit ($\mathrm{DE}^*_{\mathrm{CMC(2:1)}} \leqslant 1$). This criterion is widely used in dyeing quality control to compare the color differences between two fabric samples.

3. Results and discussion

3.1. Reuse of salt

The percentages of salt reused in the different series of dyeing carried out with each individual dye and the trichromie are shown in Fig. 1. In each dyeing, an average of 60% of the initial electrolyte was saved. As expected, this percentage was from the order of the recovered water volume (70% of the initial dyebath). All the percentages of NaCl recovery were between 55 and 65% because the dyeing was started with a dry fabric and finished with a wet fabric. For this reason, the percentage of water recovered was 70%. In the same way, the unrecovered salt remained also adsorbed on the wet fabric. The reuse of this electrolyte entails a significant reduction of the salt discharged into the wastewater. Besides the environmental and economical benefits of salt reuse, the biological treatment plant can also be better operated.

3.2. Evolution of organic matter content in the effluent

The reuse of the discolored residual dyebath involved performing the operation with water containing a significant amount of organic matter, in contrast to the dyeings with decalcified tap water. This organic matter was in part due to the residual hydrolyzed dye but it was also extracted from the cotton fabrics. The fixation of dye to the fiber could be affected by it. Although the hydrolyzed dye is not able to react with the textile fiber, it can be adsorbed into it, as well as the organic matter extracted in previous dyeing, which implies a more difficult reaction of new dye.

The organic matter content of each bath for the different dyeing series is shown in Fig. 2. This figure shows the TOC evolution for the exhausted dyebath, the discolored dyebath and the water prepared to be reused. It is apparent that the TOC, after an initial increase, became stable through successive reuses. The TOC reached a steady state because the organic matter increase expected in each reuse was compensated by electrochemical treatment (which reduced the TOC by an average of 22%), and also by the 30% of fresh water (free of organic matter) added to each bath.

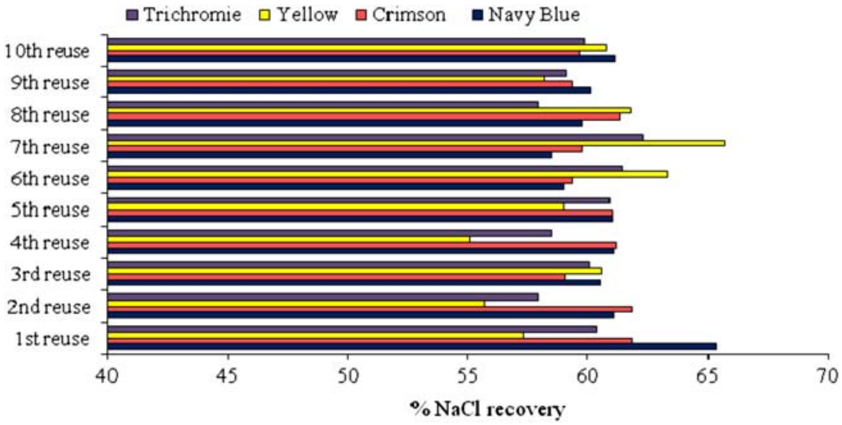

Fig. 1. Percentage of salt saved in the four series of reuse.

3.3. Color reproduction

All dyeings were carried out in duplicate. In all cases, $DE^*_{CMC(2:1)}$ between the duplicates were always lower than 0.3. This value is very low with respect to the acceptance limits of the textile industry ($DE^*_{CMC(2:1)} \leqslant 1$).

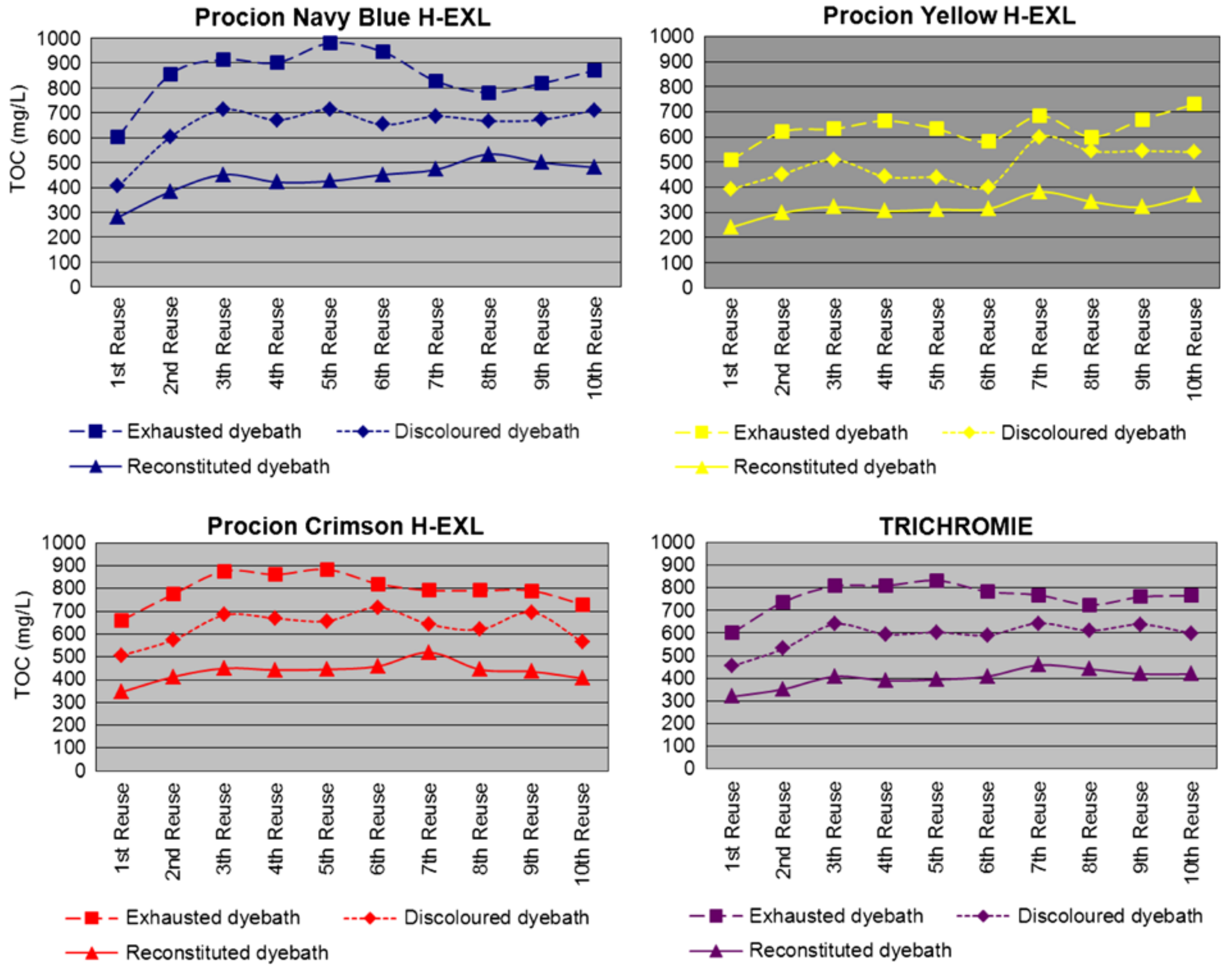

Fig. 2. Evolution of TOC in the four series of dyeing.

Color differences in each reuse with respect to the standard for the different dyeing series are shown in Fig. 3. These color differences were calculated as DE* $_{\text{CMC(2:1)}}$.

From the evolution of DE* $_{\text{CMC(2:1)}}$, the influence of consecutive reuses of discolored dyebaths on the dyeing processes can be established in the four dyeing series. For all dyes, the first reuse produced dyeings with low color differences (DE* $_{\text{CMC(2:1)}} \leq 1$) with respect to standard dyeing. When the reuse process was repeated, color differences increased in all cases until the 4th or 5th reuse. At that point, DE* remained practically constant until the last reuse, that is to say, DE* became independent of the number of reuses.

With respect to DE* $_{\text{CMC(2:1)}}$ values, in the dyeing series in blue and in the trichromie, color differences observed were high except in the first reuse where the dyeing presented DE* $_{\text{CMC(2:1)}}$ equal to 1. In the red dyeing, the first three reuses produced dyeings of high quality and the dyeings obtained in the following reuses had DE* $_{\text{CMC(2:1)}}$ values very close to 1. Finally, all yellow dyeings were acceptable, as DE* $_{\text{CMC(2:1)}}$ was bellow 1 in all the reuses. The calculations of color differences DE* $_{\text{CMC(2:1)}}$ are based on the sensitivity of the human eye to perceive color differences. This sensitivity is higher for blue shades and it is lower for red and yellow shades. The human eye discriminates better among different kinds of blue than among different kinds of red, and has difficulties to detect different kinds of yellow. For this reason, color differences DE* $_{\text{CMC(2:1)}}$ are more pronounced for blue dyeing and trichromies than for red dyeing and yellow dyeing.

Color differences were attributed to the differences in the three parameters that constitute the chromatic coordinates: Lightness (DL*), Chroma or saturation (DC*) and hue (DH*) on the basis of the chromatic diagram (Fig. 4) [30,31]:

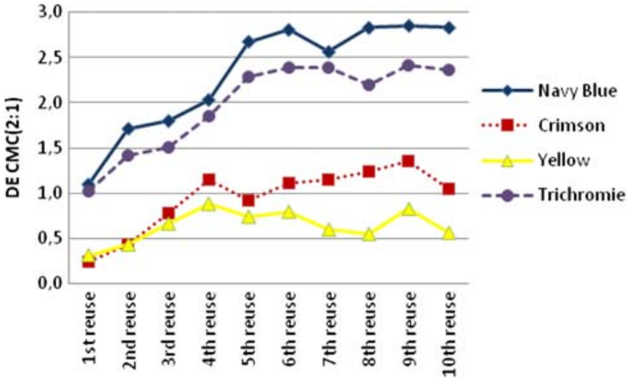

Fig. 3. Evolution of color differences for the four series of reuse with respect to the standard dyeing.

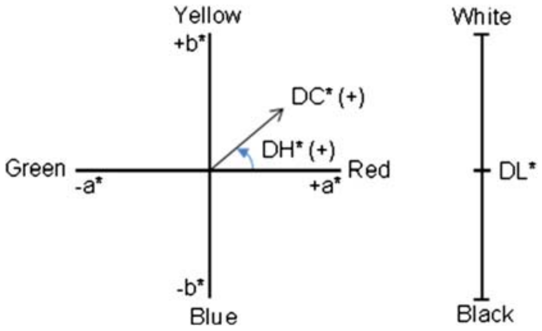

Fig. 4. Chromatic diagram of the CIELab color space.

Table 1 shows the differences in the chromatic coordinates for each reuse series which are useful to evaluate the influence of different parameters in the colour differences.

From these results, it is clear that the evolution in color difference was directly related to the DL* (lightness) evolution as they both increased in the first reuses until they reached a stable value whereas the two other parameters (DC* and DH*) show a different tendency (they exhibit a lower variability apparently not correlated with the reuses). That is, the main color differences were due to the lower intensity of dyed samples. This fact implied a lower dyeing exhaustion, probably caused by the residual organic matter (products of dye degradation and/or other compounds extracted from the fabric). Some dye by-products could act as residual direct dye when the water is reused or it could also react with the new reactive dye, decreasing the final dye fixation. In this way, the TOC evolution confirms this hypothesis, as it also followed the same tendency as DL*.

All studied dyes exhibited a similar behavior with respect to DE* $_{\text{CMC(2:1)}}$, DL* and TOC values along the reuse series. Moreover, in the case of the blue dyestuff, DL* values were higher than in the other dyes and consequently, DE* $_{\text{CMC(2:1)}}$ differences were found to be higher.

With respect to the rest of the chromatic parameters, negative DC* values indicate lower color intensity or less saturated color. Thus, with reused dye baths, the color intensity fall increased according to the following sequence:

Crimson < Trichromie < Navy Blue < Yellow

Negative DH* values with respect to the reference color (clean water) indicate a change of hue in the clockwise direction, that is to say:

For the Navy Blue dye, the color became slightly more green (or yellowish). For the Crimson, the hue

Table 1
Differences in chromatic coordinates in the four series of dyeing

	Navy Blue			Crimson			Yellow			Trichromie		
Sample	DL	DC	DH	DL	DC	DH	DL	DC	DH	DL	DC	DH
1st reuse	1.4	−0.8	−0.2	0.4	0.1	−0.6	0.7	−1.1	0.1	0.7	−0.4	−0.9
2nd reuse	2.3	−0.9	0	0.7	−0.1	−1.1	0.9	−1.3	0.6	1.4	−0.4	−1.0
3rd reuse	2.4	−0.9	−0.3	1.3	−0.4	−1.7	1.5	−0.9	0.7	1.4	−0.6	−1.1
4th reuse	2.7	−1.2	0	1.9	−0.5	−2.7	2	−1.9	0.8	1.9	−0.7	−1.2
5th reuse	3.6	−1.2	−0.4	1.6	−0.9	−1.7	1.6	−0.9	1.1	2.1	−1.1	−1.6
6th reuse	3.8	−1.2	−0.3	1.8	−0.7	−2.7	1.8	−2.5	0.4	2.3	−1.1	−1.6
7th reuse	3.4	−1.4	−0.4	1.9	−0.5	−2.7	1.3	−1.6	0.7	2.3	−1.1	−1.6
8th reuse	3.8	−1.4	−0.3	2.2	−0.1	−2.1	1.2	−1.8	0.5	2.4	−0.7	−1.3
9th reuse	3.8	−1.5	−0.4	2.3	−0.6	−2.9	1.8	−2.5	0.9	2.5	−1.0	−1.5
10th reuse	3.8	−1.4	−0.3	1.8	−0.2	−2.1	1.2	−2.3	0.5	2.4	−1.0	−1.5

was less red or more greenish, and it was more sensitive to the water reuse. For the Yellow, the color was less reddish and more greenish (more yellowish). For the trichromie, the hue was more greenish and more yellowish and it was less reddish and less bluish. Trichromies and Crimson dyeings were more sensitive to the reuse. In general, all the hues became more yellowish due to the higher organic matter content (TOC) in the following order of sensitivity:

Crimson > Trichromie > Yellow > Navy Blue

The total effect on the color differences $DE^*_{CMC(2:1)}$ is explained by the following aspects:

- Yellow: lower total differences (always acceptable) were obtained since the change was to the same hue and the differences of intensity were less perceptible in yellow and green colors.
- Crimson: The level of yellowing did not produce perceptible and unacceptable differences.
- Trichromie: Due to the variations of hue, intensity and lightness, the total color differences were clearly perceptible and they were not acceptable.
- Navy blue: Although hue differences were minimal, the loss of intensity and the increase of lightness produced clearly perceptible color differences in such a dark shade, which implied the variation from Navy Blue to Sky Blue.

In order to consider the possibility of reusing the maximum amount of water and salt in unlimited dyeing cycles, some actions should be carried out to compensate the major content of organic matter of the reused water and to reduce color differences, mainly for the blue color and the trichromie. Two solutions can be proposed to improve the dyeing quality: the application of a higher intensity in electrochemical treatment or the addition of a higher concentration of dye in the initial recipe.

In the first case, the application of a higher current density in a prolonged electrochemical treatment leads to organic matter mineralization, obtaining water free of organic matter. In our previous studies [24], 81% of TOC was removed after electrochemical treatment was conducted for 10 h at 24 mA/cm^2. The required treatment time and its high electrical consumption (700 Wh/L) would make industrial application of this degradation process difficult.

On the other hand, increasing dye concentration in the reuses to compensate for their lower exhaustion can be especially interesting in Mediterranean areas where the hydric resources are scarce and salinity is a severe problem. For this reason, environmental regulations are very restrictive to the discharge of high-salinity effluents [2]. The consequent increase in

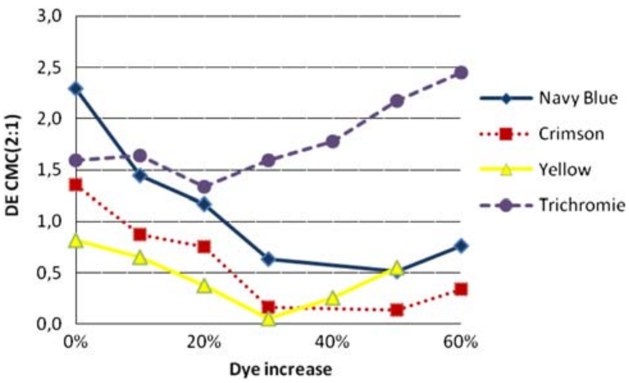

Fig. 5. Influence of the dye increase on color differences. Dyeing with reused water (10 reuses) versus standard dyeing.

Table 2
Differences in chromatic coordinates with respect to the dye increase. Dyeing with reused water (10 reuses) versus standard dyeing

	Navy Blue			Crimson			Yellow			Trichromie		
Dye increase (%)	DL	DC	DH	DL	DC	DH	DL	DC	DH	DL	DC	DH
0	3	−0.9	−0.8	2.5	−2.1	0.3	1.9	−1.4	0.6	1.5	0.4	−1.2
10	1.9	−0.8	−0.3	1.6	−1.6	0.2	1.5	−0.7	0.6	1.1	0.4	−1.5
20	1.5	−0.6	−0.4	1.4	−0.9	0.5	0.9	−0.5	0.2	0.0	0.4	−1.4
30	0.8	−0.4	−0.2	0.2	0.3	0.6	0.1	0.2	−0.1	−1.0	0.8	−1.4
50	−0.7	−0.1	0.1	−0.1	0.5	0.5	−1.3	0.9	0.3	−2.2	0.9	−1.4
60	−1	−0.1	0.3	−0.4	1.2	1				−2.7	1.1	−1.3

dyeing costs can be compensated with salt saving, and with lower wastewater discharge costs [32].

3.4. Dye increase

As indicated, color differences became practically constant from the fourth/fifth reuse in an apparent steady state. Thus, for a cyclic process, it can be assumed that DE* is independent from the number of reuses. The amount of dye to be added to the initial dyeing formula was determined with respect to this point. Dyeing processes were carried out with water that had already been reused 10 times (11th reuse). Different amounts of dye were added. Color differences ($DE^*_{CMC(2:1)}$) with respect to the standard obtained with different dye increases are shown in Fig. 5.

In this figure, it can be seen that the blue dyeing requires a 30% increase to provide an acceptable color difference ($DE^*_{CMC(2:1)} = 0.6$), whereas for the red color, it was only necessary to add 10% of the dye. In the case of yellow dyeing, the dye increase was not necessary, as color differences were lower than 1 in all reuses. However, an almost null $DE^*_{CMC(2:1)}$ was obtained when yellow dye was increased by 30%. Finally, in the trichromie, it was not possible to obtain $DE^*_{CMC(2:1)}$ lower than 1, the lowest color differences were obtained when all the dye concentrations were increased by 20% ($DE^*_{CMC(2:1)} = 1.4$), and in this case, the percentage needed for each dyestuff should be studied to obtain the new formula to reproduce the desired color.

The values in the chromatic coordinates are shown in Table 2. As in the previous experiments, in this case, DL* also exhibited the same tendency of $DE^*_{CMC(2:1)}$ and, consequently, color differences with respect to the standard can be again attributed to this parameter.

DL* values decreased when increasing the amount of dye until they reached negative values. At this point, the dyeing became darker than the standard which means that too much dye had been added. It can be concluded that color differences (DE*) were directly related to the absolute value of DL*.

For the three individual dyes, the other two coordinates, DC* and DH*, have a lower influence on the total color differences $DE^*_{CMC(2:1)}$. However, they reached the value zero at the same point that DL*.

In the trichromie an equal increase of the three dyes did not lead to acceptable color differences ($DE^*_{CMC(2:1)}<1$). Due to the higher DH* values obtained (almost constant in all the percentage of dye addition studied) the appropriate colour formula for the reused baths should be revised, as it is usual in the textile dyeing industry.

In summary, while it was not necessary to increase the concentration of yellow dye, the 30% increase in blue dye and 10% for red dye allowed for acceptable color differences to be obtained independent of the number of consecutive reuses carried out. Also, getting a steady state, after 4–5 reuses, meant that with a usual reuse of dyebaths, the reproducibility and repeatability of dying colors should not be adversely affected.

4. Conclusions

Savings of 60% of NaCl on average were achieved with the reuse of discoloured dyebaths after electrochemical treatment.

The first reuse always provided good quality dyeings ($DE^*_{CMC(2:1)} \leq 1$). In the subsequent reuses, the color differences were not significant for yellow. For red, three reuses produced color differences lower than 1 and after the 4th process, $DE^*_{CMC(2:1)}$ was always lower than 1.4. Finally, for blue and trichromie, color differences were higher than 1 after the 2nd reuse, showing a different sensitivity to the residual products in the dyebath than the other two dyestuffs.

In all cases, color differences increased in each reuse until they stabilized from the 4th or 5th reuse. At this point, DE* became independent of the number of reuses. The organic matter content (TOC) in the dyebath showed a similar evolution and the behavior of DL* exhibited a parallel tendency. Dyeings with reused water were less intense due to a minor dye exhaustion, which can be attributed to the presence of dye treatment by-products or to organic compounds extracted from the fabric. In any case, a final steady state was obtained.

An increase of dye was proposed in the dyeing when water was reused in order to reduce the color differences with respect to the original standard dyeing with fresh water. A 30% increase of blue dye and 10% for red dye provided dyeings with acceptable color differences independent of the number of consecutive reuses. Thus, the reuse became a cyclical process where the maximum amount of recoverable water and salt was used. In the yellow dyeing, the addition of dye was not necessary. After 10 reuses, the amount of blue dye to be added was higher than the red dye and it was not necessary to increase the amount of yellow. This different behavior is also due to the different sensitivity of the human eye with respect to the shade.

For the trichromie, the lowest color differences were obtained when the dye was increased by 20%. However, differences of hue with respect to the reference were observed, independent of the dye increase. The influence of the reuse process was more significant in the hue of the trichromie than in the hue of the individual dyeing, due to higher visual sensitivity to hue variations in achromatic colors.

Acknowledgments

This work was supported by the Spanish Ministry of Education and Science (projects CTM2004-05774-C02-01/TECNO and CTM2007-66570-C02-01).

References

[1] European IPPC Bureau, European Commission. Integrated Pollution Prevention and Control (IPPC), Reference Document on Best Available Techniques for the Textiles Industry, Institute for Prospective Technological Studies, Sevilla, 2003.

[2] Spanish government, Royal Decree 849/1986, Regulation of the hydraulic public domain, 1986.

[3] L.F. Greenlee, D.F. Lawler, B.D. Freeman, B. Marrot, P. Moulin, Reverse osmosis desalination: Water sources, technology and today's challenges, Water Res. 43 (2009) 2317–2348.

[4] K. Madwar, H. Tarazi, Desalination techniques for industrial wastewater reuse, Desalination 152 (2002) 325–332.

[5] Y.M. Chao, T.M. Liang, A feasibility study of industrial wastewater recovery using electrodialysis reversal, Desalination 221 (2008) 433–439.

[6] A. Gurses, Ç. Dogar, S. Karaca, M. Açikyidiz, R. Bayrak, Production of granular activated carbon from waste Rosa canina sp. Seeds and its adsorption characteristics for dye, J. Hazard. Mater. 131 (2006) 254–259.

[7] S. Wang, Z.H. Zhu, Effects of acidic treatment of activated carbons on dye adsorption, Dyes Pigm. 75 (2007) 306–314.

[8] E.A. Oliveira, S.F. Montanher, M.C. Rollemberg, Removal of textile dyes by sorption on low-cost sorbents. A case study: sorption of reactive dyes onto Luffa cylindrica, Desalin. Water Treat. 25 (2011) 54–64.

[9] A.Y. Zahrim, C. Tizaoui, N. Hilal, Evaluation of several commercial synthetic polymers as flocculant aids for removal of highly concentrated C.I. Acid Black 210 dye, J. Hazard. Mater. 182 (2010) 624–630.

[10] M. Khayet, A.Y. Zahrim, N. Hilal, Modeling and optimization of coagulation of highly concentrated industrial grade leather dye by response surface methodology, Chem. Eng. J. 167 (2011) 77–83.

[11] C. Allègre, P. Moulin, M. Maisseu, F. Charbit, Treatment and reuse of reactive dyeing effluents, J. Membr. Sci. 269 (2006) 15–34.

[12] Y. He, G. Li, H. Wang, J. Zhao, H. Su, Q. Huang, Effect of operating conditions on separation performance of reactive dye solution with membrane process, J. Membr. Sci. 321 (2008) 183–189.

[13] T. Visa, M. Sánchez, V. López-Grimau, R. Navarro, S. Reche, M.C. Gutiérrez-Bouzán, Photocatalysis with titanium dioxide to remove colour of exhausted reactive dyebaths without pH modification, Desalin. Water Treat. 45 (2012) 91–99.

[14] J. Chung, J.O. Kim, Application of advanced oxidation processes to remove refractory compounds from dye wastewater, Desalin. Water Treat. 25 (2011) 233–240.

[15] H.Y. Shu, M.C. Chang, Decolourization effects of six azo dyes by O_3, UV/O_3, and UV/H_2O_2 processes, Dyes Pigm. 65 (2005) 25–31.

[16] M.S. Lucas, J.A. Peres, Decolorization of the azo dye Reactive Black 5 by Fenton and photo-Fenton oxidation, Dyes Pigm. 71 (2006) 236–244.

[17] M.G. Neelavannan, M. Revathi, A.C. Basha, Photocatalytic and electrochemical combined treatment of textile wash water, J. Hazard. Mater. 149 (2007) 371–378.

[18] M.S. Morsi, A.A. Al-Sarawy, W.A. Shehab El-Dein, Electrochemical degradation of some organic dyes by electrochemical oxidation on a Pb/PbO_2 electrode, Desalin. Water Treat. 26 (2011) 301–308.

[19] C.A. Martínez-Huitle, E. Brillas, Electrochemical alternatives for drinking water disinfection, Angew. Chem. Int. Ed. 47 (2008) 1998–2005.

[20] A.I. del Río, J. Fernández, J. Molina, J. Bonastre, F. Cases, Electrochemical treatment of a synthetic wastewater containing a sulphonated azo dye. Determination of naphthalenesulphonic compounds produced as main by-products, Desalination 273 (2011) 428–435.

[21] M.C. Gutierrez, M. Pepio, M. Crespi, N. Mayor, Control factors in the electrochemical oxidation of reactive dyes, Color. Technol. 117 (2001) 356–361.

[22] M.C. Gutierrez, M. Pepio, M. Crespi, Electrochemical oxidation of reactive dyes: Method validation and application, Color. Technol. 118 (2002) 1–5.

[23] M. Riera-Torres, M.C. Gutierrez, Colour removal of three reactive dyes by UV light exposure after electrochemical treatment, Chem. Eng. J. 156 (2010) 114–120.

[24] V. Lopez-Grimau, M.C. Gutierrez, Decolourisation of simulated reactive dyebath effluents by electrochemical oxidation assisted by UV light, Chemosphere 62 (2006) 106–112.

[25] V. López-Grimau, M.C. Gutiérrez-Bouzán, J. Valldeperas, M. Crespi, Reuse of water and salt of reactive dyeing effluents after electrochemical decolourisation. Color Technol. 128 (2012) 36–43.

[26] DyStar, Inc., Work procedures, Industrial Washing Procedure, Excel Washing, p. 36.

[27] APHA–AWWA–WEF, Method 4500 Cl- (B) Chloride. Argentometric Method. Standard Method for the Examination of Water and Wastewater, 20th ed., American Public Health Association, Washington, DC, 1998.

[28] APHA–AWWA–WEF, Method 5310 (B) Total Organic Carbon (TOC). Combustion-Infrared Method, Standard Methods for the Examination of Water and Wastewater, 20th ed., American Public Health Association, Washington, DC, 1998.

[29] AENOR,UNE-EN ISO105-J03: 1997, Textiles. Ensayos de solidez del color: Cálculo de las diferencias de color, Asociación Española de Normalización y Certificación, Madrid, 1997.

[30] M.R. Luo, B. Rigg, Chromaticity-discrimination ellipses for surface colours, Color. Res. Appl. 11 (1986) 25–42.

[31] J. Valldeperas-Morell, F. Carrillo-Navarrete, Colour fastness (Chapter 5), In: P.A. Annis (Ed.), Understanding and Improving the Durability of TextilesWoodhead Publishing Series in Textiles, The Textile Institute, Cambrigde, pp. 82–103, 2012.

[32] V. López-Grimau, B. Amante García, M.C. Gutiérrez, Estudio de viabilidad de la reutilización de baños de tintura textil, Afinidad 67 (2010) 182–186.