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Electrochemical decolourisation of cotton dye baths for reuse purposes: a way to reduce salinity of the textile wastewater

Víctor López-Grimau[a,*], Carmen Gutiérrez[b], Mireia Sala[b], Martí Crespi[b]

[a]*Departement of Projects Engineering ETSEIAT, Universitat Politècnica de Catalunya, Terrassa 08222, Spain*
Email: victor.lopez-grimau@upc.edu
[b]*INTEXTER, Institute of Textile Research, Universitat Politècnica de Catalunya, Terrassa 08222, Spain*

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ABSTRACT

Electrochemical techniques offer many advantages for the treatment of industrial effluents. These processes are clean, operate at room temperature, and in most cases, do not need the addition of reagents (as in the case of reactive dyeing effluents). In particular, the electrochemical treatment of textile effluents is an efficient method to remove colour. In this work, diverse synthetic effluents containing reactive dyes were treated in an electrochemical cell with Ti/PtO_x electrodes. The efficiency of the process to remove colour and the use of an additional UV irradiation were evaluated. Once the conditions were established in synthetic effluents, they were applied on two types of exhausted reactive dye baths collected from a cotton mill. Instead of the effluent discharge, another possibility is to reuse the decoloured effluents for a new dyeing process. In this sense, diverse experiments were carried out and conditions for the effluents reuse were established. The reuse of dyeing effluents implies an important reduction of the salt and water consumption as well as a reduction of the salinity of the discharged effluents.

Keywords: Textile wastewater; Dye baths; Reactive dyes; Colour removal; Electrochemical treatment; Salt reuse; Water reuse

1. Introduction

The textile industry produces large volumes of wastewater in its dyeing and finishing processes. These effluents have as common characteristic their high colouration. The high consumption of reactive dyes, mainly in the cotton industry, increases this environmental and aesthetic problem, due to their low degree of exhaustion.

Reactive dyes, as well as many of textile dyes, are only partially removed under the aerobic conditions of the conventional biological treatment, and only a small part of them is removed by adsorption on the activated sludge. As biological treatment is insufficient to remove the colour and to accomplish with current regulations, the application of specific treatments is required. There are different techniques to achieve colour removal and among them, the most used are as follows: use of organic adsorbents [1,2], filtration with membrane [3,4], coagulation–flocculation processes [5,6], selection of microorganisms able to degrade dyes [7], application of advanced oxidation processes [8–11] or the development of electrochemical decolourisation [12–14]. The electrochemical decolourisation is an

*Corresponding author.

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advanced oxidation method which provides great advantages in the treatment of high coloured textile wastewater, namely, the addition of chemical compounds (organic or inorganic) is not required and wastes are not generated. The electrochemical oxidation of dyes can also be assisted by photocatalysis [15].

This work was focussed on the optimisation of the electrical consumption, by applying low current densities during the electrochemical treatment, followed by irradiation of solar light or UV light. Initially, synthetic effluents containing reactive dyes were treated in an electrochemical cell with Ti/PtO_x electrodes to remove colour. Once the electrochemical treatment was optimised, it was applied to exhausted reactive dye baths collected from a cotton dyeing mill with the objective to study the efficiency of the decolourisation process in industrial residual dye baths. In these effluents beside the hydrolysed reactive dye and the dyeing electrolyte, there is an important part of organic matter original from the fibre that can compete with the dye oxidation.

The aim of electrochemical treatment combined with UV irradiation is not only the colour removal but also the reuse of the decoloured effluent. The reuse process is especially interesting in the dyeing of cotton and other cellulosic fibres where high amounts of salt are required to obtain a good dye exhaustion and fixation to the fibre. Generally, a concentration of 5–80 g L^{-1} of NaCl or Na_2SO_4 is added depending on the type of dye (direct or reactive dyes) and the shade of the dyeing. The salt does not have affinity to the fibre, 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. The presence of high concentrations of salt is very harmful for the aquatic ecosystems, and it causes operational problems to the biological wastewater treatment plants. Moreover, its elimination is only possible by applying costly treatments such as inverse osmosis or electrodialysis.

In this work, the reuse of the decoloured dye baths for a new dyeing process is proposed as an alternative for the reduction of the discharge of high salinity effluents. The reuse procedure implies an important saving of salt and water consumption (about 70% of dyeing water and 60% of salt are recycled).

2. Methodology

2.1. Electrochemical treatment

The decolourisation treatment was carried out in an undivided electrolytic cell ECO-75 (Elchem, Germany) with a vessel volume of 1 L and total electrodes surface of 486 cm^2. The cathodes were plates of titanium, and the anodes were made of titanium, covered by platinum oxide (Ti/PtO_x anodes). The reactor operated at a continuous flow rate fixed at 20 L/h. The power supply Grelco GVD310 0-30Vcc/0-10A allowed to apply intensities up to 10 A (current densities up to 20 mA/cm^2). The experimental plant was completed by a pump to feed the cell and a tank to store the treated wastewater. To reduce the electrical consumption of the treatment, the effluent was only partly decoloured. The full decolourisation was then achieved after the treatment by exposition of the wastewater, stored in a tank, to solar light or UV irradiation. The UV light source was a Philips TUV lamp (PL-S, UV-C) of 8 watts which emitted at 254 nm and which generated an electrical consumption of 1.6 Wh/L.

Initially, the electrochemical treatment was optimised in synthetic effluent prepared to simulate an industrial dyeing effluent. Three reactive dyes were selected: Navy Blue Procion H-EXL, Crimson Procion H-EXL and Yellow Procion H-EXL at a dye concentration of 1 g/L. Dyes were hydrolysed at alkaline pH by addition of NaOH, and 20 g/L of NaCl were added as electrolyte. Decolourisation was calculated by measuring the absorbance of treated and untreated samples at the wavelength of maximum absorbance of each dye (605 nm for Navy Blue Procion H-EXL, 522 nm for Crimson Procion H-EXL and 413 nm for Yellow Procion H-EXL). The absorbance measurements were carried out with a UV-visible spectrophotometer (Shimadzu UV-240 SP 1,750 model, Germany).

Once the conditions of treatment were established in synthetic effluents, they were applied on two types of exhausted reactive dye baths collected from a cotton mill. Both of them were constituted by a trichromie of Sumifix dyes (a trichromie is a mixture of a red dye, a yellow dye and a blue dye at different concentrations depending on the desired shade). The dyeing liquor ratio was 1/10. One dye bath was more concentrated than the other one. The dye concentration of each dye bath was as follows:

- LC (low concentrate dye bath): Yellow 0.11 g/L + Red 0.30 g/L + Blue 0.85 g/L.
- HC (high concentrate dye bath): Yellow 0.52 g/L + Red 2.00 g/L + Blue 1.12 g/L.

The dyeing recipe also included a commercial sodium chloride solution and a mixture of sodium carbonate and sodium hydroxide as alkali.

The electrochemical treatment was applied at current densities of 3, 6 and 12 mA/cm^2. Colour removal was evaluated by absorbance measurements at their

maximum wavelength (552 nm for LC dye bath and 542 nm for HC dye bath).

2.2. Dyeing with reused water

Dyeings of cotton knitted fabrics were carried out at a liquor ratio (L/R) 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. Three reactive dyes were selected according to the three primary colours (commercial grade, 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) which corresponds to ($3\,g\,L^{-1}$ at a LR of 1/10). As dyeing electrolyte, $80\,g\,L^{-1}$ of NaCl was selected. A mixture of $5\,g\,L^{-1}$ Na_2CO_3 and $0.5\,g\,L^{-1}$ NaOH was used as dyeing alkali.

The 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°C for 15 min; then, the temperature was raised to 80°C at a gradient of 1.4°C/min. The alkali was added after 30 min at 80°C, 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 [16].

The electrochemical treatment of the exhausted dye baths was applied at a current density of $6\,mA/cm^2$ and a flow rate of 20 L/h, with an electrical consumption of 7 Wh/L. A colour 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 decolourisation according to the optimisation experiments carried previously.

Once decoloured the dye bath was prepared to be reused as indicated in the following steps:

(1) Addition of the volume of water lost in the dyeing (30%).
(2) Quantification of residual NaCl and addition of the necessary amount of NaCl.
(3) Adjust to pH 7.
(4) Addition of the dyes and beginning of a new dyeing.

In order to study the feasibility of reusing the discoloured residual dye bath, 10 successive reuses with each dye were carried out. Each series of reuse started with a standard dyeing with soft water. In each reused bath, the organic matter content and the percentage of recovered salt were calculated. The organic matter content was determined as Total Organic Carbon (TOC) with a TOC analyser (Shimadzu TOC-5050A, Germany). In the dyed fabrics, colour reproducibility was studied from colour differences (DE) calculated with respect to the standard dyeing. Colour differences (DE) of each dyeing were obtained with a Colorimeter (Elrephomat Carl Zeiss, Inc., Germany) by evaluating chromatic coordinates. Chromatic coordinates are defined by three parameters: L, C and H, which represent luminosity, chroma and hue, respectively, according to UNE-EN ISO 105-J03: 1997 [17].

In general, in the textile industry, the acceptance limit for colour differences is one unit ($DE \leq 1$). This criterion is widely used in dyeing quality control to compare the colour differences between two fabric samples.

3. Results and discussion

3.1. Optimisation of the decolourisation in synthetic dye baths

Colour removal values higher than 80% were obtained immediately after an electrochemical treatment at $6\,mA/cm^2$ (electrical consumption: 6.7 Wh/L). The complete decolourisation was reached after three hours of water exposition to the solar light. This period of exposition could be reduced to 1 h when the solar light was substituted by UV light (Table 1), since UV light promotes the homolytic breaking of chlorine bonds to generate new $^{\bullet}Cl$ radicals that continue the dye oxidation.

Table 1
Colour removal (%) in the treatment of synthetic dye baths

Treatment	Decolourisation (%)		
	Navy Blue	Crimson	Yellow
After electrochem. ($6\,mA\,cm^{-2}$)	81	83	84
Solar light (3 h)	100	100	100
UV light (1 h)	100	100	100

Table 2
Characterisation of the exhausted reactive dye baths

Parameter	LC dye bath	HC dye bath
Colour (Pt–Co units)	10,000	20,000
TOC (mg/L)	238.2	243.6
NaCl (g/L)	58	71
Conductivity (mS/cm)	79.3	84.7
pH	11.30	11.29

3.2. Decolourisation of exhausted reactive dye baths

The two exhausted dye baths, collected in the mill, were characterised as indicated in Table 2.

According to the previous study carried out with synthetic effluents, the selected optimal conditions were applied to the treatment of LC and HC dye baths: low current densities, followed by an UV irradiation to obtain a full decolourisation at a low cost. Exhausted dye baths were treated in the electrochemical plant at two different current densities: 3 and 6 mA/cm^2 for LC and 6 and 12 mA/cm^2 for HC. Values of decolourisation, electrical consumption and TOC removal obtained immediately after the electrochemical process are presented in Table 3.

High degrees of colour removal were reached in all the experiments. Thus, the presence of organic matter extracted from the cotton did not interfere on the dye oxidation. Further exposition to UV light for 1 h provided full decolourisation. The evolution of the decolourisation by UV light irradiation implies that dye degradation did occur not only by oxidation with hypochlorite and free chlorine, but also through the reaction with high reactive radicalarian species catalysed by the solar light (such as $Cl^{\bullet}$, $Cl_2^{\bullet -}$ and $^{\bullet}OH$).

On another hand, in Table 3 can be seen that values of TOC removal obtained after the electrochemical treatment were low. Of course, they can be increased by increasing the current density, but in this case, the cost of the treatment would be too high. It must be considered that the electrochemical treatment is proposed to remove colour, but not to reduce the organic matter, as the biological treatment is much more inexpensive for this purpose. That is to say, the main objective of the electrochemical treatment is to break down the dye molecules into smaller and biodegradable colourless species, able to be treated in the biological plant.

Table 3
Electrochemical treatment applied at different current densities

	LC dye bath		HC dye bath	
Current density (mA/cm^2)	3	6	6	12
Decol. (%)	93	96	89	96
Decol. after solar exp. (%)	100	100	100	100
Consumption (Wh/L)	4.4	7.2	7.2	12.3
Reduction TOC (%)	11	17	15	24

3.3. Reuse of decoloured wastewater

Ten consecutive reuses of the decolourised dye bath were performed with each one of the three selected dyes. In each dyeing, 70% of the process water and an average of 60% of the initial electrolyte were saved. 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.

The reuse of the discoloured residual dye bath involved performing the operation with water containing a significant amount of organic matter, in contrast to the dyeings with soft fresh water. This organic matter can interfere in the fixation of the new dye to the cotton fibre. The organic matter content of each reuse for the dyeing with Navy Blue dye is shown in Fig. 1. This figure shows the TOC evolution for the exhausted dye bath, the discoloured dye bath and the water prepared to be reused. The TOC, after an initial increase, became stable through successive reuses. The TOC reached a steady state because the electrochemical treatment reduced the TOC by an average of 22%, and also because a 30% of fresh water (free of organic matter) was added to each bath. The TOC evolution for the dyeing series with the other two dyes followed a similar behaviour.

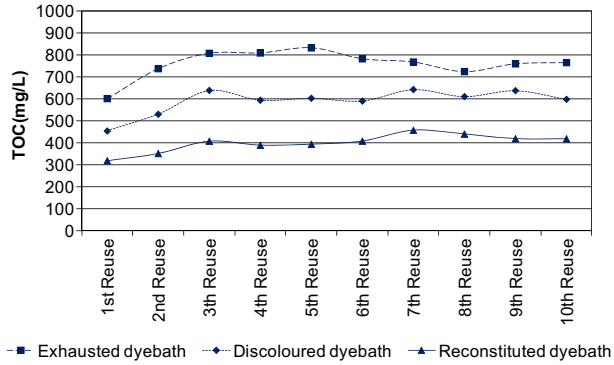

Fig. 1. TOC of each reuse for the dyeing with Navy Blue dye.

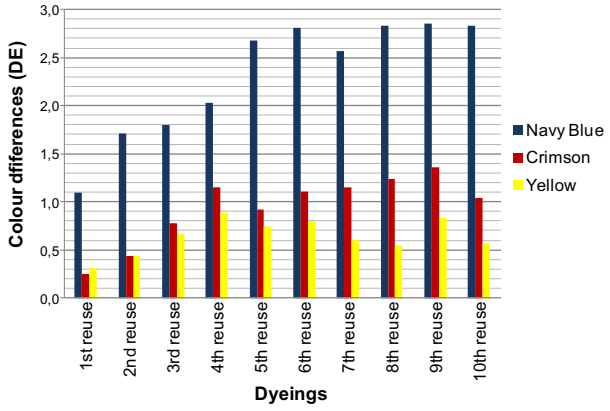

Fig. 2. Colour differences (DE) for each reuse respect to the reference.

Colour differences (DE) in each reuse with respect to the standard for the different dyeing series are shown in Fig. 2. From the evolution of DE, the influence of consecutive reuses of discoloured dye baths on the dyeing processes can be established. For all dyes, the first reuse produced dyeings with low colour differences ($DE \leq 1$) with respect to standard dyeing. When the reuse process was repeated, colour 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.

In the blue dyeing series, colour differences were high except in the first reuse (DE equal to 1). In the red (crimson) dyeing, the first three reuses produced dyeings of high quality and the dyeings obtained in the following reuses had DE values very close to 1. Finally, all yellow dyeings were of high quality, as DE was bellow 1 in all the reuses. The calculations of colour differences (DE) are based on the sensitivity of the human eye to perceive colour 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, colour differences (DE) are more pronounced for blue dyeing and than for red dyeing and yellow dyeing.

In the case of Navy Blue dyeing, colour differences were easily reduced by addition of an extra amount of dye. For instance, an addition of 30% of dye in the 10th reuse allowed to obtain a $DE = 0.7$. For Crimson, dyeing only was necessary to increase the dye concentration a 10% to obtain DE bellow 1. In this case, the increase in the dyeing cost was compensated by the saving of water and salt.

4. Conclusions

The electrochemical treatment of exhausted reactive dye baths using Ti/PtO_x electrodes provides high decolourisation levels immediately after the electrochemical process. The exposure of the partially decoloured effluent to UV light allows to apply lower densities during the electrochemical treatment, which implies a reduction of the electrical consumption.

The exhausted dye baths, once decoloured, can be reused for new dyeing processes which implies an important saving of water and salt, of the order of 70% of water and 60% of salt. In all cases, colour differences increased in each reuse until they stabilised from the 4th or 5th reuse. At this point, DE became independent of the number of reuses. The organic matter content TOC in the dye bath showed a similar evolution. After 10 reuses, a 30% increase of blue dye and 10% for red dye provided dyeings with low colour differences independent of the number of consecutive 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 behaviour is also due to the different sensitivity of the human eye with respect to the shade.

These studies to save water and salt are particularly important in Mediterranean countries, where salinity of rivers is increasing and, nowadays, represents a serious environmental problem.

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References

[1] F. Banat, N. Al-Bastaki, Treating dye wastewater by an integrated process of adsorption using activated carbon and ultrafiltration, Desalination 170 (2004) 69–75.
[2] 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.
[3] C. Allègre, P. Moulin, M. Maisseu, F. Charbit, Treatment and reuse of reactive dyeing effluents, J. Membr. Sci. 269 (2006) 15–34.
[4] G. Capar, U. Yetis, L. Yilmaz, Membrane based strategies for the pre-treatment of acid dye bath wastewaters, J. Hazard. Mater. 135 (2006) 423–430.
[5] F. Harrelkas, A. Azizi, A. Yaacoubi, A. Benhammou, M.N. Pons, Treatment of textile dye effluents using coagulation-flocculation coupled with membrane processes or adsorption on powdered activated carbon, Desalination 235 (2009) 330–339.
[6] D.J. Joo, W.S. Shin, J.H. Choi, S.J. Choi, M.C. Kim, M.H. Han, T.W. Ha, Y.H. Kim, Decolorization of reactive dyes using inorganic coagulants and synthetic polymer, Dyes Pigm. 73(1) (2007) 59–64.

[7] S. Sumanthi, B.S. Manji, Uptake of reactive textile dyes by *Aspergillus foetidus*, Enzyme Microb. Technol. 27 (2000) 347–355.
[8] 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.
[9] I. Arslan, I.A. Balcioglu, D.W. Bahnemann, Advanced oxidation of a reactive dyebath effluent: Comparison of O_3, H_2O_2/UV-C and TiO_2/UV-A processes, Water Res. 36 (2002) 1143–1154.
[10] J. Chung, J.O. Kim, Application of advanced oxidation processes to remove refractory compounds from dye wastewater, Desalin. Water Treat. 25 (2011) 233–240.
[11] T. Visa, M. Sánchez, V. López-Grimau, R. Navarro, S. Reche, C. Gutiérrez-Bouzán, Desalin. Water Treat. 45 (2012) 91–99.
[12] V. Lopez-Grimau, M.C. Gutierrez, Decolourisation of simulated reactive dyebath effluents by electrochemical oxidation assisted by UV light, Chemosphere 62 (2006) 106–112.
[13] 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.
[14] 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.
[15] M.E. Osugi, G.A. Umbuzeiro, F.J.V. de Castro, M.V.B. Zanoni, Photoelectrocatalytic oxidation of remazol turquoise blue and toxicological assessment of its products, J. Hazard. Mater. 137 (2006) 871–877.
[16] DyStar, Inc. Work procedures. Industrial washing procedure, excel washing, p. 36.
[17] AENOR. UNE-EN ISO105-J03. Textiles. Tests for colour fastness: Calculation of colour differences. Madrid: Spanish Association of Normalisation and Certification, 1997.