

ELECTROCHEMICAL TREATMENT AND REUSE OF DYEING EFFLUENTS

M.C.Gutiérrez, V.López-Grimau, M. Riera-Torres, M.Vilaseca, M.Crespi

INTEXTER, Institut d'Investigació Tèxtil de Terrassa

UPC, Universitat Politècnica de Catalunya

Colom 15, 08222 Terrassa, Spain.

gutierrez@intexter.upc.edu

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.

With the electrochemical treatment, large molecules of dyes are oxidised into smaller ones. The uncoloured compounds produced must be further removed in a biological plant before effluent discharge.

In this work, diverse synthetic effluents containing reactive dyes were treated in an electrochemical cell with Ti/PtOx electrodes. The efficiency of the process to remove colour and the use of an additional UV irradiation were evaluated. Moreover, it was shown that the treated effluents do not produce inhibition effects on a biological plant. The yield of a further biological treatment is also discussed.

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. It was shown that the reuse of decoloured washing effluents is easy and that also dyeing effluents can be reused. The reuse of these effluents implies an important reduction of the salt and water consumption as well as a reduction of the salinity of the discharged effluents.

KEYWORDS

Colour removal, wastewater, reactive dyes, electrochemical treatment, oxidation/reduction, biological treatment, biodegradability, respirometry.

1. INTRODUCTION

The textile industry produces large volumes of wastewater in its dyeing and finishing processes. These effluents have as common characteristic their high coloration. 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: activated carbon adsorption, membrane filtration, coagulation-flocculation processes, treatment with ozone, use of organic adsorbents, selection of microorganisms able to degrade dyes, application of advanced oxidation processes -Fenton and Photo-Fenton reactions, H₂O₂/ UV light systems and heterogeneous photocatalytic oxidation- or development of electrochemical decolourisation.

Some of these methods have been applied at industrial scale. They provide a good colour removal, but generally they have a high cost. Others technologies are still studied at laboratory and pilot plant scale. This is the case of the electrochemical decolouration, which could be done by reduction or by oxidation. In the case of reduction, the chromophore of azo dyes is broken to generate two amino groups (Bechtold et al., 2001). In the second case, the indirect oxidation by hypochlorite ions generated in a brine solution is reported (Vijayaraghavan et al., 2001; Vlyssides et al., 1999). The electrochemical oxidation of dyes can also be assisted by photocatalysis (Pelegri et al., 1999; Shen et al., 2002).

Last years, the uses of electrochemical techniques for the industrial effluents treatment have increased (Kim et al., 2002, 2003; Sakakibara and Nakayama, 2001). Such processes are clean, operate at low temperatures, and in most cases, do not need the addition of reagents (as in the case of reactive dyeing effluents). For this reason, the electrochemical treatment of textile effluents is an efficient method to remove colour, especially when the wastewater contains reactive dyes.

Electrochemical techniques are based on effluent electrolysis. The molecules are only partially broken to avoid excessive power consumption. In general, the destruction of organic compounds in effluents by electrochemical treatment is achieved by oxidation, which can occur directly at the anode and/or indirectly by species generated by the anode (Gutierrez et al., 2002), but simultaneously, a reduction can also occur when anode and cathode are not separated.

During the dyeing process with reactive dyes, the addition of high concentrations of salt is necessary to obtain a better fixation and exhaustion (up to 80 g L⁻¹ of NaCl or Na₂SO₄, as most common electrolytes). This amount of salt also acts as electrolyte during the electrochemical process. In our previous studies, electrodes constituted by Titanium/ Platinum oxides (Ti/PtOx) were employed to discolour simulated dyehouse effluents with reactive dyes (Gutiérrez et al., 2002; Gutiérrez et al., 2003). The results obtained with these electrodes were satisfactory, especially when NaCl was chosen as dyeing electrolyte. The better efficiency of the treatment in the presence of NaCl was attributed to an indirect oxidation of the dyes by Cl₂, ClO⁻ and other oxidising species formed from the oxidation of Cl⁻.

On the basis of our previous studies (Gutierrez and Lopez-Grimau, 2003), we propose the electrochemical treatment as a short step previous to the biological treatment, in which only the coloured effluents are treated. Consequently, these effluents are treated with the rest of wastewater in the biological plant.

In a part of this work, a synthetic effluent containing a reactive dye was treated in an electrochemical cell with Ti/PtOx electrodes to remove colour. The discoloured effluent was mixed with other textile mill process effluents (scouring, bleaching, washing, etc), according to the rate of each effluent in the mill, and was submitted to biological treatment. This biological treatment was carried out by activated sludge plant. The yield of the method to remove the organic matter was evaluated.

In addition, the electrochemical treatment was applied to exhausted reactive dyebaths collected from a cotton dyeing mill with the objective to study the efficiency of the decolourisation process in industrial residual dyebaths. 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.

This work was also focussed on the optimisation of the electrical consumption, by applying low current densities during the electrochemical treatment, followed by irradiation of solar light.

Finally, the biodegradability of the treated effluents and the presence of toxic compounds were studied to ensure that these effluents could be send to the biological treatment plant of the factory. Responses of different types of dyes to biological treatments are not alike. The ones that are insoluble in water (disperse, vat, sulphur, azoic, etc.) are first removed in a decantation step and the soluble ones go to the biological treatment. Although they are no biodegradable (aerobically) part of them can be retained with a mechanism called "bioremoval" that consists in their adsorption in the biomass and removal of the dye during slug deposition.

2. METHODOLOGY

2.1. Electrochemical treatment

Firstly, the electrochemical treatment was optimised with synthetic hydrolysed solutions of the reactive dye Procion MX-2R at 0.1g/L I (pH and conductivity: 9 and 35000 μ S/cm, respectively). Once the conditions of treatment were established, they were applied on two types of exhausted reactive dyebaths collected in a cotton dyeing process mil. Both of them were constituted by a trichromy of Sumifix dyes, the liquor ratio was 1/10 and the dyes and auxiliaries amounts as follows:

- LC (low concentrate dyebath): Y.3RF 0.11% + R.3BF 0.30% + BI.N. BF 0.85%
- HC (high concentrate dyebath): Y. 3RF 0.52% + R. 3BF 2% + BI.N. BF 1.12%
- Electrolyte: 200-250 mL/L NaCl sol. (trisaline sol.™)
- Alkali: 5 g/L Na₂CO₃+ 0.8 -1.35 mL/L NaOH sol. 50% (w/v).

The electrochemical system was constituted by the electrochemical cell, the pump and the deposit to store the treated wastewater. The electrolytic cell was undivided (Eco 75 - Elchem, Germany) with a vessel volume of 1L and total electrodes surface of 486 cm². The cathodes were plates of titanium and the anodes were made of titanium, covered by platinum oxide (Ti/PtOx anodes). It operated at a continuous flow rate fixed at 25 L h⁻¹. The current intensity was regulated from 1.5 to 6 A. To reduce the intensity of the treatment, the effluent was only partly decoloured. The full decolorisation was then achieved after the treatment by exposition of the wastewater, stored in a tank, to solar light or UV irradiation.

Colour of synthetic solutions was evaluated by absorbance measurements at their maximum wavelength (552 nm for LC dye bath and 542 nm for HC dye bath).

2.2. Biological treatment

The conventional biological study was carried out with two laboratory biological pilot plants (reactor vessel: 5L). Initially, they were inoculated with urban activated sludge. The feeding flow rate was 1.6 L/day. The whole effluent submitted to biological treatment was constituted by a 10% a discoloured synthetic effluent, mixed with other textile process effluents collected from the a Spanish cotton mill (scouring: 10%, washing: 40%, soaping: 30% and softening: 10%), according to the rate of each effluent in the production process.

In the first biological plant (A) a stoichiometric amount of sodium bisulphite was added to the discoloured dyeing synthetic effluent, followed by an aeration (2h) to remove residual chlorine, before preparing the whole effluent A. In the second biological plant (B) the discoloured effluent was not treated to remove residual chlorine in order to compare the influence of this step on yield of the biological process. The yields of both plants were evaluated by measuring the following parameters: COD, mixed-liquor suspended solids (MLSS), reactor biomass and food-microorganism ratio (F/M).

Simultaneously to the biological treatments, the biodegradability and the inhibitory effects of the effluents A and B were evaluated by electrolytic respirometry. An electrolytic respirometer BI-1000 of Bioscience was used, which consists of an 8 reactors module with a thermostatic bath, connected to a computer. The respirometric tests were carried out during 232 hours at 20°C, using the same inoculum than BOD₅ test (APHA-AWWA-WEF, 1997). For each experiment, a blank was also registered.

3.2. Dyeing with reused water

Dyeing were performed at a liquor ratio of 1/10 with the following trichromy: 1% Blue Navy Procion H-EXL, 1% Crimson Procion H-EXL, 1% Yellow Procion H-EXL, electrolyte: NaCl 80g/L and alkali: Na₂CO₃ 5g/L + NaOH 0.5g/L.

The electrochemical treatment was applied at a current intensity of 3 A and a flow rate of 20 L/h, with an electrical consumption of 7 Wh/L. Next, decolourised water 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.

3. RESULTS AND DISCUSSION

3.1. Decolourisation of exhausted reactive dyebaths

The two exhausted dyebaths collected in the mill, were characterised as indicated in table 1.

Table 1. Characterization of the exhausted reactive dyebaths.

Parameter	LC dyebath	HC dyebath
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

According to the previous study carried out with synthetic effluents, the selected optimal conditions were applied to the treatment of LC and HC dyebaths: low intensity electrochemical treatment, followed by an UV irradiation to obtain a full decolourisation at a low cost. Exhausted dyebaths were treated in the electrochemical plant at two different current densities: 3 and 6 mA/cm² for LC and 6 and 12 mA/cm² for HC. Values of decolourisation, electrical consumption and TOC removal obtained immediately after the electrochemical process are presented in table 2.

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. However, higher current densities were necessary for the electrochemical treatment of HC dyebaths to reach the same decolourisation levels.

Table 2. Electrochemical treatment applied at different current densities.

Current density (mA/cm ²)	LC dyebath		HC dyebath	
	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

The exposure of the partially decoloured effluent to the solar light allows to reduce the electrical consumption to reach the total decolourisation, as the current density applied during the electrochemical treatment can be lower. The evolution of the decolourisation by solar 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 radical species catalysed by the solar light (such as Cl[•], Cl₂^{•-} and [•]OH).

By another hand, in table 2 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.

3.2. Biological treatment with activated sludge

A two months study was performed on each pilot plant (A and B). The retention time was 2.5 days. It was shown that, after a reasonable period, there are no differences of COD removal efficiency and food-microorganism ratio (F/M) between pilot plant A and B: the COD removal is a 65% in both cases

These results indicate that the residual chlorine contained in the effluent B (20-40 mg/L), produced during the electrochemical decolourisation of the dyeing effluent, do not have any influence on the final biological treatment efficiency.

However, respirometric studies carried out showed that adaptation of micro-organisms was easier in the case of effluent A. The effluent A exhibited a high biodegradability level, whereas the effluent B showed, at the beginning, inhibition of micro-organisms activity (oxygen consumption was lower than the blank test).

In opposite, when respirometric tests were carried out with an adapted inoculum (sludge from the own plant), after 5 days, the effluent B had a respiration rate higher

than the blank. This behaviour indicates that a period of adaptation is required when effluent contains a residual amount of chlorine (figure 1).

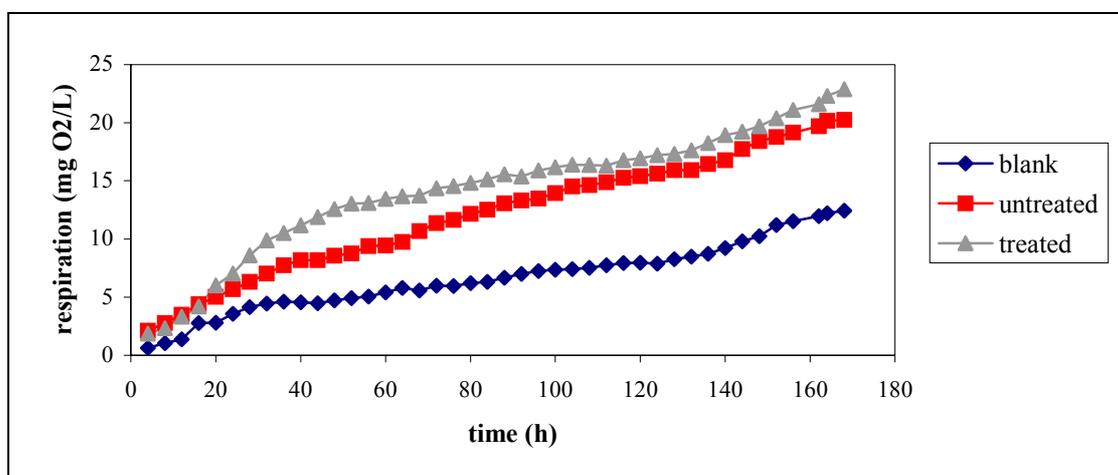


Fig. 1. Respirometries of treated and untreated exhausted reactive dyebaths.

3.3. Reuse of decoloured wastewater

Dyeing wastewater and residual dyebaths were characterized and it was concluded that the reuse of residual dyeing effluents would be more advantageous than washing baths because a much higher amount of electrolyte is reused. However, this dyebaths are more difficult to be decoloured as they have a higher amount of organic matter. The reuse of the first washing bath was thought to be also interesting because its concentration in organic matter is much lower than the residual dyebath but it still contains a certain amount of NaCl able to be reused (about 15%).

Firstly, a dyeing was performed using this first washing bath previously decolourised. The colour differences obtained between the new dyeing obtained and the reference (carried out with clean water) were very low (DE CIELab = 0.3).

Next, 10 reuses of the decolourised dyebath were performed. This allowed to save 70% of the process water and 60% de electrolyte in each dyeing. It was verified that from the 4th or 5th reuse, the TOC did not increase any more (figure 2).

The colour differences (DE CIELab) in each reuse shown a variation respect to the reference. The values varied from 1 in the 1st. reuse to 2-3 from the 5th reuse (figure 3).

However, these 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 CIELab= 0.7. In this case, the increase of the dyeing cost was compensated by the saving of water and salt.

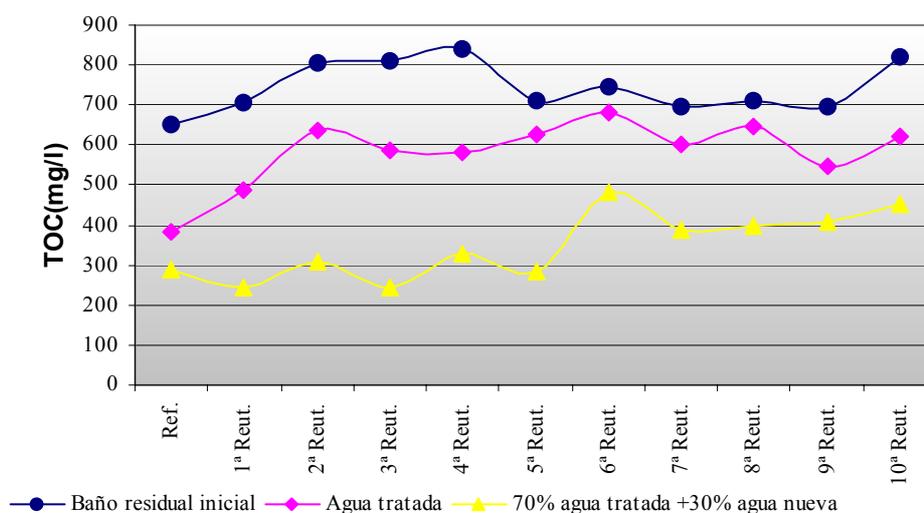


Figure 2. TOC values obtained in each reuse



Figure 3. Colour differences (DE CIELab) for each reuse respect to the reference

4. CONCLUSIONS

One of the main conclusions of this study is that the electrochemical treatment of exhausted reactive dyebaths using Ti/PtO_x electrodes provides high decolourisation levels immediately after the electrochemical process. The exposure of the partially decoloured effluent to the solar light allows to apply lower densities during the electrochemical treatment, which implies a reduction of the electrical consumption.

Also, the exhausted dyebaths treated in this way showed a similar biodegradability level than untreated samples, which indicates that the electrochemical process did not generate toxic products. For this reason, the discoloured wastewater can be submitted to the further biological treatment to remove the remaining organic matter. Moreover, another important conclusion is that the presence of residual chlorine in the discoloured effluent did not affect the yield of the biological treatment, although the biological treatment plant required a longer adaptation of the sludge in the case of chlorine containing effluents.

Finally, the third promising conclusion is that exhausted dyebaths, 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. After 4-5 reuses cycles, an additional amount of dye must be required to obtain the expected colour.

It was also shown that the first washing baths, once decoloured, are easier to reuse than the exhausted dyebaths because of their lower content of organic matter. In this case, colour differences obtained were much lower although only a 15% of salt was reused and the same amount of water was saved.

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.

5. ACKNOWLEDGEMENTS

This work was supported by the Spanish Ministry of Science and Technology (projects: REN2001-2304-C02-01/TECNO; CTM2004-05774-C02-01/TECNO); and CTM2007-66570-C02-01/TECNO).

6. REFERENCES

Bechtold, T., Burtscher, E., Turcanu, A., 2001. Cathodic reduction of Cl Acid Red 27 and Cl reactive black 5 – basic investigations of decoloration and textile waste water. *Text. Res. J.* 71 (10), 870-877.

Gutiérrez, M.C., Pepió, M., Crespi, M., 2002. Electrochemical oxidation of reactive dyes: method validation and application. *Color. Technol.* 118 (1), 1-5.

Gutiérrez, M.C., López-Grimau, V., 2003. Evolution of the Decolorisation of Textile Wastewaters after Electrochemical Treatment. *Chem. Eng. Technol. ECCE-4: Abstracts on-line.*

Kim, S., Park, C., Kim, T.H., Lee, J.W., Kim, S.W., 2003. COD Reduction and decolorization of textile effluent using a combined process. *Journal of Bioscience and Bioengineering.* 95 (1), 102-105.

Kim, T.H., Park, C., Lee, J., Shin, E.B., Kim, S., 2002. Pilot scale treatment of textile wastewater by combined process (fluidized biofilm process-chemical coagulation-electrochemical oxidation). *Water Research.* 36, 3979-3988.

Pelegri, R., Peralta-Zamora, P., R. de Andrade, A., Reyes, J., Durán, N., 1999. Electrochemically assisted photocatalytic degradation of reactive dyes. *Appl Catal B-Environ.* 22, 83-90.

Sakakibara, Y., Nakayama, T., 2001. A novel multi-electrode system for electrolytic and biological water treatments: electric charge transfer and application to denitrification. *Water Research.* 35, 768-778.

Shen, Z., Wang, W., Jia, J., Feng, X., Hu, W., Peng, A., 2002. Catalytically Assisted Electrochemical Oxidation of Dye Acid Red B. *Water Environ. Res.* 74 (2), 117-121.

Vijayaraghavan, K., Ramanujama, T.K., Balasubramanian, N., 2001. In situ hypochlorous acid generation for the treatment of textile wastewater. *Color. Technol.* 117, 49-53.

Vlyssides, A.G., Loizidou, M., Zorpas, A.A., Papaioannou, D., 1999. Electrochemical oxidation of a textile dye wastewater using a Pt/Ti electrode. *J. Hazard. Mater.* B70, 41-52.