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Effect of chloride on the one step electrochemical treatment of an industrial textile wastewater with tin dioxide anodes. The case of trichromy Procion HEXL

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ABSTRACT

The resulting solutions from the cotton fabrics dyeing using the trichromy Procion HEXL, with NaCl as electrolyte, were electrochemically treated. These dyes have two azo groups as chromophores and two monochlorotriazinic groups as reactive groups in their structure. The combined oxidation/reduction at 125 mA cm^{-2} in a filter-press cell without compartment separation was carried out using an anode of Ti/SnO_2-Sb-Pt and a cathode of stainless steel. This procedure has been effective in previous experiments using sulphate as electrolyte. A significant decrease in total organic carbon (TOC), chemical oxygen demand (COD), and total nitrogen (TN) was obtained. Moreover, the process took place efficiently. The average oxidation state (AOS) and the carbon oxidation state (COS) data confirmed the presence of stable oxidized intermediates in the electrolysed solution. The chromatography and the UV-Visible spectrophotometry assays indicated that full decolourisation is obtained at a loaded charge of around 0.81 Ah L^{-1} which is associated with an electrical energy per order (EEO) of 1.20 kWh m^{-3}.

Keywords: Tin dioxide anodes, electrochemical treatment, dyestuff wastewater, trichromy, chloride.

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1. Introduction

In environmental terms, the textile industry generates a great deal of solid, gaseous and contaminated wastewater (Drumond Chequer et al., 2013; Lacasse, 2004). But, it is in wastewater pollution that the textile sector has the greatest environmental impact (Ghaly, 2014; Shukla, 2007). Research into treatments to bleach and degrade colouring agents in textile wastewater is currently an important topic of study in the textile industry.

Generally, wastewater discharged from dyestuff is characterized by colour, BOD, COD, pH, and salinity (Blanco et al., 2014; De Jager et al., 2014). Pollution by discharges of dyes occurs because part of the dye present in dyestuff baths is not fixed to the textile fibre and then, passes to effluents. The ability to fix the dye to the fibre varies depending on the nature of the dye and the type of dye process. Reactive dyes have a particularly low percentage of fixation (European Comission, 2005). These dyes are mainly used in cotton dyestuff and the consumption of these represents approximately 20-30% of the total consumption of dyes (Carneiro et al., 2005). The

reaction between the fibre and dye takes place at an alkaline pH. Under these conditions, the dye also reacts with the water giving rise to a competitive reaction of hydrolysis. In this process, part of the dye is not fixed to the fibre, so that, once the dyestuff is finished, the resulting bath contains dye in its hydrolyzed form that can no longer be fixed to the fibre.

To improve the performance of these dyestuffs, bifunctional reactive dyes have been developed. This type of dyes presents two reactive groups in their structure with which the percentage of dye that reacts with the fibre is significantly increased. The percentage of fixation of a monofunctional reactive dye is around 60%, and in the case of a bifunctional reactive dye, it increases to values of around 80% (Allen, 1971). Therefore, the use of bifunctional reactive dyes leads to a reduction in the amount of dye discharged with the effluent. Nevertheless, this poor performance means that much of the dye used is discharged in its hydrolyzed form (Guaratini et al., 2001a, 2001b).

The presence of dyes in natural water resources strongly colours the water since small concentrations of dyes (of the order of mg L^{-1}) can produce a significant colouring. This produces not only an unpleasant visual effect but also prevents that light reach to the beds of natural waters, with consequent damage to flora and fauna. In addition, colouring of these wastewaters prevents direct reuse.

In recent years, increasingly effective methods of removing contaminants from textile wastewater have been developed. The main objective of these methods is to achieve the highest possible mineralization or, at least, to produce less aggressive intermediates for the environment. Therefore, the ideal treatment is one that does not

generate any additional polluting waste that persists in the environment and, furthermore, that is as economical as possible (Brillas and Martínez-Huitle, 2009; Miklos et al., 2018)

The use of electrochemical treatments (Brillas and Martínez-Huitle, 2015; García Segura et al., 2018; Ling et al., 2016; Moreira et al., 2017; Sala and Gutiérrez Bouzán, 2014) achieved complete decolourisation. It is reported in the bibliography that these objectives are strongly conditioned by the presence and concentration of chloride in the treated effluent (Chatzisymeon et al., 2006; Malpass et al., 2007). It is reported that in some cases the addition of sodium chloride in concentrations of up to 0.1 M allows total decolourisation and an important increase of COD abatement (Malpass et al., 2007; García Segura et al., 2018). Moreover, the effluent conductivity, the applied current density, and the anode material influence the power consumption. In general, it is reported that anodes such as boron doped diamond (BDD) reduce COD and TOC in a shorter operation time and energy consumption ranged between 16 and 100 kWh m^{-3} (Ling et al., 2016; Martínez-Huitle et al., 2012).

In previous works (Orts et al., 2018, 2019), the electrochemical treatment of a real dyestuff wastewater using Na_2SO_4 as electrolyte was carried out. Ti/SnO_2-Sb-Pt non-active anodes were used. Under these conditions, the $^{\bullet}OH$ radicals are the main electroactive species physisorbed on the anode surface. A complete decolourisation was obtained in the successive reuses of treated wastewater. Moreover, a significant incineration of organic molecules into CO_2 was obtained. It was concluded that the electrochemical treatments saved consumption of water and electrolyte (up to 70%) since the reuse of wastewaters (from the dyeing baths) prevents the discharge into the

environment of this effluents charged with a high content of salts. Nevertheless, energy consumption, current efficiency, and electrochemical mineralization must be improved. For these purposes, the use of chloride as electrolyte is examined in the present work. In addition, it should be noted that sodium chloride is the preferred electrolyte in the textile industry for cotton dyeing processes with reactive dyes. The main hypothesis of the present work is that the electrogeneration of active chlorine species for the indirect electrooxidation of real dyestuff wastewater would resolve the weaknesses of previous electrochemical treatments.

2. Experimental

2.1 Reagents, materials and dye procedure

Solutions obtained from the dyestuff baths of cotton fibres with bifunctional reactive dyes belonging to the trichomy Procion HEXL were used for the study. The molecular structures of the dyes of the trichromy Procion HEXL (Yellow, Crimson and Navy) are shown in Fig. 5. Their C.I. name or CAS number of the European Chemicals Agency are: Reactive Yellow 138:1, Reactive Red 231, and 190914-23-9 (C.I. name non-registered), respectively. The dyes were supplied by Dystar Company (Singapore).

The initial concentration of each dye was 0.50 g L^{-1}. As electrolyte, NaCl or Na_2SO_4 (Fluka quality of analysis) was used in a concentration of 32.0 g L^{-1} or 45.0 g L^{-1}, respectively, with a specific conductivity of around 42 mS cm^{-1}.The initial pH of the solution was 7. This pH has to be raised during the dyestuff (in the dye fixation process) to an interval between 10.8 and 11.0 by the addition of NaOH.

For the dyeing procedure, seven stainless steel test tubes (40 mm diameter and 160 mm height) containing 125 mL of a 0.5 g L^{-1} solution of each dye, 10 g of semi-milled cotton fabric 100% (the cotton fabric is previously washed with a solution of H_2O_2 and NaOH) are prepared. The liquor ratio is 1:12.5 (g fabric mL dye^{-1}) and a percentage of dye in relation to the fabric of 1.87 (g dye g $fabric^{-1}$). These test tubes are placed in a RED-TEST equipment (UNGOLINI RT-P). For the dyestuff procedure, the initial temperature of 15 ºC was increased, following a 1.5 ºC min^{-1} gradient, up to 80 ºC. About 60 min later, a pH=10.8 was adjusted with a NaOH solution. The dyeing process continued for about 120 min.

NaOH, H_2O_2 and HCl (quality of analysis) were supplied by the company Fluka. Distilled water (5.3 µS cm^{-1}) was used for the preparation of the solutions.

2.2 Electrolysis

The bath solutions obtained after dyeing process were electrochemically treated in galvanostatic conditions applying a current density of 125 mA cm^{-2} in a filter press cell without compartment separation. The choice of this electrochemical conditions was based on previous researches carried out with various reactive dyes (del Río et al., 2009a, 2009b, 2012).

The volume of the treated solution and the flow rate were 0.45 L and 5.60 L min^{-1}, respectively. The temperature during the electrolysis was 40ºC. The pH of the treated solutions started with values close to 11.0 and decreased until values close to 7.0 at the end of the electrolysis. During the course of electrolysis, samples were extracted to evaluate the decolourisation and the degradation of the remaining hydrolyzed dyes in the dyestuff baths. The anode used was an electrode type DSA of Ti/SnO_2 doped with Sb and with small amount of Pt obtained by pyrolysis of the salts of Sn, Sb and Pt on a

substrate of titanium as described in (Orts et al., 2018). The results obtained by our research group during the development of previous projects, have demonstrated the efficiency of the use of these anodes in the decolourisation/degradation of reactive dye solutions (Sala et al., 2012). The incorporation of platinum provides high stability to the anode thus extending its useful life (del Río et al., 2010). The cathode is made of 11.0 cm x 9.5 cm stainless steel (Cr 18-19% and Ni 8.5-9%) which was pretreated and cleaned. These pretreatments consist of mechanical polishing and degreasing in an acetone bath subjected to the action of ultrasound in order to eliminate surface fats and oxides. A Grelco GVD310 0-30Vcc/0-10 UNA power supply was used for the control and measurement of the applied current under galvanostatic conditions.

2.3 Analysis and instruments

The degree of degradation of the dyes was evaluated by measurements of total organic carbon (TOC), chemical oxygen demand (COD), and total nitrogen (TN). The average oxidation state (AOS) was obtained from the equation (1) (Bilińska et al., 2016; Clesceri L. S., Eaton, A. D., 1995; Stumm and Morgan, 2013),

$$AOS = 4 \bullet (TOC_t - COD_t)/TOC_t \qquad (1)$$

The carbon oxidation state (COS) (Comninellis and Pulgarin, 1991) and the average current efficiency (ACE) (Akrout and Bousselmi, 2012; Fóti and Comninellis, 2010; Jarrah and Mu'azu, 2016; Xu et al., 2016; Li et al., 2017) were calculated by means of the equations (2) and (3).

$$COS = 4 \bullet (TOC_0 - COD_t)/TOC_0 \qquad (2)$$

$$ACE = 100 \bullet F \bullet V \bullet (COD_0 - COD_t)/8 \bullet I \bullet t \quad (3)$$

where COD_0 and COD_t are the initial value and the COD measured in a selected loaded charge during electrolysis (g O_2 L^{-1}), respectively, F is the Faraday constant (96487 C mol^{-1}), V is the volume of the wastewater (L), I is the applied current (A), t is the time of electrolysis (s) and 8 is the equivalent weight of oxygen. AOS variations are related with the modifications that take place in the composition and in the toxicity/biodegradability of the sample. COS and ACE help in estimating the efficiency of the process. COS provides an estimate of the efficiency with which the carbon structure of the dye molecule is degraded. The ACE value provides information on the efficiency of the degradation not only of the carbon structure but also of the functional groups containing heteroatoms.

The equation (4) was chosen for the calculus of EEO according to the report of James R. Bolton (Bolton et al., 2001), considering that the concentration of initial and final dyes are directly proportional to the areas of the main chromatographic peaks. Therefore, the area of this peak was used in calculus instead of concentration (del Río et al., 2017).

$$EEO = P \bullet t/V \bullet log(A_i/A_f) \quad (4)$$

where: P is the electric power (kW), t is the time of electrolysis (h), V is the volume treated (L), A_i and A_f are the initial and final area of the chromatographic peak associated to the pollutant of interest.

To quantify the amount TOC and TN in a sample, analyses were performed on a Shimadzu TOC-VCSN model equipped with a TNM-1 unit. The TN analysis was carried out to evaluate the elimination of the triazine groups present in the structure of the dyes. All samples analyzed were diluted (1:5) to obtain concentrations within the operational range of the equipment. The measurements were made at 1193 K. A volume of 20.0 µl of sample was injected with an air flow rate of 0.150 L min^{-1} (CO_2 free). The COD measurements were performed with a MERCK TR-320 Spectroquant Thermo reactor by digesting the samples with potassium dichromate and sulfuric acid. Then the spectrophotometric method was applied, consistent with EPA 410.4, US Standard Methods 5220 D and ISO 15705. All the reagents were supplied by Merck.

High Performance Liquid Chromatography (HPLC) using a Hitachi Lachrom-Elite dispositive allowed the monitoring of the degradation of the samples during the electrolysis. The working procedure was the procedure described in the standard EN 14362-2:2003/A. The measurement conditions are described in previous works (Orts et al., 2018). With this procedure, the area of the chromatographic peaks associated with the chromophores groups of each dye at its corresponding wavelengths was obtained. Such wavelengths are 420 nm, 549 nm and 610 nm for Yellow, Crimson, and Navy, respectively. The chromatographic area is in direct relation to the concentration of the dye. So, we could obtain information about the amount of dye that remains in the solution from its unaltered chromophore group. The evolution of these areas provides information about the disappearance processes of those chromophore groups. If a wavelength of 230 nm is fixed during the chromatographic analysis, the evolution of aromatic structures can be studied.

The UV-Visible spectrophotometry measurements were performed using the same chromatographic equipment Hitachi Lachrom-Elite replacing the chromatographic

column with a tubular piece of stainless steel without any infill inside. This device allowed sample volumes of the order of μL to be analysed. The comparison of the UV-Visible spectra allowed the tracking of the decolourisation from the initial to the final state throughout the electrolysis, and the evolution of the functional groups and aromatic structures that absorb in the UV-region.

3. Results and discussion

3.1. Chromatographic study

Figs. 1a-c show the evolution of the chromatographic profile during the electrolysis at the three wavelegths corresponding to the maximum of absorption of each dye of the trichromy. The maximum loaded charge was 15.6 Ah L^{-1} because for higher load no peaks are detected. In fact, at loaded charges higher than 0.81 Ah L^{-1}, an accurate calculus of the area of the chromatographic peaks is not possible. For this reason, the kinetic study is not shown. The results confirmed the rapid disappearance of the colour of the solution during the electrolysis.

Fig. 1d shows the evolution of the chromatographs at a wavelength of 230 nm. The initial peaks at a retention time of 13.4-13.8 min. disappear during the electrolysis. At the same time, some new peaks appear at retention time of 1.0-2.0 min. These peaks change their shape during the electrolysis and remain at the end of it. Thus, it seems that some organic species with aromatic structure, that evolve during the electrolysis, remain in solution when the process finishes.

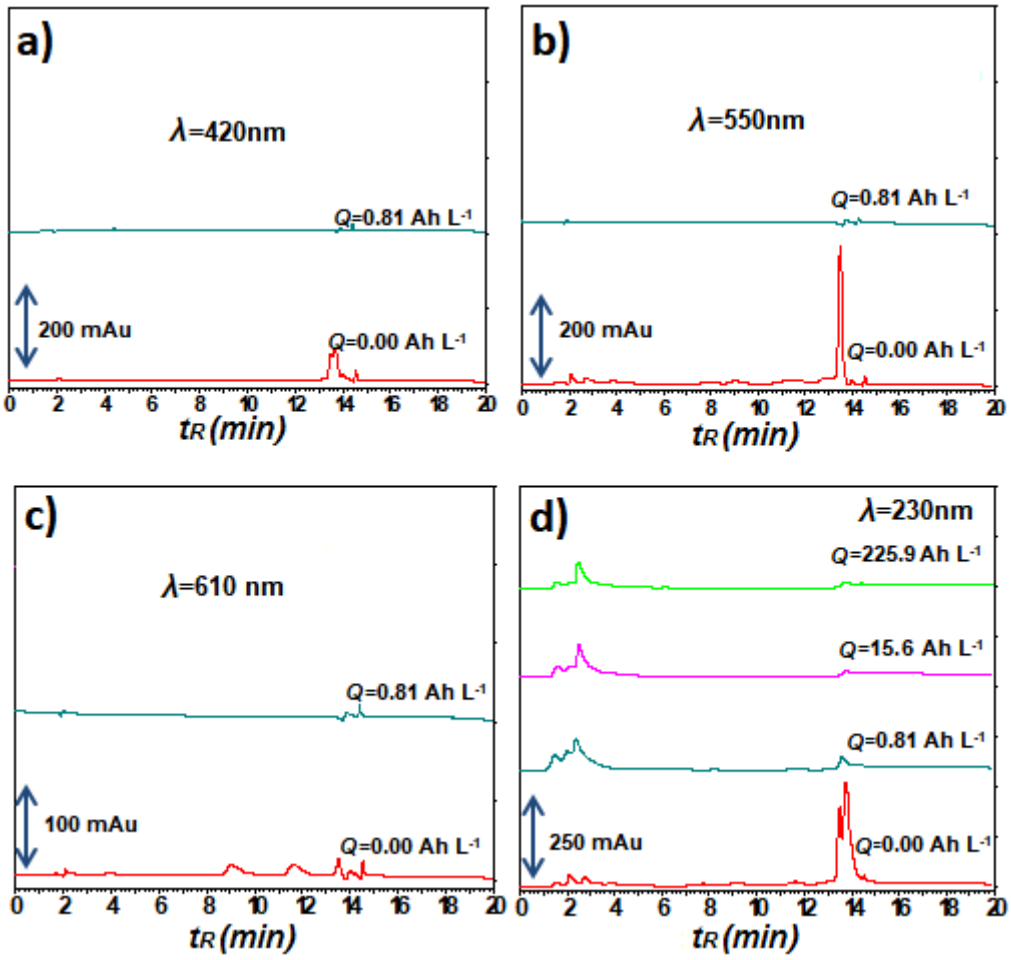

Fig. 1. Evolution of the chromatographic profile during the electrolysis using chloride as electrolite (30.0 g L^{-1})at the maximum absorptium wavelegth of: a) Procion Yellow. b) Procion Crimson. c) Procion Navy. d) Aromatic structures. The initial concentration of each dye was 0.50 g L^{-1}. The applied current density was 125 mA cm^{-2} and the volume of electrolysed sample was 0.45 L.

3.2. Comparative study of the evolution of electrolysis parameters in sulphate and chloride media.

Fig. 2a shows the photography of different samples extracted during the electrolysis with sulphate and chloride. A visual inspection is enough to conclude that the loaded charge needed for decolourisation drastically decreased in the case of chloride. Fig. 2b shows the decrease in TOC, COD and TN for both electrolytes at a similar loaded charge to that needed for total decolourisation in sulphate medium (to ensure similar experimental conditions) (Orts et al. 2018). The removal efficiency is higher in the

presence of chloride, particularly in the decrease of TN and COD. This higher efficiency is due to the fact that, in the electrolysis, chloride is oxidized giving rise to highly oxidizing species (such as hypochlorite or hypochloric acid, depending on the pH) (García Segura et al., 2018). These species are those that subsequently react with the organic pollutant to degrade it acting as electroactive substances mediating the electronic transfer. In both cases the elimination of COD is greater than that of TOC and TN. This involves the generation of fairly oxidized species that remain stable in solution.

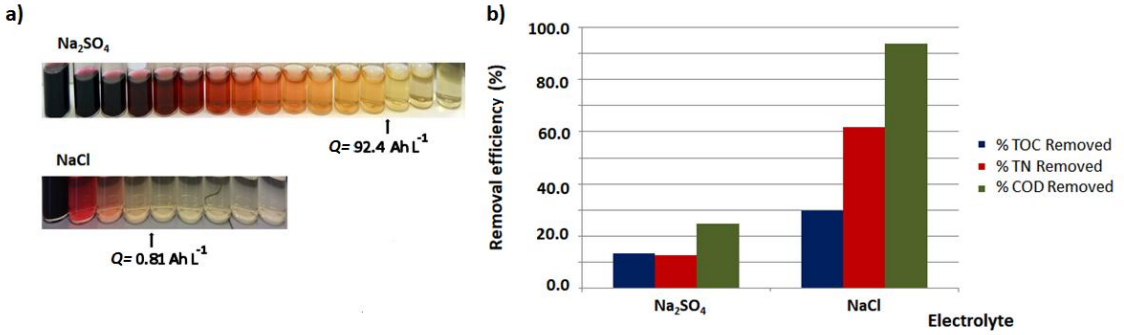

Fig. 2. a) Photography of samples extracted during the electrolysis with sulphate (45.0 g L^{-1}) or chloride (30.0 g L^{-1}) as electrolytes. The loaded charge needed in each decolourisation is shown in Figure b) Removal efficiency (%) of TOC, TN and COD with sulphate or chloride as electrolyte, after a loaded charge of around the needed for total decolourisation in sulphate medium. The initial concentration of each dye was 0.50 g L^{-1}. The applied current density was 125 mA cm^{-2} and the volume of electrolysed sample was 0.45 L. The flow rate was 5.60 L min^{-1}.

Moreover, Table 1 shows the values of %TOC, %TN and %COD removed at different values of loaded charge. At a loaded charge in which decolourisation occurs in chloride medium (0.81 Ah L^{-1}) the %TN and %TOC removed are high. So, in the first stage of electrolysis, not only the chromophore groups are degraded but also, nitrogenated groups (such as chlorotriazines) are removed from the molecular structure

and, subsequently, the carbon atoms present in its structure. This will be corroborated by the spectroscopic results.

Table 1
Values of %TOC, %TN and %COD removed at different values of loaded charge, with both chloride and sulphate electrolytes.

ELECTROLYTE	Q (Ah L^{-1})	%TOC	%TN	%COD
NaCl	0.81	19.1	33.4	0.87
	101.7	29.7	61.8	93.9
Na_2SO_4	92.4	13.3	12.7	24.8

Fig. 3a shows the variation of COS and AOS with sulphate (Orts et al. 2018) or chloride as electrolyte, after a loaded charge corresponding to that needed for total decolourisation in sulphate medium. Positive trends in AOS relative to the initial value indicate that the final compounds are more oxidized than the untreated dye molecules (del Río et al., 2009a). Changes in COS values are related to changes in the composition of the solution as a result of electrochemical treatment. For both electrolytes an increase in COS and AOS values were observed, although this variation is much more pronounced in the presence of chloride. Fig. 3b-c show the evolution of COS and AOS with loaded charge during the electrolysis with sulphate (Orts et al. 2018) and chloride as electrolytes, respectively. The evolution of both parameters occurs in a more pronounced way with chloride. At the beginning of the electrolysis, COS and AOS increase, so, oxidation occurs changing the oxidation state of the dye. Later COS and AOS remain practically constant. Therefore, can be concluded that the electrolysis continues oxidising and mineralising the samples and that both processes take place at similar rate.

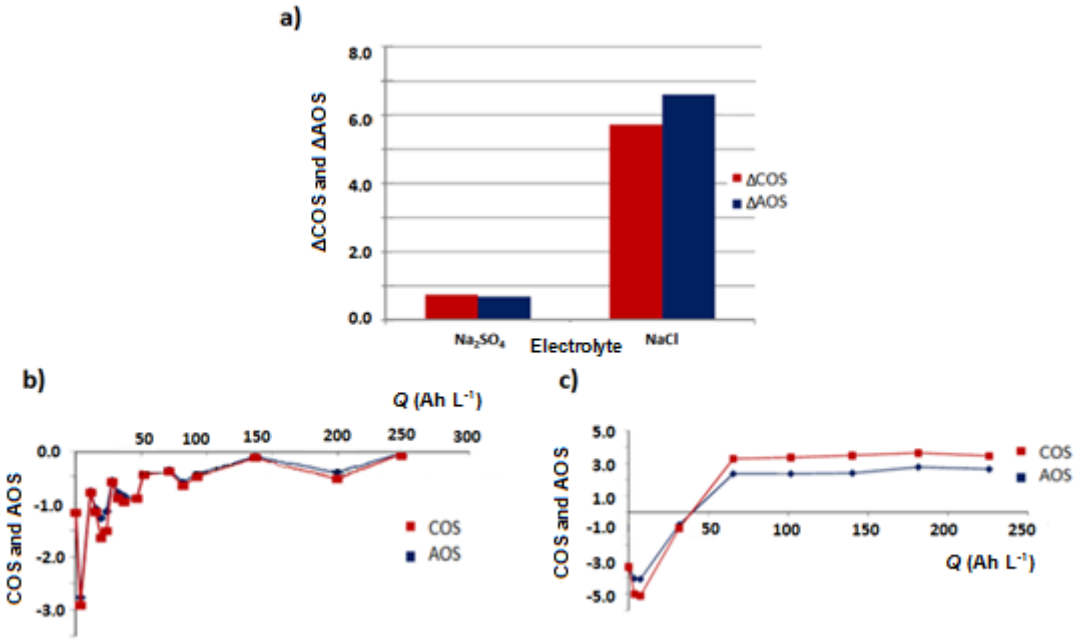

Fig. 3. a) Variation of COS and AOS with sulphate (45.0 g L^{-1}) or chloride (30.0 g L^{-1}), after a loaded charge corresponding to the need for total decolourisation in sulphate medium. b) Evolution of COS and AOS with loaded charge during the electrolysis with sulphate as electrolyte. c) Evolution of COS and AOS with loaded charge during the electrolysis with chloride as electrolyte. The initial concentration of each dye was 0.50 g L^{-1}. The applied current density was 125 mA cm^{-2} and the volume of electrolysed sample was 0.45 L. The flow rate was 5.60 L min^{-1}.

The average current efficiency (ACE) indicates the fraction of current that has been used to decrease COD by a certain percentage, while COS provides information on the efficiency with which the carbon structure of the dye is degraded. The ACE values provide an estimate of the degradation efficiency of the whole molecule. For a loaded charge similar to that needed for total decolourisation in sulphate medium, the value of ACE is 1.4% whereas in similar loaded charge conditions, the ACE value in chloride medium increases up to 5.6%. When the electrolysis process passes from the decolourisation stage increasing the loaded charge values, there is a decrease in the percentage of ACE during the time of electrolysis. For instance, for a value of loaded charge of around 230 Ah L^{-1}, the percentages of ACE were 2.5% and 0.97% with

chloride and sulphate, respectively. This could be because in the initially stages of the electrolysis, the main reactions are the degradation of chromophores and reactive groups of dye molecules. But, as their concentration decreases, they give way to more complex degradation reactions and to water electrolysis. This is consistent with the spectroscopic results. Nevertheless, the process continues being more efficient in the presence of chlorides by the generation of chloride oxidation products during the electrolysis.

As a consequence of the increase in efficiency and the faster decolourisation observed when chloride electrolyte is used, the Electrical Energy per Order (EEO) decreased significantly. Thus, after total decolourisation the value of EEO obtained is 1.2 kWh m^{-3} with chloride and 152.0 kWh m^{-3} with sulphate.

3.4. Evolution of the UV-Vis spectra

Figs. 4a-b show the UV-Vis spectra evolution during the electrolysis with sulphate (Orts et al. 2018) and chloride as electrolytes, respectively. In the initial spectra, bands associated with the azo groups are observed. These bands are around 420 nm, 549 nm, and 610 nm for Procion Yellow, Procion Crimson, and Procion Navy, respectively. These bands quickly disappear in the presence of chloride while in the case of sulphate a higher loaded charge (higher than 0.81 Ah L^{-1}) is needed. These results confirmed the HPLC results.

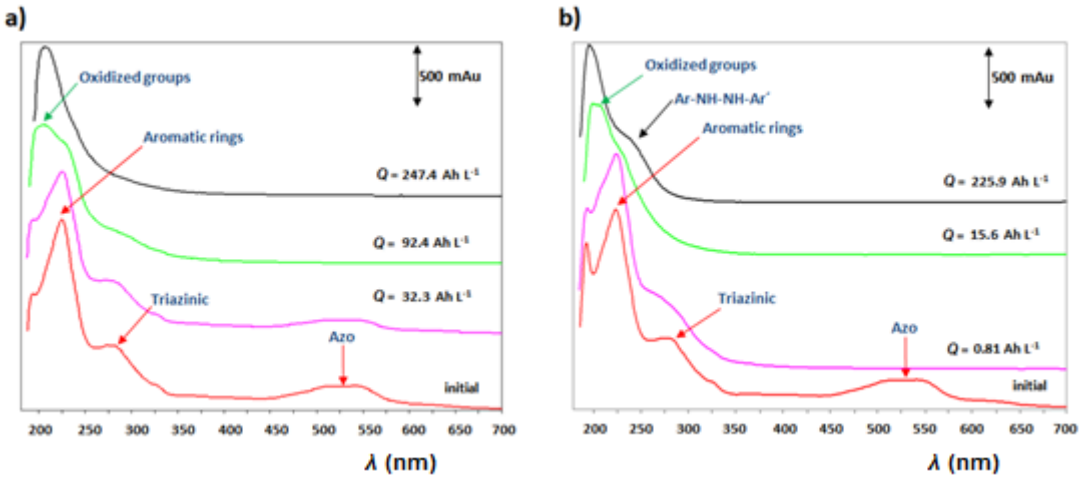

Fig. 4. UV-Vis spectra evolution of a) during electrolysis with sulphate (45.0 g L^{-1}) as electrolyte. b) During electrolysis with chloride (30.0 g L^{-1}) as electrolyte. The initial concentration of each dye was 0.50 g L^{-1}. The applied current density was 125 mA cm^{-1}.

The band centered at 280 nm (triazinic groups) (Chapman, 2005) completely disappears during electrolysis, which is also confirmed by the decrease of TN. The band at 230 nm ($\pi \rightarrow \pi^*$ transitions of benzenic and naphthalenic rings) (Stylidi et al., 2004) diminishes indicating a loss of aromaticity. Although in the presence of sulphate this band is still detected, in the presence of chloride it completely disappears. At the end of the electrolysis in presence of chlorides, two bands corresponding to the Ar-NH-NH-Ar´ structure (Feng et al., 2000), at 245 nm is clearly noted. A $\pi \rightarrow \pi^*$ transition at 210 nm of highly oxidized groups, such as carbonyl (Chapman, 2005) is also observed.

From all these results, an oxidation/reduction reaction mechanism with chloride and sulphate as electrolyte is shown in Fig. 5.

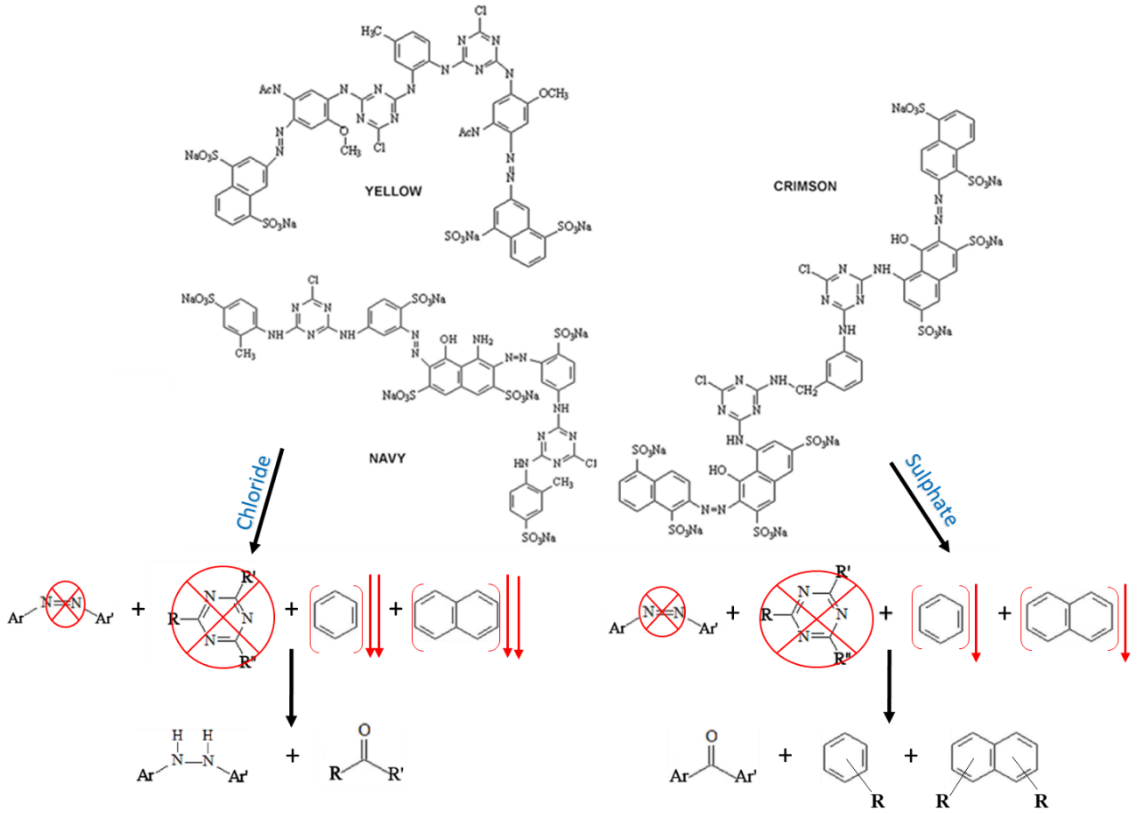

Fig. 5: Oxidation/reduction reaction mechanism with chloride and sulphate as electrolyte.

3.5. Reuse experiments

In contrast with what occurred when sulphate is used (Orts et al., 2018, 2019), the evaluation of colour matching after dyeing processes with the reusing water from the electrolysis in the presence of chloride, gives values outside the limits accepted in the textile industry. The evolution of the composition of the electrolyzed solution due to the presence of oxidation intermediates of chloride whose nature and concentration changes with time and the appearance of photochemical reactions may be the reason for this behavior (López Grimau and Gutiérrez, 2006). This is not to say that the reuse water cannot be used in dyeing processes, but simply that for the requirements of the colour matching, the reused water requires a treatment with UV-light to eliminate the

remains of chlorinated species. It is also possible to adjust the initial quantities of dye used in the dyeing process to match the requirements of colour matching.

4. Conclusions

In the present work the results obtained using sulphate or chloride as electrolyte in the electrolysis of real textile wasterwater after dyeing with the trichromy Procion HEXL cotton yarns are compared. As anode, a DSA electrode of Ti-SnO_2-Sb-Pt was used and as cathode a stainless steel plate was selected. As shown in previous studies, when sulphate is chosen as electrolyte, a moderate decrease of COD, TOC, and TN together with a complete decolourisation was obtained. Moreover, a good colour matching in the successive dyeing was also obtained. So, it can be concluded that in the presence of sulphate reuse is possible, saving water and electrolyte. Nevertheless, the loaded charge needed for that purpose, and as such, the electrical energy per order are high and the current efficiency is poor.

In the other hand, the results obtained in the present work show a higher degradation of organic matter, rapid decolourisation, better current efficiency, and lower energy consumption (1.2 kWh m^{-3}) when chloride is used as electrolyte. Nevertheless, the elimination of COD is greater than that of TOC and TN. This indicates the generation of fairly oxidized carbon and nitrogen species that remain stable in the solution. The efficiency of the process in terms of oxidation and mineralisation can be assessed by analyzing the variation of carbon oxidation state (COS) and the variation of the average oxidation state (AOS). These variations are always higher than in the case of using sulphate and the results indicate that in a first phase both parameters continuously increase which means that the oxidation mainly occurs rather than mineralisation.

Subsequently, a second phase of the experiments showed that COS and AOS remain constant. This implies that, although the process is able to continue to oxidize and mineralize the sample, both processes happen at similar rates. Moreover, it is possible to use reused wastewater when chloride is used as electrolyte in dyeing processes. To comply with the textile industry requirements of colour matching, two successful strategies are possible: Pretreatment of the reused wastewater with UV-light to eliminate the remains of chlorinated species or modifying the proportions of the initial quantity of dyes used in the dyeing process.

Acknowledgments

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Graphical Abstract