Electrochemical investigations of *C.I. Reactive Orange 4* focused on textile wastewater reuse.

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Abstract

The electrochemical behaviour of the azo/dichlorotriazine reactive dye Procion Orange MX-2R (*Colour Index Reactive Orange 4)* on stainless steel electrodes was investigated. This dye shows only a 6% of biodegradability. Textile wastewaters were simulated as real conditions of industrial effluents considering Na_2SO_4 and NaCl as background electrolyte. Different concentrations of the commercial dye were studied. The electrochemical behaviour has been investigated by Cyclic Voltammetry (CV). Besides, the decolourization/degradation degree was evaluated in several electrolyses in a divided and undivided electrolytic cell at controlled current density. UV-Visible Spectroscopy of the initial dye solution allowed determining the maximum absorbance wavelength of the azo group. Therefore, High Performance Liquid Chromatography (HPLC) permitted monitoring the dye solution decolourization during the electrolytic process and the decolourization kinetic was established. Also, Fourier Transform Infrared Spectroscopy (FTIR) was used to analyse the functional group evolution after all the electrolysis assays. TOC, TN and COD parameters were studied in order to evaluate the mineralization degree. Finally, with the objective of reusing the dyestuff waters, three successive dyestuffs have been carried out on 100 % cotton samples without any change in the dyestuff conditions.

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1. Introduction

Colour in textile effluents involves a continuing problem for dyestuff manufacturers, dyers and finishers and water companies because of the impact on the ecosystem. For this reason academia and industry have been researching new technologies to remove colour for over five decades. Thought it is difficult to calculate the exact amount of dyes produced in the world, in 1978 it was estimated about 50.000 tonnes of dyes which were discharged in effluents. Assuming that dyes production increase with cotton consumption and considering that cotton is the first fibre produced worldwide (from 1978 to 2000 cotton consumption rose to 23 million tonnes), it is easy to have an idea of the scale of the colour discharge [1-4].

Reactive dyes have been one of the most significant technological innovations of the 20th century but also one of the major responsible of coloured rivers. These dyes have been widely used for the last four decades since they are

easy to apply because of their high reactivity. However, the fixation reaction is hindered by the dye hydrolysis. For this reason reactive dyes are only retained from 60% to 90% at best case on cellulose fibres. Besides, an additional problem is that reactive dyes in both the ordinary and hydrolysed forms are not easily biodegradable and thus even after extensive treatment colour from unexhausted reactive dyes may still remain in textile wastewater.

Since every possible chromophore could be used in reactive dyes synthesis, most reactive dyes fall in the category of azo dyes (around 80%). Azo dyes are by far the most important class accounting for over 60-70% of all commercial dyes [5].

The electrochemical techniques have been found of special interest for the treatment of different effluents. Among all their advantages it is interesting to notice the high yields of elimination/degradation of polluting substances with maximum energy resource management. Moreover, these techniques show facility and precision on control of the electrochemical process (the electron is the main reagent) and the reactors are compact [6]. The degradation products in the oxidation of azo dyes are typically carbon dioxide, nitrogen and sodium sulphate, with the possible formation of aromatic esters, phenols, aromatic amines, etc. First of all, the oxidation of the azo group occurs, followed by the oxidation of the decomposition products [7]. On the other hand, electrochemical reduction of dyes could be an attractive alternative for the decolourisation of highly coloured concentrated dyestuff solutions [8-11]. Besides, it is important to notice that removal of dyes from wastewaters in an economic way using low-cost electrodes remains a major concern. In this sense, stainless steel electrodes represent an interesting alternative.

In the present work, the electrochemical behaviour on stainless steel electrodes of an azo/dichlorotriazine reactive dye was studied. Its commercial name is Procion Orange MX-2R (*Colour Index Reactive Orange 4*). It was selected as a representative dye with a 1, 3, 5-triazinyl group as functional group and because of its low fixation efficiency on cellulose. In spite of this, this dye has been widely used for decades.
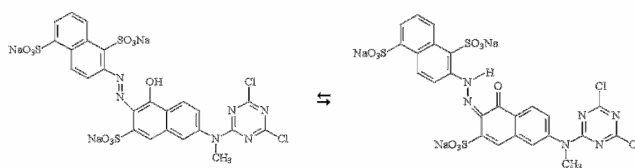

Fig. 1. Molecular structure of Procion MX-2R and its tautomeric equilibrium. Structure of its non-hydrolysed form.

2. Experimental

The commercial dye was supplied by Zeneca. All solutions were prepared from commercial dye using ultrapure water from a Milli-RO/Milli-Q water purification system. Different concentrations of the commercial dye Procion Orange MX-2R were prepared: 0.08 $g \cdot l^{-1}$ as a typical dye concentration in a real wastewater, 0.8 $g \cdot l^{-1}$and 3.9 $g \cdot l^{-1}$ in order to observe in a better way all the processes which

take place in the electrode-solution interface. These simulated dye solutions allowed the research to be carried out at constant composition. All dye solutions were previously hydrolysed where final pH must be higher than 10 for an efficiently hydrolysed solution. Results corresponding to the dye solutions were compared to those obtained for blank solutions consisted on a 0.5M NaOH and 0.1M / 0.5M Na_2SO_4 (Merck p.a.) or 0.1M NaCl (Fluka) .

Besides, different solutions of commercial products which structure is similar to some dye moieties (postulated as products of electrolysis) were also studied at similar conditions. These commercial products were supplied by Acros Organics, Fluka, Aldrich, Sigma and Merck.

All voltammetric and potentiostatic polarisation experiments were performed using an Eco-Chemie Autolab PGSTAT30 potentiostat/galvanostat. A three electrode electrochemical cell was used with a stainless steel working electrode and Ag/AgCl (KCl 3M) reference electrode. A platinum wire was used as counter electrode. Voltammetric measures revealed similar results when both 0.1M and 0.5M Na_2SO_4 were used as background electrolyte. So only those results obtained with 0.1M Na_2SO_4 will be showed.

Electrochemical degradation experiments were conducted in an electrolytic cell at room temperature. Investigation of the electro-oxidation and electro-reduction of the dye was carried out in a divided mode of the cell (using a cationic membrane) and combined processes were studied in an undivided mode. The solution volume was 55 ml and constant stirring was kept. All the experiments were current density controlled. Different values were applied: 125, 150 and 250 $mA·cm^{-2}$. The charge loaded was always 227 $A·h·l^{-1}$. A $Ti/SnO_2/Pt$ electrode doped with antimony was employed as anode and a stainless steel electrode was employed as cathode. Different types of electrolyte were used: NaCl 0.1M and Na_2SO_4 0.1M and 0.5M.

The UV-Visible spectra were recorded by using a Genesys 10 UV Scanning spectrophotometer. Fourier Transform Infrared Attenuated Total Reflection (FTIR-ATR) experiments were performed with a Nicolet Magna 550 Spectrometer equipped with DTGS detector. Chromatographic analyses were performed in accordance with the norm EN 14362-2:2003/AC on a Hitachi Elite Lachrom chromatographic system equipped with diode array detector. The column used was Lichrospher 100 RP-18 (5 μm packing). TOC analyses were realised in a Shimadzu equipment model TOC-VCSN with an additional module for TN measures, model TNM-1. COD results were obtained with a Spectroquant $^®$ photometric system (kits CSB/COD 25-1500 $mg·l^{-1}$ supplied by Merck).

For dyestuffs samples of cotton 100 % were used. Washing fastness assays were done in according with the norm ISO 105-E01:1996.

3. Results and discussion

3.1 Electrochemical behaviour. Voltammetric characterisation

A voltammetric characterisation was carried out taking into account different parameters such as dye concentration, electrolyte concentration, scan rate, pH,

etc. Thus, dependence with dye concentration was found as shows Fig. 2. In the absence of dye (blank solution), the oxidation and reduction of the electrode surface at -0.70V and -1.04V respectively take place. Besides, redox behaviour of chromium contained on the working electrode appeared at 0.48V and 0.36V for oxidation and reduction respectively. In presence of dye, a strong peak appears at about -0.55 V related to the dye oxidation. The dye reduction peak is also observed at -0.69 V. However, a new cathodic process at -0.83 V is clearly observed when concentration is 3.9 g·l^{-1}. This could be related to the intermediate species generation.
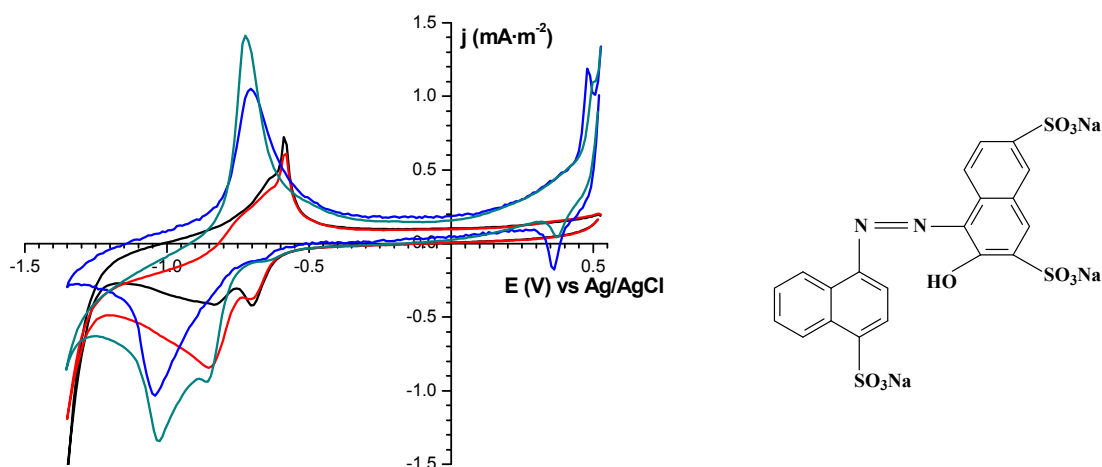

Fig. 2. Left: Cyclic voltammograms recorded on a stainless steel electrode immersed in aqueous solutions of NaOH 0.5M and Na$_2$SO$_4$ 0.5 M with amaranth 0.6. g·l^{-1} (——), Procion MX-2R 0.8 g·l^{-1} (——) and Procion MX-2R 3.9 g·l^{-1} (——). Blank solution (NaOH 0.5 M and Na$_2$SO$_4$ 0.5 M) (——). Right: Chemical structure of amaranth.

Simultaneously, a voltammetric study of different commercial products with similar structure to some fragments of the dye molecule was developed. The cyclic voltammogram of amaranth (Fig. 2, left) shows the same reduction peak at -0.83 V as Procion MX-2R 3.9 g·l^{-1}. Consequently it could be assumed that the intermediate generated from dye degradation presents a very similar structure to amaranth.

The kinetic study of the reduction process of Procion MX-2R (at -0.69 V) was carried out at different scan rates: from 10 mV· s^{-1} to 200 mV· s^{-1} and at different concentrations of the dye. For 0.08 g·l^{-1} Procion MX-2R, the regression of log Ip$_c$ versus log v gave a slope value of 0.64 (correlation coefficient 0.991) indicating that the reduction process are both diffusion and adsorption controlled. As concentration was increased to 0.8 g· l^{-1} and 3.9 g· l^{-1}, the corresponding plots of log Ip$_c$ versus log v gave a slope of 0.89 and 0.80 respectively (R: 0.997 and 0.991 respectively). Thus the reduction process is mainly an adsorption controlled process but diffusion control must be considered too. Besides, the adsorption control contribution of the electrochemical process when concentration is increased, was confirmed by the linearity of Ip$_c$ versus v curves for each case, according to the equations: Ip$_c$ (mA) = 0.058 + 0.006v (mV·s^{-1}), R = 0.998 for 0.8 g·l^{-1} solutions and Ip$_c$ (mA) = 0.085 + 0.005v (mV·s^{-1}), R = 0.997 for 3.9 g·l^{-1} solutions. The scan rate

dependence of the peak current at -0.83V observed at higher concentration was also evaluated. For 3.9 g·l^{-1} Procion MX-2R, the log Ip$_c$ versus log v presents a linear tendency with a slope value of 0.42 (R = 0.988). This reveals that the diffusion mass transport to the electrode surface controls the reaction [12-14].

3.2. Electrolyses.

Depending on the electrolysis process which is wanted to study two different electrolytic cells were used. The electrolyses assays allow understanding how the different interphases studied above act in the decolourisation process.
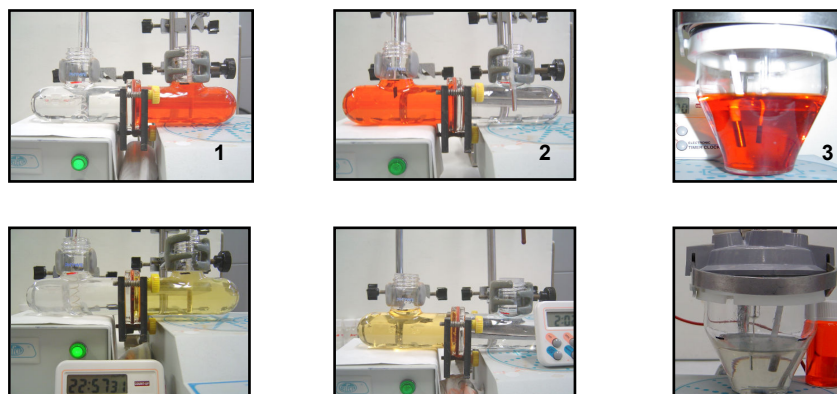

Fig. 3. Images of the decolourisation degree obtained after: 1) an electro-reduction 2) an electro-oxidation 3) a combined process. Charge loaded: 227 A·h·l^{-1}. Initial concentration: Procion MX-2R 0.8 g·l^{-1}. Background electrolyte: Na$_2$SO$_4$ 0.1 M

3.2.1. TOC, TN and COD measures

The variations in TOC and TN values were determined before and after the different electrolyses as a measure of the mineralisation/decolourisation capacity of the electrodes. Fig. 4 represents the results obtained for the three processes studied at 125 and 250 mA·cm^{-2}. As suggest these results, both oxidation and oxido-reduction process showed a better TOC removal than reduction process at the two current densities studied. This could be explained by the OH$^·$ generation from water hydrolysis on the anode surface. When current density was 250 mA·cm^{-2} TOC elimination, in every process, was higher than at 125 mA·cm^{-2}. TN measures were also made for the three processes (figure not showed). Results were better for oxidation or oxido-reduction. Reduction processes gave no significant changes of TN at any current density. The reduction of COD (Table 1) was also influenced by the process which took place. Oxido-reduction gave the best results (until 94%) while COD removal of a reduction process was only a 9.7% since no oxidant species are generated.
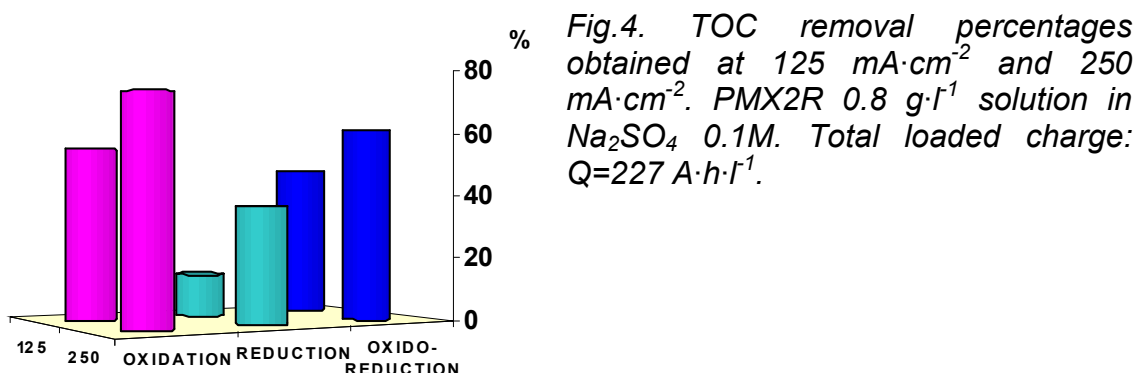

Fig.4. TOC removal percentages obtained at 125 mA·cm^{-2} and 250 mA·cm^{-2}. PMX2R 0.8 g·l^{-1} solution in Na$_2$SO$_4$ 0.1M. Total loaded charge: Q=227 A·h·l^{-1}.

Table 1. COD removals obtained at 125 mA·cm^{-2}. PMX2R 0.8 g·l^{-1} solution in Na$_2$SO$_4$ 0.1M. Total loaded charge: Q=227 A·h·l^{-1}.

PROCESS	-ΔCOD (mg O$_2$·l^{-1})
OXIDATION	75.0%
REDUCTION	9.7%
OXIDO-REDUCTION	93.9%

3.2.2. UV-Visible

Assuming that the degradation reaction is the predominant process, the UV-Visible spectroscopy permitted to monitor the dye solutions decolourization during the electrolytic process. The maximum absorbance wavelength of the azo group before any electrolysis was determined at 486 nm. The aromatic structures were centred at 200-300 nm.
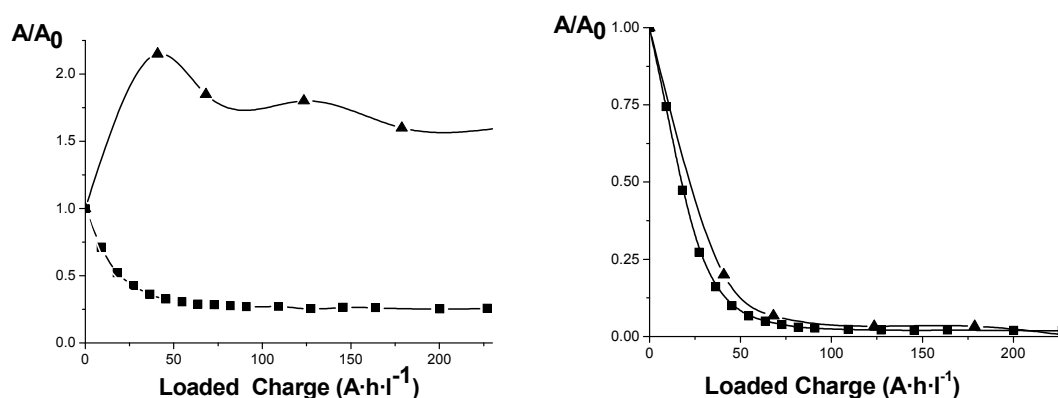

Fig 5. UV-Visible spectra obtained after an electro-reduction process at 150 mA·cm^{-2} (—▲—▲—) and an electro-oxidation process at 125 mA·cm^{-2} (—■—■—). Total charge loaded: 227 A·h·l^{-1}. Procion MX-2R 0.8 g·l^{-1}. Background electrolyte: Na$_2$SO$_4$ 0.5M. Left: evolution of the naphthalene groups. Right: evolution of the azo group.

Fig. 5 illustrates the evolution of the two principal structures present at dye molecule. It is clear that the azo group was completely destroyed after an oxidation process just as the aromatic rings in the structure. However, the reduction process showed a total degradation of the azo group but aromatic rings remained in the structure. Attention must be paid to the fact that a superficial brown layer appeared onto the stainless steel electrode when electro-reduction of Procion MX-2R was carried out (sodium sulphate as electrolyte). This resulted in a diminution of the decolourisation efficiency because of a partial block of the electrode surface. However in presence of chloride ion, no superficial layer was observed so an increase of the decolourisation efficiency took place.

3.2.3. High Performance Liquid Chromatography

The progress of the electrolyses was followed by HPLC analyses of the samples at different values of loaded charge. Taking into account the proportional relation between the dye concentration and the area of the

chromatographic peak at 486 nm (azo group), the decolourisation degree was studied by the evolution of the chromatographic area. Combined and separate processes were studied at 125 and 250 mA·cm^{-2} and sodium sulphate 0.1M and sodium chloride 0.1M were used in both cases. The log A_t/A_0 versus loaded charge (A·h·l^{-1}) curve was obtained (figure not showed) which confirmed the pseudo-first order kinetics in every case.

The fastest decolourization process was the combined process in an undivided electrolytic cell at 250 mA·cm^{-2} in presence of chloride ion. Chlorine was generated onto the electrode so the dye degradation occurs as a result of a chemical oxidation coupled to the electronic transfer. However, organochlorated compounds are formed during the electrolysis and a faster deterioration of the anodes occurs. When sodium sulphate was used the faster decolourization process was oxido-reduction at 125 mA·cm^{-2} in an undivided electrolytic cell. Oxido-reduction with sodium sulphate and current density 250 mA·cm^{-2} was the slowest combined process. The reason could be the major generation of O_2 and H_2 onto the surface electrodes. These phenomenons compete against the degradation of the dye slowing this reaction down. With regard to the separate processes, the electro-reduction presents a decolourization rate higher than electro-oxidation. This fact could be explained by the higher number of chromatographic peaks appeared in the chromatograms obtained after the electro-oxidation.
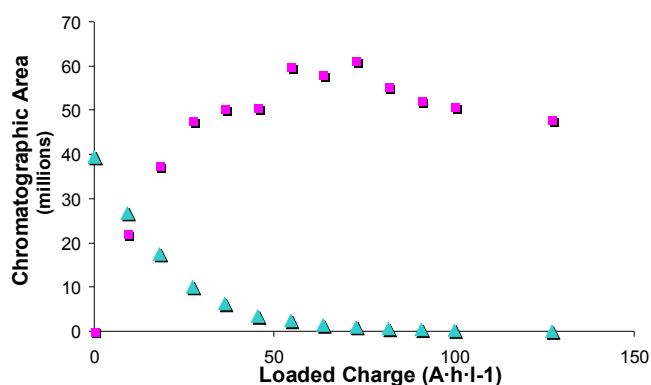

Fig. 6. Evolution of the chromatographic areas corresponding to the azo group (486 nm) (▲) and to the intermediate generated (■) after an electro-reduction process (246 nm). Current density: 250 mA·cm^{-2}. Background electrolyte: sodium sulphate 0.1M. Total loaded charge 227 A·h·l^{-1}. Dye concentration: 0.8 g·l^{-1}.

In all cases, the azo group disappeared completely since its chromatographic area diminished entirely as the loaded charge increased. Fig. 6 shows the evolution of the azo group until its complete disappearance. Besides, chromatograms obtained at λ=246 nm (aromatic rings wavelength) after an electro-reduction process showed a predominant peak which area increased as the loaded charge did. Then, it is logical to associate this peak to an electro-reduction product. Fig. 6 shows the evolution of this peak too. From about 55 A·h·l^{-1} on up, the concentration of the reduction product presents stabilized

values. It is important to notice that this behaviour coincides with the complete disappearance of the azo group.

On the other hand, similar studies of several compounds postulated as electrolysis products revealed that 2-amine-1, 5-naphthalenedisulfonic acid presented the most similar retention time to the reduction product. In fact, their UV-Visible demonstrated that the similarity degree between them was around 99.7%. Besides, internal patron assays were carried out with this commercial product which confirmed the results obtained. Therefore, the reduction product must be structurally similar to this commercial compound.

3.2.4. Horizontal FTIR-ATR

This technique has also been employed to monitor the evolution of functional groups during the electrolysis. The spectrum was collected at 4 cm^{-1} resolution as a result of an average of 100 scans with a ZnSe prism. Fig. 7 illustrates the differences between the spectrum of the initial dye solution with a concentration of 0.8 g·l^{-1} and those obtained from the samples resulted from both the reduction and oxidation process at 227 A·h·l^{-1}.

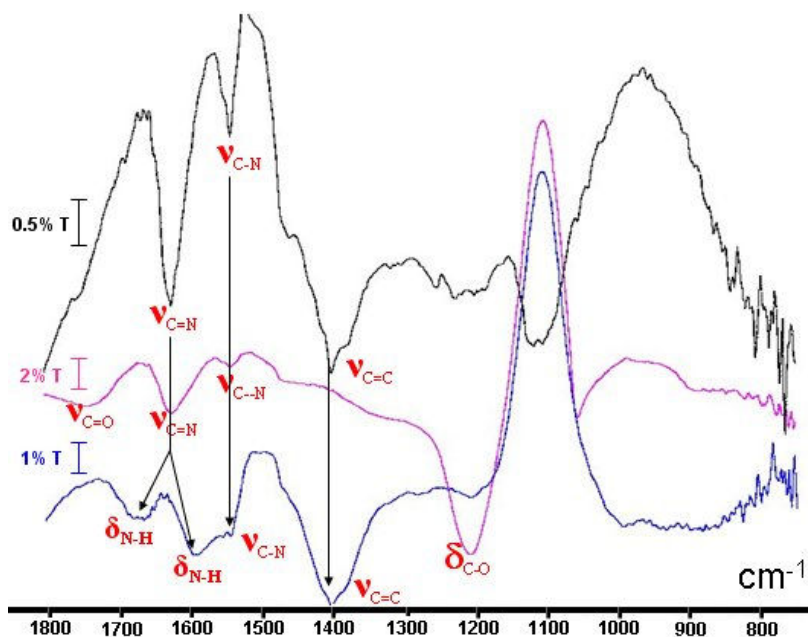*Fig. 7. Comparison of the horizontal FTIR-ATR spectra obtained for the initial dye 0.8 g·l^{1} (—) and final solution after an electro-oxidation process (—) and an electro-reduction process (—) at 250 mA·cm^{-2} and sodium sulphate 0.1M. Loaded charge 227 A·h·l^{1}. Electrolytic cell divided by a cationic membrane.*

Different points can be concluded [15]:

- The strong band at 1400 cm^{-1} in the original dye spectra could be related to the aromatic structures -C=C- stretching vibration ($\nu_{C=C}$). Oxidation process is able to eliminate these structures since this band was not observed. However, after the reduction process the spectrum showed the same band indicating the presence of the aromatic rings.

- After the oxidation process a weak band at 1740 cm^{-1} is observed. This could be ascribed to -C=O stretching vibration ($\nu_{C=O}$) maybe related to carbonyls groups appeared during the oxidation. On the other hand, an intense band at 1200 cm^{-1} appeared increased in intensity. This could be because of the partial relation of this band with -C-O bending mode of the carbonyl groups (δ_{C-O}). These bands do not appear after the reduction process.
- The band at 1530 cm^{-1} could be associated to the -C=N- stretching vibration mode of the triazinic group (ν_{C-N}). Both the oxidation and the reduction processes are able to degrade partially this group, since this band diminishes in both cases.
- The initial dye spectrum showed a very sharp strong band at 1620 cm^{-1} which could indicate the stretching vibration of the imine bond ($\nu_{C=N}$) present in the corresponding tautomeric form of the dye (see Fig. 1). After the electro-reduction process this band turns into two weak bands at 1590 cm^{-1} and 1670 cm^{-1} which may be attributed to N-H bending mode (δ_{N-H}) as a result of the azo rupture and amino group formation.

3.3. Dyestuffs reuse

With the objective of reusing wastewater generated as a result of dyestuff, three successive dyestuffs have been carried out on 100 % cotton samples without any change in the dyestuff conditions. A good reproducibility between initial and first reused dyestuff was observed. However, as the number of reuses goes up, changes in the dyestuff conditions are needed. Washing fastness assays (ISO 105-E01:1996) demonstrated that Procion MX-2R presents an excellent fixation to the fibres after every dyestuff reuse.
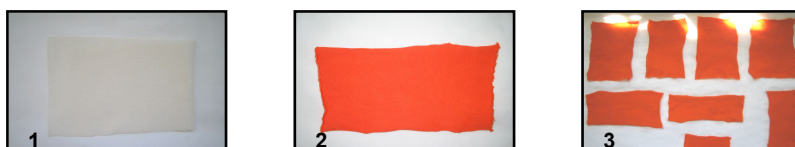

Fig. 8. 1) Sample of cotton 100%. Initial appearance before the dyestuffs. 2) Sample after the dyestuff. 3) Samples after the first reuse of the dyebath.

4. Conclusions

As a consequence of an oxidation or reduction process adsorbed species were observed onto the electrode surface. In addition, at low concentrations the reduction process presents contributions from both diffusion and adsorption currents but at higher concentration the reduction of the dye is predominantly adsorption controlled. Moreover, it has been demonstrated which part of the dye molecule could be responsible of the reduction peak at -0.83V.

The most probable product generated as a result of a reduction process presented a chemical structure similar to 2-amino-1, 5-naphthalenedisulfonic acid as HPLC results and UV-Visible spectra indicated.

Spectroscopy studies indicate that both the oxidation and reduction treatments are able to degrade triazinic and azo groups. Besides, oxidation treatment causes aromatic group degradation. Nevertheless, colour removal is faster by reduction treatments. The decolourisation always follows a pseudo-first order kinetic for all the processes studied. Moreover the fastest process was the oxido-reduction in presence of chloride ion.

Compounds with carbonyl groups are detected as intermediates in the electrochemical oxidation of the dye. Naphthalene amines formed during azo group rupture are detected as products of the reduction of the dye.

The initial dyestuff and that performed by reusing the dyebath for first time gave a good reproducibility. The second reuse of the dyebath indicated the necessity of modifications in the dyestuff formula. After each dyestuff, a very good dye fixation was obtained.

5. References

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