Study of the Reuse of Industrial Wastewater After Electrochemical Treatment of Textile Effluents without External Addition of Chloride

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The interference of human beings in the environment is causing rapid intense environmental damage which is particularly evident in the depletion of natural resources. Research into powerful practical treatments to decolorize and degrade colored textile wastewater is an important challenge nowadays for the textile industry due to environmental considerations, along with the potential water saving. It has been verified, in previous studies, that electrochemical oxidation-reduction treatment with doped SnO_2 anodes was effective. In particular, those belonging to a trychromy (mix of three reactive dyes) achieved a significant reduction in Chemical Oxygen Demand (COD) and Total Organic Carbon (TOC), as well as the decolorization of the treated solutions. Subsequently, the next step is to proceed to study and verify that these treated waters can be reused in subsequent dyes and that acceptable values of color equalization in the dyed fabrics can be achieved. The color differences obtained in the dyed fabrics in the four studied reuses are below the threshold of acceptance of color differences in the textile industry, which is one unit. The only electrolyte used was sodium sulphate. Chloride was not added externally in order to avoid as far as possible indirect oxidation. This allows a true test of the electrooxidantion power of the anodes. In these conditions, the Ti/SnO_2-Sb-Pt DSA electrode is stable. The degree of mineralization is evaluated by measurements of TOC and COD. These data also allow the Average Oxidation State (AOS) at the end of each electrolysis, as well as information on the efficiency in each case through the Carbon Oxidation State (COS) and Average Current Efficiency (ACE) to be established. High Performance Liquid Chromatography (HPLC) was used to study the decolorization kinetics and the evolution of the generated intermediates. Comparison of the spectra obtained by UV-Visible Spectroscopy allows the decolorization from the initial state to the end of the electrolysis to be monitored.

1. INTRODUCTION

In the textile finishing and dyeing industry, large quantities of water and energy are consumed. This industry also produces large amounts of waste water with a high content of organic matter which biodegrades slowly and with great difficulty and which has a persistent color which is resistant to light, temperature, detergents or microbial attack.

The textile dyeing industry has always sought systems that provide maximum efficiency. It is known that these industries have used over 100,000 different dyes with a production of 700,000 tons per year [1]. Up to 15% of this is discharged as waste water [2]. Therefore, it can be estimated that around 50,000 tons of dyes are discharged as waste water annually due mainly to ineffective processes of dyeing or dyes with low affinity with fibers.

Cotton is the substrate that requires the most water in this process. The cotton dyeing industry mainly uses reactive dye reagents. These dyes represent approximately 20-30% of the total consumption of dyes [3]. This type of dye reacts chemically with the fiber, causing a covalent bond between involving oxygen, nitrogen, or sulfur atoms present in the fiber in the form of groups: amino, hydroxyl or thiol, respectively. In the dyeing process, a percentage of non-reactive dye is not fixed to the fiber because there is a parallel hydrolysis reaction. This reaction involves a competitive process with the reaction between the dye and the fiber. Thus, once the dyeing process finishes, the resulting residual bath contains a given concentration of dye in its hydrolyzed form that is no longer able to react with the fiber and is removed with the washing process. This percentage of non-fixed dyes has been determined by various authors and is shown in table (1) [4]

Table 1. Percentages of non-fixed dyes [4].

Dye	EPA	OECD	ETV	Bayer[1]	Euratex	Spain
Acid: - in wool - in poliamide	10 20	7-20	7-20	---	5-15	5-15
Basic	1	2-3	2-3	2	---	0-2
Direct	30	5-20	5-30	10	5-35	5-20
Disperse: - in acetate - in polyester 1 bar - in polyester HT	25 15 5	8-20	8-20	5	1-15	0-10
Azoic	25	5-10	5-10	---	10-25	10-25
Reactive[2]: - in cotton - in wool	50-60	20-50	5-50	5-50	20-45 3-10	10-35
Pre-metallised	10	2-5	2-5	5	2-15	5-15
Mordant	---	---	1-2	---	---	5-10
Vat	25	5-20	5-20	---	5-30	5-30
Sulfur	25	30-40	30-40	---	10-40	15-40
EPA: US Environmental Protection Agency OECD: Organisation for Economic Cooperation and Development ATV: Abwasser Technishe Vereinisung (Waste Water Technical Association) Footnotes: (1) Now Dystar (including BASF) (2) Nowadays, there are new reactive dyes with higher efficiencies (bifunctional dyes).						

In general, reactive dyes have an affinity of around 50-80% with cellulosic fibers. This poor performance is responsible for the noticeable quantity of the non-fixed dye that is discharged into waste water in its hydrolyzed form [5-7]. This problem is solved in part with the use of bifunctional reactive dyes. These dyes have two fixing points to fix to the fiber structure and this increases their affinity to up to 80% [7]. As consequence, the amount of dye discharged into waste water diminishes. However, the total disappearance of unfixed dye from the waste water is not possible.

From the environmental point of view, reactive dye wastewater is water-colored, with high concentrations of salt, and high values of COD and TOC. Moreover, many of these dyes are toxic and can cause mutagenic effects, often causing harm to aquatic life [8-10]. The dye molecules contain aromatic rings which are refractory to the traditional treatments of degradation and elimination. For these reasons, research into powerful practical treatments to decolorize and degrade dyeing textile wastewater nowadays represents a problem of broad interest to the textile industry due to the beneficial effects for the environment.

The conventional biological treatments [11-14], physical (such as adsorption processes) [15] or chemical (flocculation, precipitation, reverse osmosis and chemical oxidation-reduction) [16], are ineffective in decolorization and complete mineralization of these discharges and subsequent treatments are usually required.

For some time, the scientific community has focused increasingly on electrochemistry to solve environmental problems directly related to the textile industry and its wastewater treatment. Electrochemical treatment has been the subject of numerous studies showing significant benefits in terms of cost and safety [17-21].

Besides the electrolyte and the design of the cell, the electrode material is the main factor influencing electrochemical treatment. The use of Dimensionally Stable Anodes (DSA) has proven to be an effective technique. Nowadays, this is an active area of research in the degradation of organic dyes [22-24].

The main objective of this work is the study of the reuse of effluents containing the trichromy of reactive dyes: C.I. Reactive Yellow 138:1 (Yellow), C.I. Reactive Red 231 (Crimson) and $C_{42}H_{27}Cl_2N_{15}Na_6O_{19}S_6$, CAS No.190914-23-9 European Chemicals Agency (Navy), after electrochemical treatment. This type of dye has two monochlorotriazninic groups as reactive groups and two azo groups ($—N=N—$) as chromophores [25]. That is to say, different cycles of dyeing using textile effluents are developed. Before each cycle, the textile effluents are electrochemically treated. This would mean a significant saving in terms of water and electrolyte used. The only electrolyte used was sodium sulphate. Chloride has not been added externally to avoid as far as possible indirect oxidation. A cathode of stainless steel (Cr 18-19% and Ni 8, 5-9%) and a DSA anode of Ti/SnO_2 doped with antimony and small amounts of Platinum (Ti/SnO_2-Sb-Pt) were used. The addition of Platinum provides high stability thus extending its service life and maintaining a great oxygen over-potential [26-27]. In previous research, these experimental conditions produced an important decrease of COD and TOC as well as the color removal of the treated solutions [28-32].

2. EXPERIMENTAL

2.1. Dyes and reagents

The Dystar company supplied the dyes used in this work and they have been used without any form of purification. Other products used in the dying process (NaOH, H_2O_2, and Na_2SO_4) were provided by the companies Merck and Fluka (analysis quality). For preparation of all solutions, distilled water or solutions from reuse of previous dyeing were used.

The initial concentration of each dye prior to dyeing was always 0.50 gL^{-1} (Yellow, Crimson and Navy). The overall concentration of dyes was 1.50 gL^{-1}, which is similar to those used by the industry in the dyeing of cotton fabrics.

For the preparation of dye solutions, the dye was dissolved in distilled water and then Na_2SO_4 electrolyte was added until values of conductivity of about 40.0 $mScm^{-1}$ were reached. The initial pH in all solutions was approximately 7.0. During the dyeing process, pH value increased up to a range between 10.8 and 11.0 with the addition of NaOH.

The solutions that were used in the part corresponding to the study of the color equalization and reuse of waste water were prepared as described above but replacing distilled water with the baths of previously electrolyzed dye.

Once these solutions were prepared, the dying process was initiated.

2.2. Dyeing process.

For the dyeing process, a RED-TEST (UNGOLINI model RT-P) that has a heating system by air and a digital controller for the control of time and temperature was used. This equipment ensured the repeatability of the tests and allowed low bath relationships.

Each of the samples contained:

- 0,125 L of the dyestuff solution.
- 10,00 g of fabric 100% cotton semi-milled (previously washed with a solution of H_2O_2 and NaOH)
- liquor ratio: 1/12,5 (g woven / mL solution)
- Percentage of dye in relation to woven: 1.87%

Each sample was placed inside a steel test tube. These specimens were then introduced into the RED-TEST equipment. The equipment had 10 sample holders in which the tubes containing the dye bath and fabric to dye were inserted. These tubes rotated around an axis to obtain a constant agitation and the following program recommended by the DYSTAR Company for dyeing cellulosic fibers was initiated:

- Initial temperature: 15.0°C-20.0°C ± 2°C. .

- Temperature gradient: 1,5 ºCmin^{-1}.
- Final temperature: 80.0°C ± 2°C.

Once the dyestuff was started, after 60 minutes, an NaOH solution was added to reach a pH of 10.8-11.0. This allowed the dye to fix to the fiber. At a lower pH, dye was deposited onto the fiber but did not react with it. The dyestuff finished after 2 hours. After the dyeing process, the fabrics were washed to eliminate the dye not attached to the fiber. The washing process consisted of a previous neutralization of samples and subsequent treatment with a solution of 2gL^{-1} of detergent AUXIDET RD for twenty minutes under boiling conditions.

2.3. Electrochemical treatment

The choice of electrochemical treatment was based on previous research carried out with various reactive dyes. These results indicate that the best working conditions correspond to the oxidation-reduction process applying a current density of 125 mA cm^{-2}; obtaining the strongest degradation of the dyes as well as a faster decolorization of the solutions. The experimental conditions and the filter press cell configuration were analogous to those used previously [32].

The electrochemical processes were carried out using a stainless steel cathode (Cr 18-19% and Ni 8.5-9%) in the form of a plate of dimensions 11.0 cm x 9.5 cm. This electrode was pretreated to ensure the elimination of surface contamination [32]. A DSA electrode of Ti/SnO$_2$ doped with antimony and with small amounts of platinum in its composition was used as the anode. The thermal method used in previous works was chosen to prepare these electrodes using a mesh geometry [33].

2.4. Reuse process

For the reuse tests five consecutive dyeings were carried. For each of them, the solution from the previous bath was used. The bath contains the hydrolyzed dyes that did not reacted with the fiber and that were electrochemically treated in a filter press cell without separation of compartments and mixed in a ratio of 70/30 with distilled water. This ratio was chosen after testing with different ratios. From these, the one with a content of 70% of electrochemically treated solution and 30% distilled water produced the optimum color matching with the highest quantity of treated solution.

In the dyeing baths, the dye concentrations were always the same: Yellow, Crimson and Navy dye mixtures, with initial concentrations prior to dyeing of 0.50 gL^{-1} for each of these three dyes (total concentration, 1.50 gL^{-1}). The concentration of Na$_2$SO$_4$ for the first dyestuff solution was 45 gL^{-1}. For the following dye processes, the amount of Na$_2$SO$_4$ necessary to maintain conductivity values of the order of 40 mScm^{-1} was added. In terms of pH values, although in each tincture it rose to values of 10.8-11, it later decreased during the electrolytic degradation process. This occurred since in this process, in addition to degrading the dye molecules, water electrolysis cannot be avoided and at the end of the electrolysis the bath always remained with pH values close to 7. Thus, it was not necessary to correct this parameter.

In each electrolysis a load charge of about 95-110 AhL^{-1} was applied. That load value was chosen on the basis of the results obtained in previous work [32], where a complete decolorization of the bath was achieved. This point is defined as the time in which there is less than 1% of the chromophore.
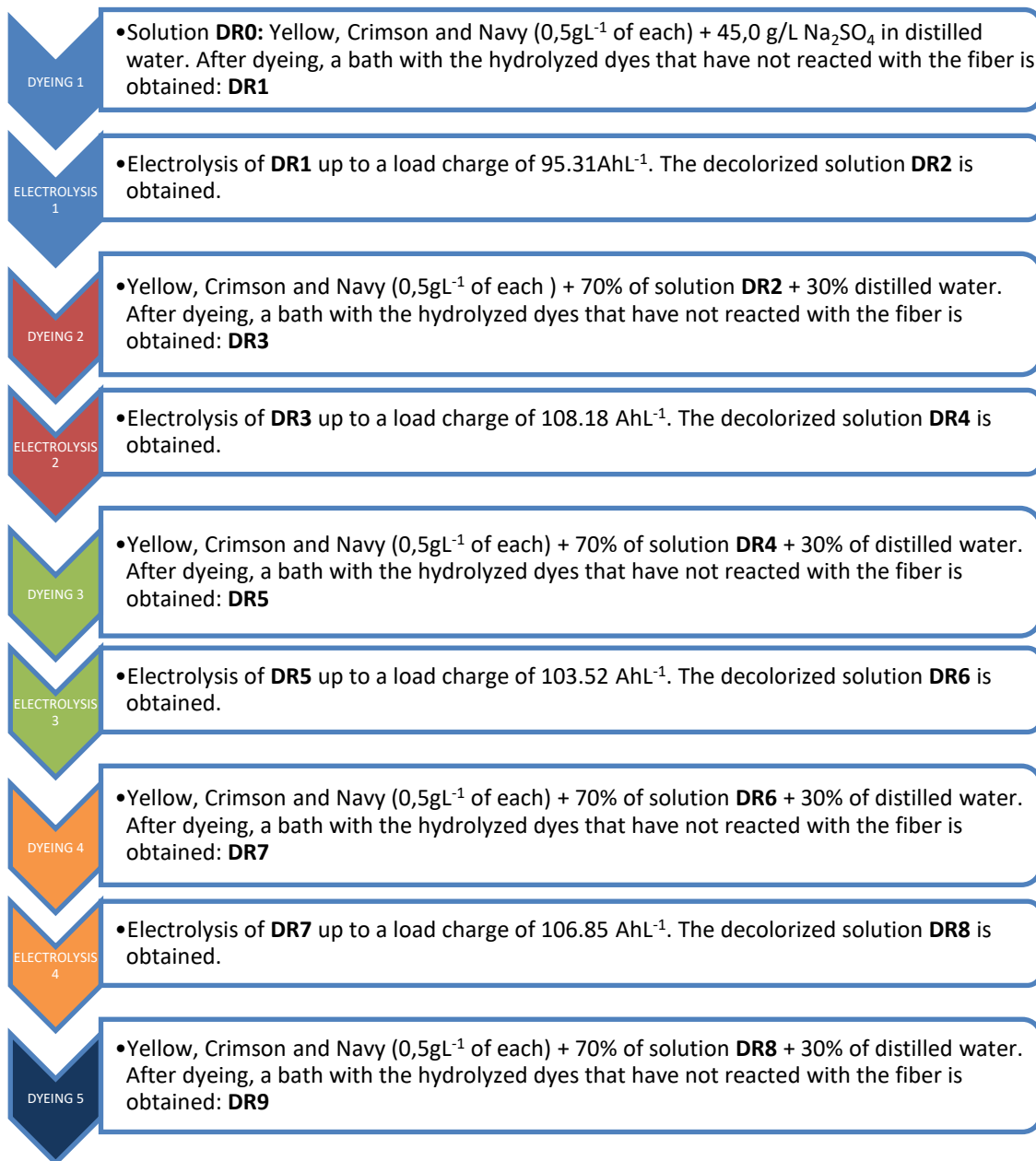
DYEING 1
- Solution **DR0**: Yellow, Crimson and Navy ($0,5gL^{-1}$ of each) + 45,0 g/L Na_2SO_4 in distilled water. After dyeing, a bath with the hydrolyzed dyes that have not reacted with the fiber is obtained: **DR1**

ELECTROLYSIS 1
- Electrolysis of **DR1** up to a load charge of 95.31AhL^{-1}. The decolorized solution **DR2** is obtained.

DYEING 2
- Yellow, Crimson and Navy ($0,5gL^{-1}$ of each) + 70% of solution **DR2** + 30% distilled water. After dyeing, a bath with the hydrolyzed dyes that have not reacted with the fiber is obtained: **DR3**

ELECTROLYSIS 2
- Electrolysis of **DR3** up to a load charge of 108.18 AhL^{-1}. The decolorized solution **DR4** is obtained.

DYEING 3
- Yellow, Crimson and Navy ($0,5gL^{-1}$ of each) + 70% of solution **DR4** + 30% of distilled water. After dyeing, a bath with the hydrolyzed dyes that have not reacted with the fiber is obtained: **DR5**

ELECTROLYSIS 3
- Electrolysis of **DR5** up to a load charge of 103.52 AhL^{-1}. The decolorized solution **DR6** is obtained.

DYEING 4
- Yellow, Crimson and Navy ($0,5gL^{-1}$ of each) + 70% of solution **DR6** + 30% of distilled water. After dyeing, a bath with the hydrolyzed dyes that have not reacted with the fiber is obtained: **DR7**

ELECTROLYSIS 4
- Electrolysis of **DR7** up to a load charge of 106.85 AhL^{-1}. The decolorized solution **DR8** is obtained.

DYEING 5
- Yellow, Crimson and Navy ($0,5gL^{-1}$ of each) + 70% of solution **DR8** + 30% of distilled water. After dyeing, a bath with the hydrolyzed dyes that have not reacted with the fiber is obtained: **DR9**

Figure 1. Process followed for four reuses of a dye bath.

Each of the solutions obtained after electrolysis was used in the subsequent dyeing process. These were denominated:

- Solution DR0→ Initial solution, 100% Water and dyes
- Solution DR1→ After 1st dyeing process
- Solution DR2→ After 1st electrolysis
- Solution DR3→ After 2nd dyeing process
- Solution DR4→ After 2nd electrolysis

- Solution DR5→ After 3rd dyeing process
- Solution DR6→ After 3rd electrolysis
- Solution DR7→After 4th dyeing process
- Solution DR8→ After 4th electrolysis
- Solution DR9→After 5th dyeing process

The process is repeated five times, as is shown in Figure 1 and in each of these successive dyeing and electrolysis processes the evolution of chromatograms, TOC, COD, efficiency values, kinetics, UV-Vis spectra were studied as well as the equalization of the color in the dyed fabrics after each dyeing process.

2.5 Analytical methods and calculated parameters.

To assess the degree of degradation and oxidation of the various samples obtained throughout the electrolysis process, TOC and COD measurements were performed.

The TOC measurements were made using a Shimadzu TOC-VCSN analyzer based on the infrared combustion method. All samples analyzed were diluted (1: 5) to bring them to concentrations within the operating range of the equipment and measurements were made at 1193 K. A volume of 20.0 μl was used in each sample injection. The airflow was 0.150 Lmin^{-1} (CO_2-free). The COD measurements were performed according to the standard ISO 15705 with a Spectroquant analyzer.

Chromatographic analyses were performed by High Performance Liquid Chromatography (HPLC) using a Hitachi Lachrom-Elite chromatography system equipped with a diode array detector. The concentrations of dyes are directly related to the area of the chromatographic peaks, so the evolution of the dye concentration during electrolysis was measured according to the normalized area of the chromatographic peak (S/S_0) associated with each dye (where S_0 is the peak area obtained before starting the electrolysis). The measuring conditions chosen in the chromatographic tests were similar to the ones used in previous works [32]. The wavelength of detection was established at the wavelength of maximum absorption (λ_{max}) of each dye, which is the one in which the azo group absorbs. They are located at 420 nm for Yellow, 549 nm for Crimson and 610 nm for Navy. In addition, in all cases, the detector was also adjusted to 250 nm to study aromatic compounds.

The UV-Visible Spectrophotometry measurements were made using the same Hitachi Lachrom-Elite chromatographic equipment, changing the chromatographic column for a tubular piece of stainless steel (without any type of packaging inside), which allowed the UV-Visible spectra of the samples analyzed using sample of low volume (of the order of μL) to be obtained.

The color matching of the different samples of dyed fabrics obtained according to the method described above was performed using the norm UNE-EN ISO 105-J03: 1997 [34]. A spectrophotometer reflection GretaMacbeth TH 7000 with an illuminant D65 and the observer standard of 10º was used for this purpose. Generally, the maximum limit of acceptance of color differences in the textile industry is one unit (DECMC (2:1) $\leq$ 1). It is a criterion widely used in the sector as a quality control when comparing color differences between two different dyeing processes.

In this study, a series of calculated parameters were used. These provide detailed information on the degree of oxidation and the efficiency of each oxide-reduction process. These parameters were calculated from the results of TOC and/or COD and were as follows: Average Oxidation State (AOS) [35-37], Carbon Oxidation State (COS) [38] and Average Current Efficiency (ACE) [38-43]. While AOS is related to variations in the composition of the sample, COS allows the degree of oxidation of the organic matter present in the samples to be estimated. Thus, information on the efficiency of the degradation of the carbon structures was obtained. Furthermore, ACE indicates the fraction of applied current that is used to decrease the initial COD. This provides an estimation of the effectiveness of the degradation of the whole molecule. These parameters are calculated as follows:

$$AOS = 4\frac{(TOC_t - COD_t)}{TOC_t}$$

$$COS = 4\frac{(TOC_0 - COD_t)}{TOC_0}$$

In both expressions, TOC and COD values are in molar units.

$$ACE = \frac{COD_0 - COD_t}{8 \cdot I \cdot t} \cdot F \cdot V \cdot 100$$

where COD_0 is the initial value and COD_t is the value from a sample obtained during the electrolysis, F is the Faraday constant (96487 C mol^{-1}), 8 is the equivalent weight of oxygen, I is the applied current (A), V is the volume of wastewater (L) and t is the time of electrolysis (s).

3. RESULTS AND DISCUSSION

In the experiments described in this section, electrochemically treated dye baths were mixed with distilled water (70/30). The electrochemical treatment consisted of an oxidation-reduction process under galvanostatic conditions applying a current density of 125 mAcm^{-2} and using a Ti/SnO$_2$-Sb-Pt electrode as anode and a stainless steel electrode as cathode. These solutions were used in successive dyeing-electrolysis processes. The choice of these conditions is based on previous work where electrolyses of reactive dyes were performed at different current density values [28]. Since the decrease of TOC and TN during the highest current density tested (250 mA cm-2) are the highest, the electrolyses at such current densities gave the worst current efficiencies and COD decrease. For these parameters, a current density of 125 mA cm-2 gave the best results. Moreover, oxidation, reduction and oxido-reduction processes were checked. From all of them, oxidation-reduction at 125 mA cm-2 of current density showed the best results for COD removal, average current efficiency and energy consumption for the same loaded charge. BOD5 was used to check the amount of biodegradable matter in solution. With this in mind, the BOD5 to COD ratio was evaluated. Oxidation-reduction process at 125 mA cm-2 increased the BOD5/COD value from 0.02 of the initial sample to 0.30 after the electrolysis, indicating an improvement in the biodegradability. All these results showed that oxido-reduction at 125 mA cm-2 is

the most appropriate process for the degradation of such dye solutions with these electrodes without external addition of chloride.
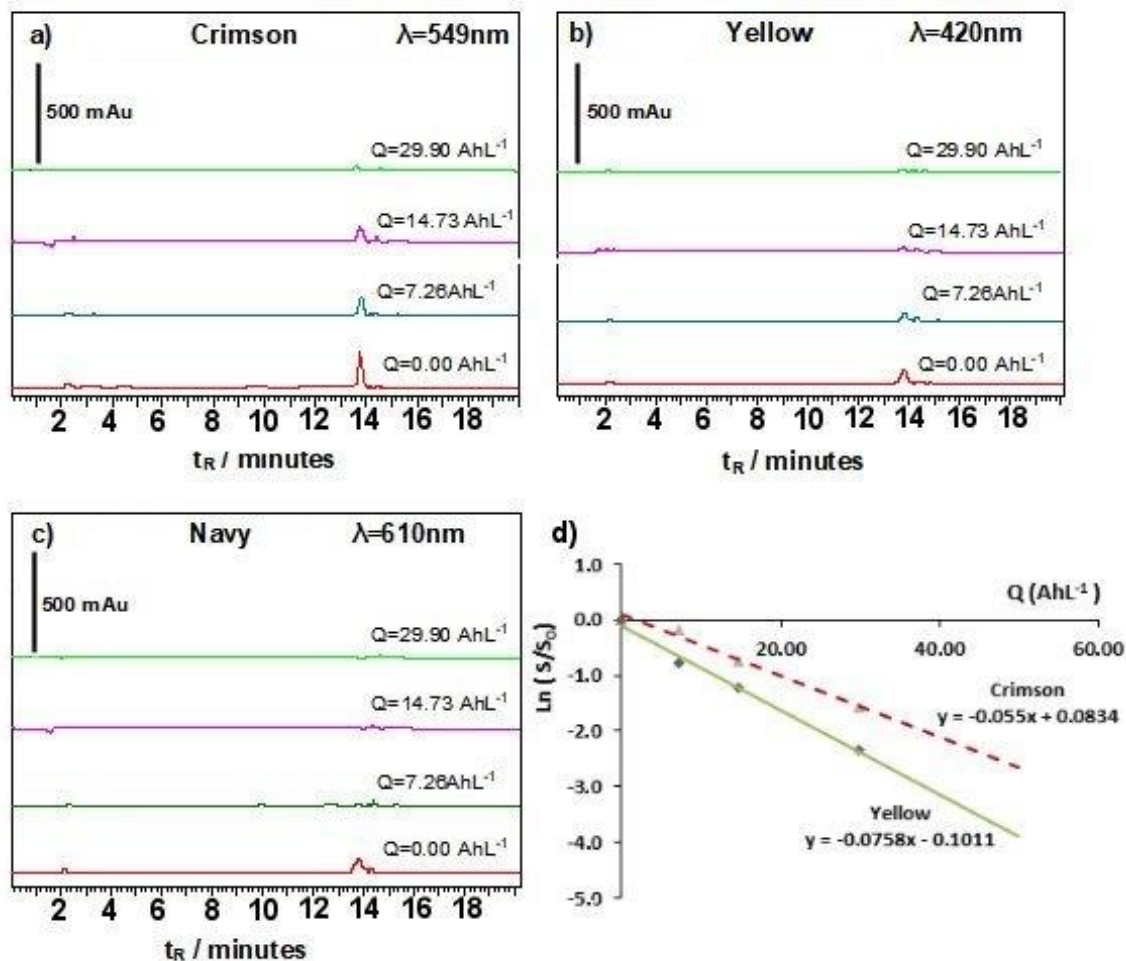
3.1 Kinetics

Figure 2. Chromatographic profile evolution during the electrolysis of solution DR1 of: a) Crimson, b) Yellow and c) Navy; d) logarithmic evolution of the normalized chromatographic peak area versus specific charge loaded before the extraction of each sample.

The different samples taken throughout the electrolyses were analyzed by HPLC. The areas of the corresponding chromatographic peaks were obtained at the wavelengths of maximum absorption (λmax) in which the molecular groups of each dye absorb. The concentration of each dye is directly related to the chromatographic area of the peak at the maximum absorption wavelength. The evolution of the amount of dye remaining in solution with its unchanged chromophore group was followed through the measurements of the normalized chromatographic areas (S/S_0) of the peaks associated with each dye (where S_0 is the peak area when Q=0.00 AhL^{-1}) throughout the four electrolyses.

Figures 2 and 3 show the evolution of the chromatograms during the first and fourth electrolyses. These figures include the representation of the evolution of the logarithm of the normalized

chromatrographic areas of the peaks associated to the chromophores versus the specified charge applied prior to the extraction of samples. The evolution of Navy is not shown because the chromatographic peak corresponding to this dye disappears immediately upon beginning the electrolysis processes and it was not possible to obtain enough chromatographic area values for it.
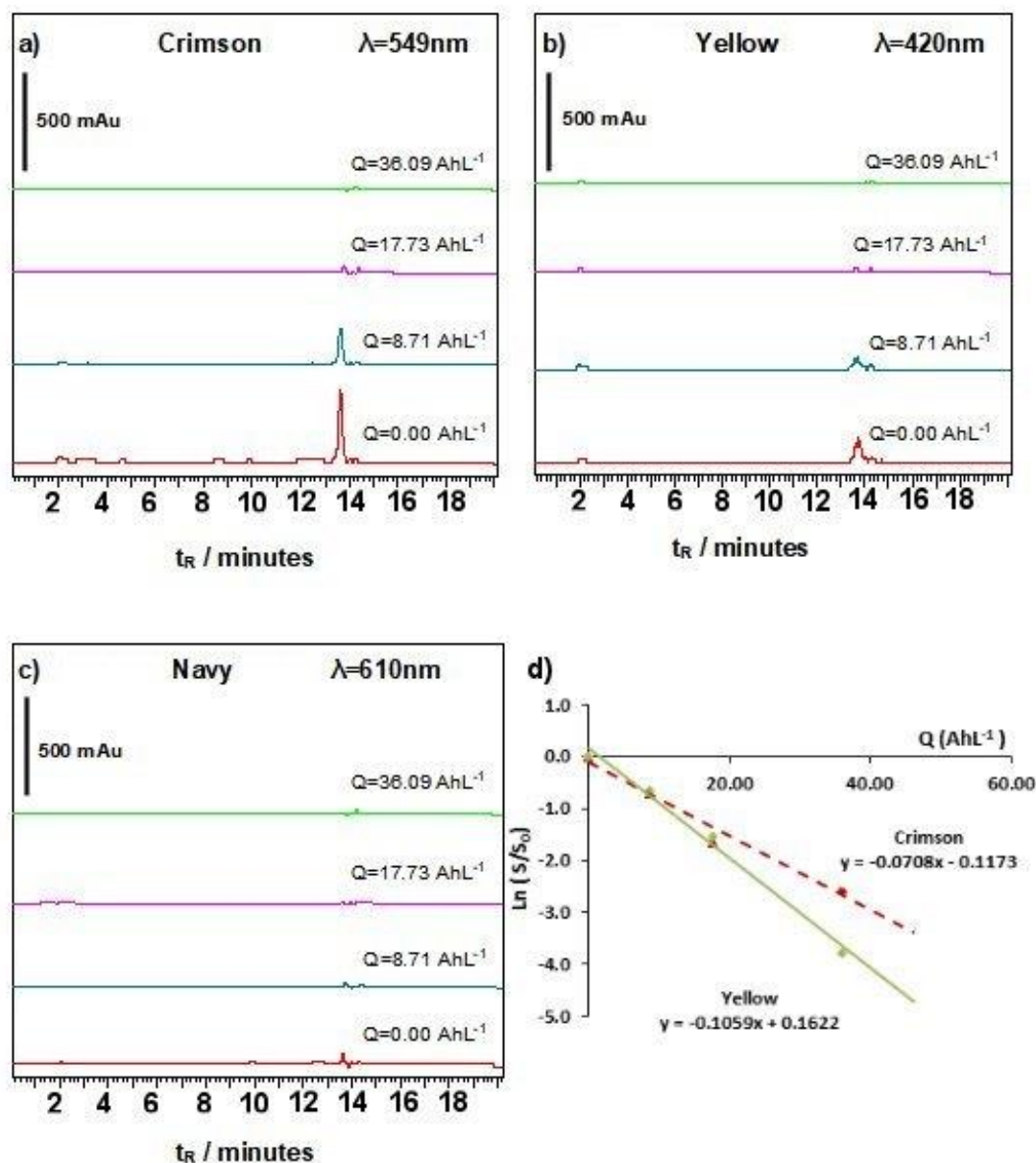

Figure 3. Chromatographic profile evolution during the electrolysis of solution DR7 of: a) Crimson, b) Yellow and c) Navy; d) logarithmic evolution of the normalized chromatographic peak area versus specific charge loaded before the extraction of each sample.

The evolution of the plots Ln(S/So) vs. Q (AhL^{-1}) indicates an exponential decrease as the loaded charge increases, which is the typical behavior of pseudo-first order decolorization kinetics.

Table 2 shows the evolution of the kinetics parameters obtained from the linear regression analysis for the plots Ln(S/So) vs. Q (AhL^{-1}) for the electrolyses of solutions DR1, DR3, DR5 and DR7.

All the decolorization kinetics rates were very close, between 0.05 and 0.10 $LA^{-1}h^{-1}$. The values of the minimum estimated specific load charge needed for decolorization (1% of chromatographic peak area) of each dye were very close throughout all the electrolyses experiments. In other words, during the successive dyeing-electrolysis processes there were no significant increases in coloration and in each electrolysis the chromophores are completely eliminated. Riera-Torres et al. [44] studied the electrochemical oxidation for color removal of the dyes studied in the present work. They used as electrolyte and Ti/Pt oxide electrodes and UV combined treatment. In this work, total color removal and organic compound degradation only occurred after UV irradiation.

Table 2. Decolorization rate constant, Kap ($LA^{-1}h^{-1}$), obtained for the electrolyses of the solutions DR1, DR3, DR5 y DR7 and values of minimum estimated specific load charge needed for decolorization, Qdec (AhL^{-1}).

SOLUTION	INITIAL CONCENTRATION(gL^{-1})	λ (nm)	Tr (min)	Kap ($LA^{-1}h^{-1}$)	Qdec (AhL^{-1})
Electrolysis 1					
Yellow	0.5	421	13.6	0.08	59.35
Crimson	0.5	549	13.4	0.05	85.15
Electrolysis 2					
Yellow	0.5	421	13.6	0.08	58.45
Crimson	0.5	549	13.4	0.07	65.64
Electrolysis 3					
Yellow	0.5	421	13.6	0.07	60.36
Crimson	0.5	549	13.4	0.06	69.66
Electrolysis 4					
Yellow	0.5	421	13.6	0.10	44.97
Crimson	0.5	549	13.4	0.07	63.31

3.2 TOC and COD removal. Efficiency studies.

Table 3. TOC, COD AOS, COS and ACE obtained from samples at the beginning and at the end of the electrolyses processes, for the electrolyses of the solutions DR1, DR3, DR5 y DR7.

SOLUTION	Q ($A.h\ L^{-1}$)	TOC (mgL^{-1})	TOC REMOVAL (%)	COD ($mg\ L^{-1}$)	COD REMOVAL (%)	AOS	ΔAOS	COS	ΔCOS	ACE (%)
Electrolysis 1	0.00	486.10	-	1467.33	-	-0.53	-	-0.53	-	-
	95.31	434.65	10.58	1152.50	21.46	0.02	0.55	0.02	0.55	1.09
Electrolysis 2	0.00	664.00	-	1888.00	-	-0.27	-	-0.27	-	-
	108.18	393.75	40.70	1012.00	46.40	0.20	0.47	0.09	0.35	2.62
Electrolysis 3	0.00	693.00	-	1803.33	-	0.10	-	0.10	-	-
	103.52	561.50	18.98	1290.00	28.47	0.55	0.46	0.45	0.35	1.64
Electrolysis 4	0.00	617.00	-	1846.67	-	-0.49	-	-0.49	-	-
	106.85	458.95	25.62	1082.00	41.41	0.46	0.95	0.34	0.83	2.35

Table 3 shows the results corresponding to TOC and COD removal as well as the AOS, COS and ACE values obtained at the beginning and the end of each electrolysis. The load values of specific charge

at the end of the electrolyses are in the range of 100.00 AhL^{-1}. The electrolyses were raised to these values because in previous studies it was verified that these values guarantee total decolorization and ensure a greater degradation of organic matter [32].

The removal average of TOC is 24.00% for the four electrolyses. For the first electrolysis the TOC value started at 486.10 mgL^{-1}. The TOC value for the second electrolysis started at 664.00 mgL^{-1}, which meant an increase of 37%, but in the following reuses no substantial increase was observed with values remaining of the order of 600-700 mgL^{-1}. That is to say, throughout the process there was continuous mineralization and degradation of the dyes.

In all cases the COD decreased, and the elimination percentages were between 21.46% in the first electrolysis to a maximum removal of 46.40% in the second electrolysis. The average elimination value for the four electrolyses was 34.45%. These are noteworthy values and it is worth commenting that the COD value does not rise significantly in the successive reuses. In the first electrolysis the COD value started at 1467.33 mgL^{-1} in the DR1 solution. In the second electrolysis we have an initial COD value of 1888.00 mgL^{-1} (DR3 solution), equivalent to an increase of 28%. However, in the following reuses the initial COD was maintained at values of the order of 1800.00 mgL^{-1}, which indicates that the process is sustainable since it does not increase the load of oxidizable material in the solutions.

The TOC and COD removal percentage are lower than those reported in the bibliography using Na2SO4 as electrolyte, synthetic textile wastewater with one only dye and anodes of boron-doped diamond (BDD) or PbO2 [19-20, 45]. The experimental conditions used in the present study: alkaline pH as obtained after dyeing and Na2SO4 as electrolyte without addition of another one, are not usual. So, comparing the results obtained in the present study with others in the bibliography is difficult. In fact, there is no noticeable number of examples in the bibliography of electrochemical oxidation of real textile wastewater with the objective of reusing the water. Nevertheless, among others, the results obtained by Gutiérrez-Bouzan et al. are interesting, combining nanofiltration membranes with electrochemical processes [46] or the results reported by Tsantaki et al. where using HClO4 as supporting electrolyte and BDD as anode, they obtain a maximum of 70% of dissolved organic carbon (DOC) removal [47].

In all cases, the elimination of COD was greater than that of TOC. This involved the generation of oxidized carbonaceous species that remain stable in the solution. These removal rates of TOC and COD were obtained due to the generation of hydroxyl radicals (OH$^{.}$) on the surface of the Ti / SnO$_2$-Sb-Pt anode. These species have a strongly oxidizing character that promotes the mineralization of the organic matter present in the solution.

The ACE values fell between 1.09 of the first electrolysis and 2.62 for the second electrolysis. These values indicate that the process is developed efficiently.

Variations in the AOS involve changes in the composition of the solution because of the electrochemical process. Positive trends of the EOP with respect to the initial value indicate that the final compounds had a more positive oxidation state than the untreated dye molecule [28]. All the treated solutions had more positive carbon oxidation states.

Changes in COS values were also related to changes in the composition of the solution as a result of electrochemical treatment. In all cases, an increase in COS values was observed.

In summary, the electrolysis products exhibited a higher oxidation state than the dyes before electrolysis and these oxidized intermediates were stable in solution, as indicated by the TOC removal results [28]. This behavior was confirmed by the increase in the AOS values associated with the processes.

3.3 Spectroscopic results.

Figure 4 shows the evolution of the UV-Vis spectra during the four electrolyses. The bands associated to the chromophore groups of each dye are 420nm, 610 nm and 549 nm for Yellow, Navy and Crimson, respectively. Due to the experimental conditions applied in the dyestuff procedure, the initial concentration of each dye is low, and so the intensity of these bands is also very low. Nevertheless, it seems that these bands completely disappeared after electrolysis.
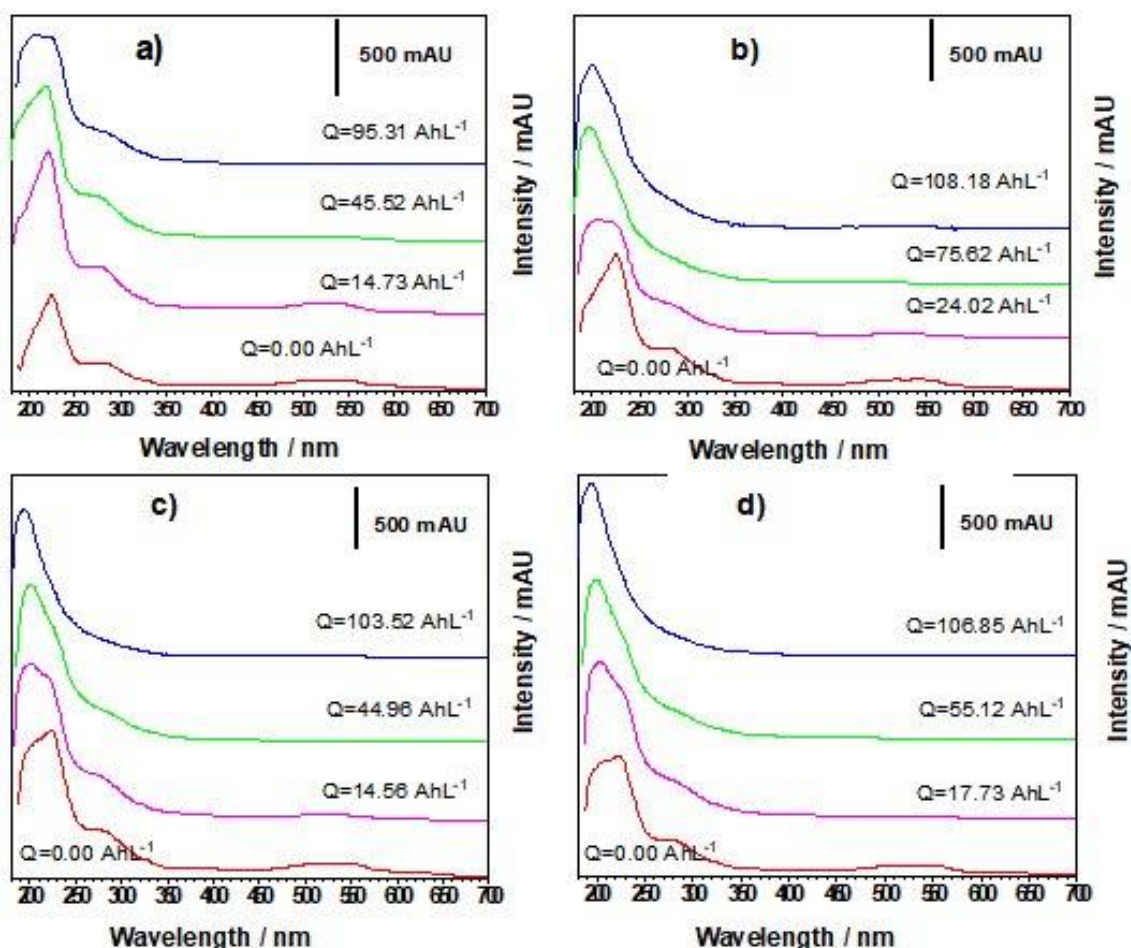
Figure 4. Evolution of the UV-Vis spectra profile during the electrolyses of: a) solution DR1, b) solution DR3, c) solution DR5 and d) solution DR7.

Bands in the UV range are more intense. In all cases, the band centered at 280 nm, related to triazinic groups [48], completely disappeared after electrolysis. The band centered at 230 nm, assigned

to $\pi \to \pi^*$ transitions of benzenic rings [49-52], remained after electrolysis. Therefore, these molecular structures were not totally degraded after electrolysis. In all cases, the band centered on 250 nm that is associated to aromatic compounds, evolved with variations in intensity and position but without disappearing. In summary, spectra evolution indicated that after all electrolysis tests complete decolorization and partial mineralization took place.

3.4 Color matching after different reuses.

Color matching in the different samples of dyed fabrics was performed according to the UNE-EN ISO 105-J03: 1997 [34], using a spectrophotometer reflection GretaMacbeth TH 7000 with a D65 illuminant and standard observer of 10º. From the different values of the parameters: Lightness (DL CMC), Chrome (DC CMC) and Hue (DH CMC), obtained for each sample, the chromatic coordinates were evaluated. This allowed the differences between the chromatic coordinates of two different samples of dyed fabrics to be evaluated. The parameter used for this purpose was the color difference values DECMC (2:1) shown in Table 4.

Table 4. Values of color matching for the different dyeing obtained from solutions DR0, DR2, DR4, DR6 and DR8, with a D65 illuminant with a tolerance 1. Reference: dyed fabric in the first reuse (dyeing 2).

NUMBER OF DYEING	DL CMC	DC CMC	DH CMC	DECMC (2:1)
DYEING 1	-1.09	0.62	-0.85	1.52
DYEING 2	-0.26	0.62	-0.59	*0.90
DYEING 3	0.82	0.36	-0.26	0.93
DYEING 4	0.80	0.51	-0.31	1.00
DYEING 5	0.34	0.42	-0.28	0.60

(*) This value corresponds to the difference between two different samples of the 2nd dyeing.

To evaluate the color matching in the different reuses, the dyed fabric in the first reuse (dyeing 2) was taken as a reference pattern. As is shown in table 4, there is a color difference (DE CMC (2:1)) of 1.52 compared to the dyed fabric using only distilled water without reuse (dyeing 2 as reference). This value is higher than 1 and is outside the limits accepted in the textile industry (DECMC (2: 1) ≤ 1). It is a factor to be taken into account but it is not important for the results of this work since it would be usual to work with dye baths from reuse. Thus, if the reference pattern is the dyed fabric in the first reuse (dyeing 2) the DECMC (2: 1), differences always give less than or equal to one, therefore they are acceptable.

Figure 5 shows the photographs of the samples of dyed fabrics included in Table 4. A good color match can be observed.
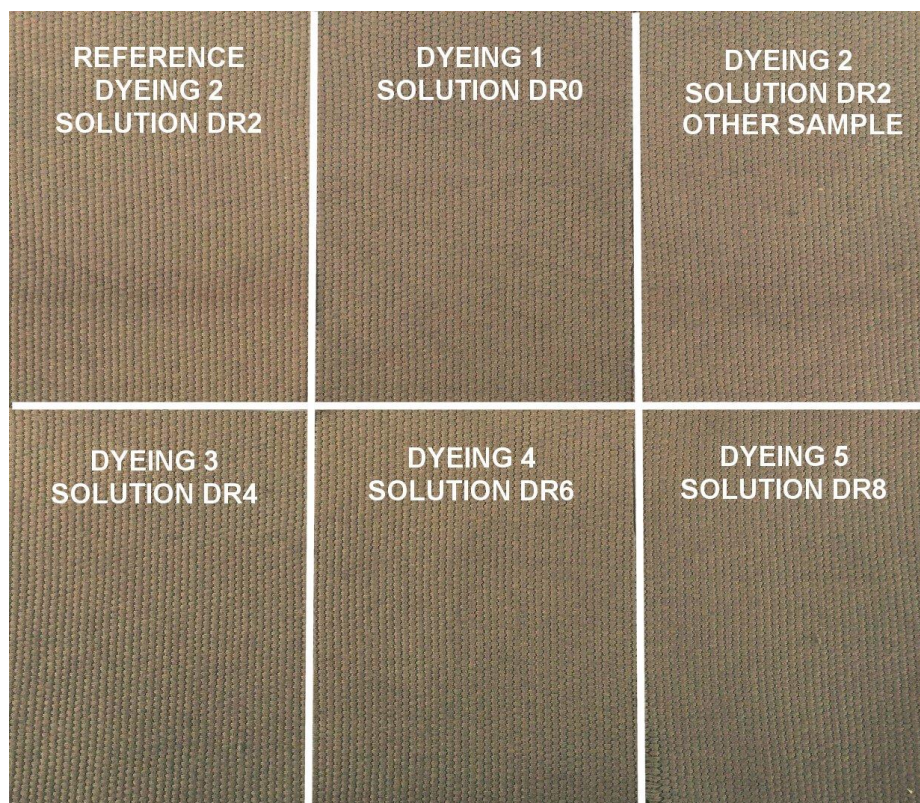
Figure 5. Samples of dyed fabrics.

Therefore, it is clear that the results of color matching obtained are within acceptable ranges, and so, the proposed hypothesis of reuse of baths consisting of 30% water and 70% dye bath after electrolysis applying a load specific charge in the range of 100.00 AhL^{-1}, according to the electrolysis procedure proposed in this work, is confirmed.

4. CONCLUSIONS

The viability of the reuse of dye baths after electrochemical decolorization and degradation of wastewater obtained from dyeing processes of cotton fabrics with bifunctional reactive azo dyes belonging a trycromy of reactive dyes, was studied.

For the dyeing processes, aqueous solutions composed of 30% water and 70% solutions obtained after each electrolysis were used. The electrolyte used was Na_2SO_4 (without external chloride addition). The electrolyses of these wastewaters was carried out in a filter-press cell under galvanostatic conditions applying a current density j = 125 $mAcm^{-2}$ and using a Ti/SnO_2-Sb-Pt electrode as an anode and a stainless steel electrode as a cathode. The applied load was in the range of 100.00 AhL^{-1}

Complete discoloration was obtained in the four electrolysis processes and there were no noticeable differences in the decolorization of the solutions obtained in the successive reuses.

In all cases, a significant decrease of COD and TOC was obtained. The elimination of COD was greater than that of TOC, indicating the presence of intermediate species (stable in solution) whose oxidation state was more positive than that of the untreated dye molecule. This was proven through the

evolution of the AOS. The AOS and COS data indicated that the oxidation state of Carbon increases in all treated solutions. The results of ACE and COS showed that this process takes place efficiently.

The decolorization kinetics of all the processes corresponded to a pseudo-first order model. The decolorization rate presented similar values of order and magnitude in all cases regardless of the number of reuses done from a dyeing bath.

The results of color matching DECMC (2:1) in the dyed fabrics in the four reuses are lower than the maximum limit of acceptance of color differences in the textile industry that is one unit (DECMC (2:1) ≤ 1.

The conclusions drawn from this work are that the electrochemical treatment under the proposed conditions of the successive dye bath could be a viable and a sustainable alternative in the purification of real textile waste water on an ongoing basis. This also prevents the discharge of textile waste water with a high content of salts into the environment, saving water and electrolyte (up to 70%).

References

1. A. S. Arun Prasad and K. V. Bhaskara Rao, *Global J. Biotech. & Biochem.*, 5 (2010) 80.
2. A. R. Elmoubarki, F.Z. Mahjoubi, H. Tounsadi, J. Moustadraf, M. Abdennouri, A. Zouhrib, A. El Albanic and N. Barka, *Water Resour. Ind.*, 9 (2015) 16.
3. P. A. Carneiro, M. E. Osugi, C. S. Fugivara, N. Boralle, M. Furlan and M. V. B. Zanoni, *Chemosphere*, 59(3) (2005) 431.
4. European Commission, "Reference Document on Best Available Techniques in the Large Volume Organic Chemical Industry February 2003", *Integr. Pollut. Prev. Control*, 1 (2003) 267.
5. C. C. I. Guaratini, A. G. Fogg and M. V. B. Zanoni, *Electroanalysis,* 13 (2001) 1535.
6. C. C. I. Guaratini, A. G. Fogg, M. Valnice and B. Zanoni, *Dyes and Pigments*, 50 (2001) 211.
7. R. L. M. Allen, Colour Chemistry, Nelson & Sons, (1971) London, England.
8. F. I. Vacchi, J. Aparecida de Souza, B. Ferreira da Silva, M. V. Boldrin, G. de Aragão, *Sci. Total Environ.,* 601 (2017) 230.
9. K. P. Sharma, S. Sharma, S. Sharma, P. K. Singh, S. Kumar, R. Grover and P. K. Sharma, *Chemosphere*, 69 (2007) 48.
10. S. M. A. G. Ulson de Souza, E. Forgiarini and A. A. Ulson de Souza, *J. Hazard. Mater.,* 147 (2007) 1073.
11. E. Forgacs, T. Cserháti and G. Oros, *Environ. Int.*, 30 (2004) 953.
12. T. Robinson, G. McMullan, R. Marchant and P. Nigam, *Bioresource Technol.*, 77 (2001) 247.
13. A. B. dos Santos, F. J. Cervantes and J. B. Van Lier, *Bioresource Technol.*, 98 (2007) 2369.
14. J. P. Saxe, B. L. Lubenow, P. C. Chiu, C.P. Huang and D. K. Cha, *Water Environ. Res.*, 78 (2006) 26.
15. C. Galindo, P. Jacques and A. Kalt, *Chemosphere*, 45 (2001) 997.
16. X. B. Zhang, W. Y. Dong and W. Yang, *Chem. Eng. J.,* 233 (2013) 14.
17. E. Brillas and C. A. Martínez-Huitle, *Appl. Catal. B: Environ.*, 166 (2015) 603.
18. A. B. S. Nossol, S. M. C. Rosa, E. Nossol, A. J. G. Zarbin and P. Peralta-Zamora, *Quim. Nova* 39

(2016) 686.

19. L. Labiadh, M. A. Oturan, M. Panizza, N. B. Hamadi and S. Ammar, *J. Hazard. Mater*., 297 (2015) 34.
20. V. M. Vasconcelos, C. Ponce-de-León, J. L. Nava and M. R. V. Lanza, J. *Electroanal. Chem*., 765 (2016) 179.
21. M. Punzi, A. Anbalagan, R. A. Börner, B. M. Svensson, M. Jonstrup and B. Mattiasson, *Chem. Eng. J.,* 270 (2015) 290.
22. M. Gonçalves, M. M. Alves, J. P. Correia and I. P. Marques, *Bioresour. Technol*., 99 (2008) 8207.
23. G. R. P. Malpass, D. W. Miwa, S. A. S. Machado and A. J. Motheo, *J. Hazard. Mater*., 156 (2008) 170.
24. N. Mohan, N. Balasubramanian and C. A. Basha, *J. Hazard. Mater*., 147 (2007) 644.
25. R. M. Christie, Colour Chemistry, RSC Publishing, (2001) London, England.
26. F. Vicent, E. Morallón, C. Quijada, J.L. Vázquez, A. Aldaz and F. Cases, *J. Appl. Electrochem*., 28 (1998) 607.
27. A. I. Del Río, J. Fernández, J. Molina, J. Bonastre and F. Cases, *Electrochim. Acta*, 55 (2010) 7282.
28. A. I. del Río, J. Molina, J. Bonastre and F. Cases, *Chemosphere*, 75 (2009) 1329.
29. A. I. del Río, J. Molina, J. Bonastre and F. Cases, *J. Hazard. Mater.,* 172(1) (2009) 187.
30. A. I. del Río, M. J. Benimeli, J. Molina, J. Bonastre and F. Cases, *Int. J. Electrochem. Sci*., 7 (2012) 13074.
31. A.I. del Río, E. Duval, M.J. Benimeli, J. Molina, J. Bonastre and F. Cases, Investigaciones en ingeniería medioambiental, Ed. Marfil (2009) Spain.
32. F. Orts, A. I. del Río, J. Molina, J. Bonastre and F. Cases, *J. Electroanal. Chem*., 808 (2018) 387.
33. A. I. del Río, J. Fernández, J. Molina, J. Bonastre and F. Cases, *Desalination*, 273 (2011) 428.
34. UNE-EN ISO 105 J03.1997.
35. L. S. Clesceri, A. E. Greenberg, A. D. Eaton, E. W. Rice, Standard Methods for Examination of Water and Wastewater, 21th ed. AWWA, (2005) Washington, USA.
36. F. Montilla, P. A. Michaud, E. Morallón, J. L. Vázquez, and Ch. Comninellis, *Electrochim. Acta,* 47(21) (2002) 3509.
37. W. Stumm and J. J. Morgan, Aquatic Chemistry: Chemical Equilibria and Rates in Natural Waters, John Wiley & Sons Inc., (1995) New York, USA.
38. Ch. Comninellis and C. Pulgarin, *J. Appl. Electrochem*, 21 (1991) 703
39. Ch. Comninellis and G. Chen, Electrochemistry for the Environment, Springer, (2010) Berlin, Germany.
40. L. S. Andrade, R. C. Rocha-Filho, N. Bocchi, S. R. Biaggio, J. Iniesta, V. García-García and V. Montiel, *J. Hazard. Mater*., 153 (2008) 252.
41. J. Iniesta, P. A. Michaud, M. Panizza, G. Cerisola, A. Aldaz and Ch. Comninellis, *Electrochim. Acta*, 46 (2001) 3573.
42. D. Rajkumar, J.G. Kim and K. Palanivelu, *Chem. Eng. Technol*., 28 (2005) 98.
43. C. Sáez, M. Panizza, M. A. Rodrigo and G. Cerisola, *J. Chem. Technol. Biot*, 82 (2007) 575.
44. M. Riera-Torres and C. Gutiérrez-Bouzán, *Sep. Purif. Technol*., 98 (2012) 375.
45. A.N. Subba Rao, V.T. Venkatarangaiah, *Environ. Sci. Pollut. Res*., 21 (2014) 3197.
46. V. Buscio, M. García-Jiménez, M. Vilaseca, V. López-Grimau, M. Crespi and C. Gutiérrez-Bouzan, *Materials*, 9(6) (2016) 490.
47. E. Brillas, F.C. Moreira,, R.A.R. Boaventura, E. Brillas, V.J.P. Vilar, *Appl. Catal. B: Environ*., 202 (2017) 217.
48. R. M. Silverstein, F.X. Webster and D.J. Kiemle, Spectrophotometric identification of organic compounds, John Wiley & Sons Inc., (2005) New York, USA.
49. J. Yang, Analysis of Dye, Chemical Industry Press, (1987) Beijing, China.
50. W. Feng, D. Nansheng, and H. Helin, *Chemosphere,* 41 (2000) 1233.
51. C. Galindo, P. Jacques, and A. Kalt, *J. Photochem. Photobiol. A: Chem*., 130 (2000) 35.

52. M. Stylidi, D. I. Kondarides and X. E. Verykios, *Appl. Catal. B: Environ.*, 47 (2004) 189.