ELECTROCHEMICAL REDUCTION BEHAVIOR OF VAT AND SULFUR DYES: A COMPARATIVE STUDY

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ABSTRACT

In the application of vat and sulfur dyes, a large amount of hazardous by-products are generated from chemical reducing agent decomposition such as sodium dithionite and sodium sulfide. The substitution of these non-regenarable by-products by cathodically regenerable reducing agents offers great ecological advantages. In this study, indirect electrochemical reduction of the most popular Vat dye (CI Vat Blue 1) and Sulfur dye (CI Sulfur Black 1) was studied in a divided electrochemical cell connected with a separated dye bath. The redox properties of the tested dyes were studied by the mean of potentiometry at imposed low current and by controlling the evolution of the redox potential. The color coordinates and the color fastness of the samples were investigated and compared with the conventional dyeing process. The electrochemical process proposed in this study permitted an improved understanding of the dyestuff reduction behavior at a molecular level. The electrochemical reduction of CI Vat Blue 1 showed better performance. The CI Sulfur Black 1 has almost good advantage, but with different reduction behavior and more complications because of different reducible sites in its molecule.

1. INTRODUCTION

In the coloration of cellulosic fibers, Vat dyes (including indigo) as well as Sulfur dyes hold a large part of the dyestuff market. Actually, Vat dyes yield colored cotton of excellent all-round fastness, particularly to light, washing and chlorine bleaching (Roessler, Jin, 2003). Also, Sulfur dyes (particularly Sulfur Black B1) present technical benefits in the coloration of cellulosic fibers. In fact, the dyed material represents a broad shade range having an excellent fastness to washing and light (Božič, Kokol, 2008), as well as a moderate cost of the dye itself (Wang et al., 2001). Vat dyes owe their name to the vatting process associated with their application, while Sulfur dyes are so named because of the essential use of sulfur in their synthesis. The structures of Vat dyes are rather well known but Sulfur dye structures are less well defined. In fact, their polymeric nature makes them unsuitable for standard methods for structure characterization. Vat and Sulfur dyes are similarly insoluble in water and require a somewhat complicated application procedure (Trivedi et al., 2013). Both dyestuffs must be converted by reduction before, or during, the dyeing process

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from their water-insoluble form into a water-soluble form having affinity to the cellulosic fiber, the so-called leuco form. Once on the fiber, they are converted back to the original insoluble form by oxidation.

It has been known that sodium dithionite and sodium sulfide are used for reducing Vat and Sulfur dyes respectively. However, the sulfide ions released from sodium dithionite and sodium sulfide decompositions affect the environment detrimentally by noxious odors, toxicity and high chemical oxygen demand of the wastewater (Božič, Kokol, 2008; Chavan, Chakraborty, 2001; Bechtold et al., 2008). Also, chemical reducing agents can be over reduced specially for delicate dyestuffs. This disadvantage leads the dyestuffs to not being re-oxidized to its original water insoluble form. In addition, chemical reducing agents do not allow clear experimental separation and isolation of the discussed parameters due to the complex reaction pathway influenced by thermodynamic and kinetics factors (Bechtold et al., 2000). Also, an another complication is caused by the undefined structural formulae of Sulfur dyes, even for the most important representatives such as Sulfur Black B1 and Leuco Sulfur Black B1. This handicap leads to an undefined and non-well known redox behavior until now (Bechtold et al., 2000). Solving these technical and environmental problems has been the main concern of many researches (Roessler, Jin, 2003; Božič, Kokol, 2008; Chavan, Chakraborty, 2001; Bechtold et al., 2008; 1997). Beginning with the need to minimize the reducing agent consumption, "eco-friendly" techniques were investigated, to study the possibility of achieving enhanced dyestuff reduction. In modern textile dyeing processes, the most attractive procedure to reduce Vat and Sulfur dyes is the electrochemical reduction method. By this way, it is possible to reduce solid dyestuff on the surface of cathode in aqueous solution. If the dyestuff present in an aqueous suspension is not immobilized it shows distinctly different reduction behavior (Bechtold et al., 1998). Under these conditions it cannot be electrochemically reduced efficiently. However, an electrochemical reduction process using a redox mediator (complexes of iron with triethanolamine or gluconic acid) has been developed (Bechtold et al., 1998). Promising results were achieved by using the indirect electrochemical process especially for Vat dyes (Bechtold et al., 2008; Haj Said et al., 2008). At first, the mediator is introduced in the medium under its oxidized form. Once the mediator is reduced at the electrode, it would diffuse and exchange electrons with microcrystal of the dispersed dye in solution. Then, the dye is reduced and the oxidized form of the mediator is regenerated (Figure 1).
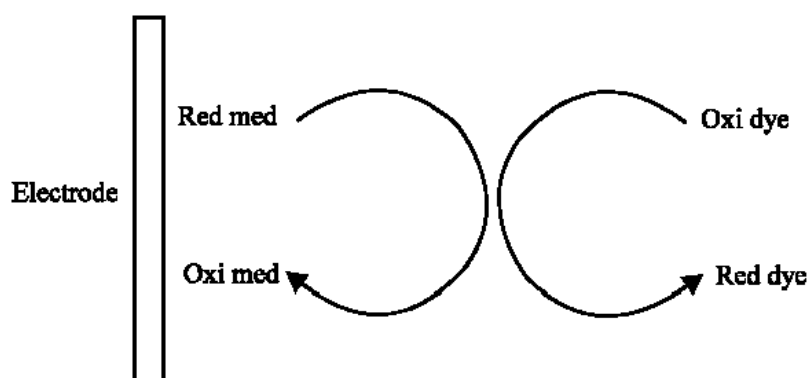

Figure 1: Reaction schema of the indirect electrolysis

An extensive literature review shows that broad research has been carried out in electrochemistry redox behavior of Vat and Sulfur dyes but a comparative study of the electrochemical reduction behavior is still lacking.

In the present study, attempts were made to understand the fundamentals of electrochemical reduction of selected Vat and Sulfur dyes using iron-TEA complex as a mediator. The evolution of the redox potential and the difference of potential were also explored. Color yields and fastness properties of the electrochemically dyed samples were compared with those of conventional method.

2. EXPERIMENTAL

2.1. Electrochemical dyeing apparatus

Electrolyses were carried out in a divided cell (catholyte volume 150 cm^3; anolyte volume 50 cm^3 and total dyeing volume 250 cm^3). The anolyte (40 g/L NaOH) was separated from the catholyte by a sintered glass diaphragm ($\emptyset$= 2cm; e=3mm; ε= 3 mm). The direction of the internal circulation and the homogenisation of the dye bath were ensured by peristaltic pumps of OSI type (flow rate D= 145 mL/min). The exchange of the solution between the reduction cell and the dyeing unit could be obtained within less than five seconds. The cathode was made from carbon fibre and had surface area of 19 cm². The anode was a stainless steel plate with a surface area of 14 cm². The electrical energy was supplied by an adjustable laboratory power supply unit (G ZIMMERMAN AG LUZERN Generator). The electrolysis cell was constructed and optimised with regard to relatively short liquor ratio (material to liquor ratio MLR= 1:40). A schema of the construction is shown in Figure 2.
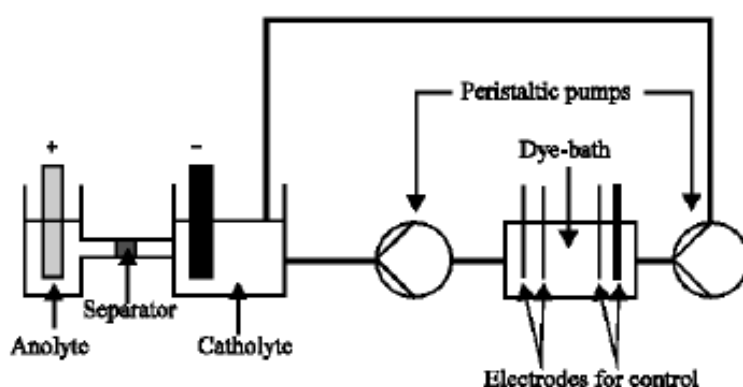

Figure 2: Electro-reduction and dyeing apparatus

2.2. Chemicals

The sodium dithionite ($Na_2S_2O_4$; BASF), sodium sulfide (Na_2S, BASF), caustic soda (NaOH; PANREAC ACS-ISO), wetting agent (Subitol LSN; BEZEMA), dispersing agent (Dispertagol SMS; BEZEMA), anhydrous sodium carbonate (Na_2CO_3; Chemi-pharma), hydrogen peroxide (H_2O_2 at 30%; Chimi-tex), acetic acid (CH_3COOH; PANREAC ACS-ISO) and soaping agent (Sultafon UNS; BEZEMA), used for conventional dyeing were of technical grade and were used as received.

2.3. Mediator composition

The complex of iron with triethanolamine FE^{III}-TEA was chosen as mediator for the indirect electrochemical reduction because it offers a very fast dye reduction (Haj Said et al., 2008; Bechtold et al., 1994). The mediator solution was prepared by dissolution of the iron sulphate $Fe_2(SO_4)_3$ 7-8 H_2O (RIELD 0F HAEN) 4.7 $g.L^{-1}$ in distilled water. Then, triethanolamine $(HOCH_2CH_2)_3N$ (ACROS) 20 $g.L^{-1}$ and caustic soda NaOH (PANREAC ACS-ISO) 34 $g.L^{-1}$ were added under magnetic stirring. After dissolution of the iron hydroxide precipitate, the solution was diluted to the required volume (Bechtold et al., 1996). All the cited chemicals were of laboratory grade.
In order to avoid the formation of iron hydroxide in an alkaline medium and to ensure better stability of the mediator, the TEA concentration must be overdosed. In an ecologically point of view, this is not an advantage. In fact, TEA is considered as a hazardous material (Miled et al., 2010). Consequently, it must be handled with care. But since we operate in a closed system and considering the possibility of recycling and reusing the whole dye bath, the environmental effect of the use of TEA ligand can be attuned.
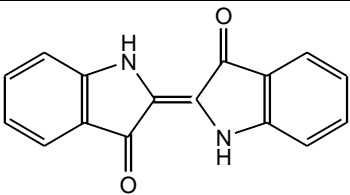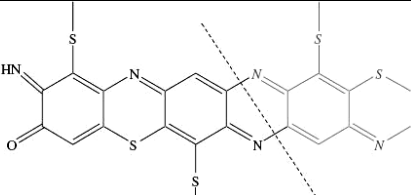
2.4. Material

Conventional and electrochemical dyeing were carried out using commercially desized, scoured and bleached cotton fabric (plain weave, mass per unit area 180 g/m², warp yarn density 35 y/cm, weft yarn density 25 y/cm; SITEX Ksar Hellal, Tunisia).

2.5. Dyes

The dye component was dispersed separately. The solution to be investigated was prepared by mixing the mediator solution with an adequate volume of the dye stock solution. The chemical structures and main features of the investigated commercial dyes are given in Table 1.

Table 1 : Technical features of Vat and Sulfur dyes

	CI. Vat Blue 1	CI. Sulfur Black 1
Chemical structure		
Commercial name	Indigo	Black B1
Constitution number	CI.73000	CI.53185
Chemical formula	$C_{16}H_{10}O_2N_2$	$C_{24}H_{16}N_6O_8S_7$ or $C_{24}H_{16}N_6O_8S_8$
Chemical class	Indigoïde	Substitute phenol
Dye house	BASF	BASF

2.6. Dyeing procedure

For _Standard procedures_ such as desizing, alkaline scouring, bleaching as well as dyestuff oxidation after Vat or Sulphur dyeing, soaping and rinsing, the dyeing apparatus worked in a separated unit for normal package processing.

The _Conventional dyeing_ experiments were performed according to BASF's technical instructions. The dyeing steps can be resumed as follow:

- Wetting (2 g.L^{-1} of wetting agent MLR 1:40; T 20-25°C, during 30 sec);
- Squeezing (60%);
- Preparation of the dye-bath by reducing the Vat Blue 1 with sodium dithionite and the Sulfur black 1 with sodium sulfide at room temperature.
- Exhaustion dyeing during 25 min (at room temperature for the Vat Blue 1 case and at 80°C for the Sulfur Black 1 case);
- Rinsing with cold water;
- Oxidizing in a separated bath with 1 ml.L^{-1} of hydrogen peroxide and 0.5 mL.L^{-1} of acetic acid for 30 min at 70°C;
- Soaping at boil during 10 min (only samples dyed with Sulfur Black 1);
- Rinsing with cold water;
- Drying at room temperature.

The reducing agent and the exhausting agent concentrations were dosed in function of the dye concentration and according to the cited dye-house technical instructions.

For Electrochemical dyeing steps, the experiments were performed under intensiostatic conditions at room temperature. In all the experiments, 3% dye (owf) was introduced in the dyeing recipe. All solutions were initially degassed with N$_2$ for 15 min in order to avoid contact between reduced dye and O$_2$ coming from ambient air. To maintain the cycle only dyes, an alkali and small quantities of additional substances, such as

dispersing and wetting agents, were added. No other chemicals active in the oxidation-reduction process were used. The material was positioned in the dyeing cell. After electrochemical dyeing experiments, samples were also withdrawn from the dye bath, oxidized, cold rinsed, soaped at boil, cold rinsed, and finally air dried.

2.7. Dye bath control

The redox potential RP/mV of the dye bath were measured with platinum electrode vs. a saturated calomel reference electrode in term of which all the potential values were quoted. Furthermore, we applied potentiometry at an imposed low current. This technique consists in measuring the variation of potential ΔE/mV between two platinum electrodes while a 1 µA current intensity is imposed between them. When the reduced and the oxidised forms of a reversible Ox/Red couple are simultaneously present in the solution, a low value of ΔE can ensure the current flow. In this study, potentiometry at imposed low current will indicate the simultaneous presence of Fe^{III}-TEA and Fe^{II}-TEA in the solution. This condition is fulfilled only when the total amount of dye is reduced. For this purpose, we used the Ipol function of a pH-meter-millivoltmeter of Methrom Herisan Switzland 691 type.

2.8. Dyed samples evaluation

Results of the dyeing experiments were characterized by color measurements in the form of CIELab coordinates by means of a colorimeter SPECTRAFLASH 300 (Datacolor International 1994) using D65 light source, 10° viewing angle.

The total color difference ΔE which represents the difference between color obtained by electrochemical and conventional dyeing procedures was calculated using equation 1 :

$$\Delta E = \sqrt{\Delta L*^2 + \Delta a*^2 + \Delta b*^2} \qquad (1)$$

L* is corresponding to the brightness (100 = white, 0 = black), a* to the red green coordinate (positive sign = red, negative sign= green) and b* to the yellow-blue coordinate (positive sign = yellow, negative sign = blue).

Dyestuff content on the dyed fabric was determined according the Kubelka–Munk function. The K/S values were calculated from the reflectance determined at 580 nm in the sulfur dye case and at 620 nm in the vat dye case.

Dyed samples were also evaluated from wash fastness (Source: ISO 105-C01: 1989), light fastness (Source: ISO 105-B02:1994) and rubbing fastness (Source: ISO 105-X12: 1993).

3. RESULTS AND DISCUSSION

All electrochemical reduction experiments were carried out in intensiostatic mode. As a consequence, the current intensity is the most crucial factor because low current values allow higher selectivity of the electrochemical reaction but longer electrolyzes (Bechtold, Brunner, 2005). However, higher current values offer shorter experiments duration but bad selectivity. In our previous studies, the electrochemical conditions such as current intensity, material to liquor ratio, dye concentration and time of immersion were optimized (Haj Said et al., 2008; Miled et al., 2010). A current intensity to about 200 mA was selected as the optimal value because it presented the best compromise between electrolyzes duration and energetic efficiency. So, in order to offer better dyeing performances (color coordinates and fastness properties), all experiments presented in this work were done in optimized conditions.

3.1. Electrochemical reduction of Vat Blue 1

Figure 3 shows the electrochemical reduction of 3% dye (owf) and the evolution of RP/mV and ΔE/mV in function of time at 200 mA. At the beginning of the experiments, the redox potential value is relatively low

(about -200 mV). After the formation of a certain amount of a soluble reduced product, the potential of the redox pair dye/leuco dye is fixed at about -700 mV. The electrochemically reduced dyestuff maintains its redox potential until complete reduction is achieved. Then the redox potential changes to more negative values defined by the Fer$^{II/III}$-TEA couple (about -1050 mV). When the redox potential of the mediator is reached, it indicates that initially insoluble Vat dye is totally reduced. At this moment, the electrochemical reduction process can be switched off to avoid over reduction. Figure 3 shows also a good accordance between the values of the total reduction time obtained with the described control methods. In both cases, this time is indicated by a sharp transition of the RP/mV and ΔE/mV values noting the presence of the Fe^{III}-TEA/Fe^{II}-TEA couple. As for ΔE/mV case, value falls to almost zero values when total amount of dye is reduced. Consequently, the total time reduction is indicated by this transition which is related to the presence of the Fe^{III}-TEA/Fe^{II}-TEA couple.
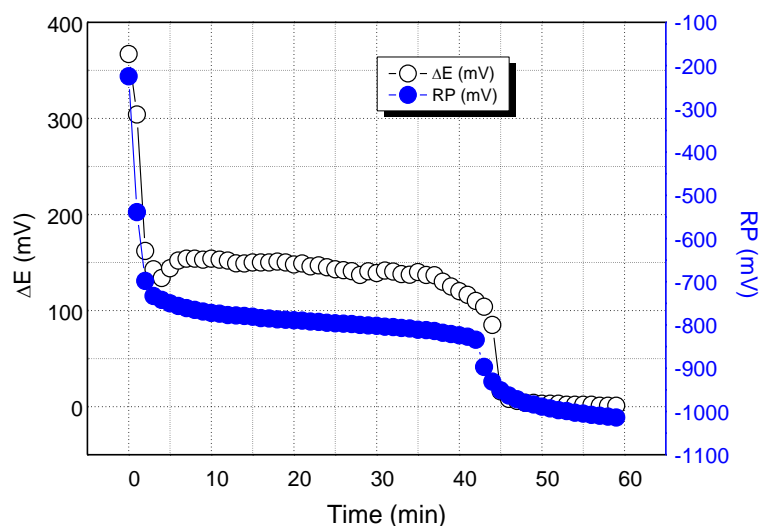

Figure 3: Difference of potential (ΔE (mV)) and redox potential (RP (mV)) vs KCl reference electrode measured in the dye bath during <u>Vat Blue 1</u> reduction as function of electrolysis time (I= 200 mA)

3.2. Electrochemical reduction of Sulfur Black B1

Figure 4 shows the build-up of the reduction capacity of 3% dye (owf) and the evolution of RP/mV and ΔE/mV during electrolyzes as a function of time at 200 mA. At the beginning of the experiment, the potential of reduction is low due to the low concentration of the soluble dyestuff. During this electrolysis, the potential decreases from -200 (measured at the beginning) and raises up to -700 mA. Then, particles dissolve completely with increasing the reduction duration and the electrochemically reduced dyestuff maintains its redox potential until complete reduction. At this time, the dyeing process takes place without switching off the current intensity in order to avoid moving the potential toward more positive values (due to the uptake of oxygen).

When comparing Figure 3 and Figure 4, we note some differences in the curves shape. In fact, unlike Vat dye experiments, for the Sulfur dye experiments both curves of RP/mV and ΔE/mV in a function of time follow a similar trend with no accordance between values of the total reduction time obtained with the control methods. The same evolution was obtained for other tested current intensities values. In all cases, we find that the total reduction time indicated by potentiometry at imposed low current (ΔE (mV) curve) is shorter than the total reduction time indicated by the evolution of redox potential (RP (mV) curve). As show in Figures 5 and 6, this is probably due to the fact that after electrochemical reduction, the Sulfur pigment molecules are broken apart at disulfide linkages and molecules become smaller. However, all the peripheral changes in Vat dye molecules leave the main structure intact. When a sufficient quantity of reduced Sulfur dye is formed in the dye bath, it reacts as a fast system (such as the mediator). Immediately, it is detected by the potentiometry at imposed low current and ΔE values fall to almost zero values behind the total reduction of the dispersed dyestuff. At this moment, the solubility of the dye is almost good but can be better when two parts of the molecule represented in Table 1 are totally reduced. This was obtained

with higher current intensity and higher reduction duration experiments. Electrolyzes done in these conditions show other complications such as over-reduction which is a parasite reaction that may results in irreversible changes.
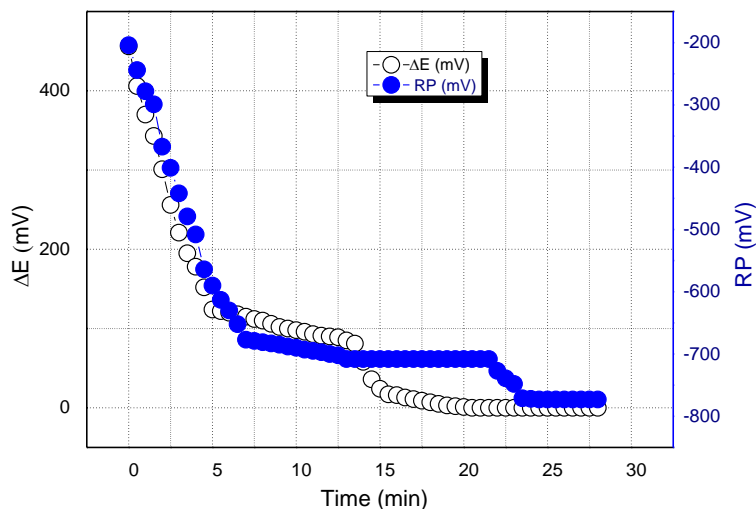

Figure 4: Difference of potential (ΔE (mV)) and redox potential (RP (mV)) vs KCl reference electrode measured in the dye bath during <u>Sulfur Black 1</u> reduction as function of electrolysis time (I= 200 mA)
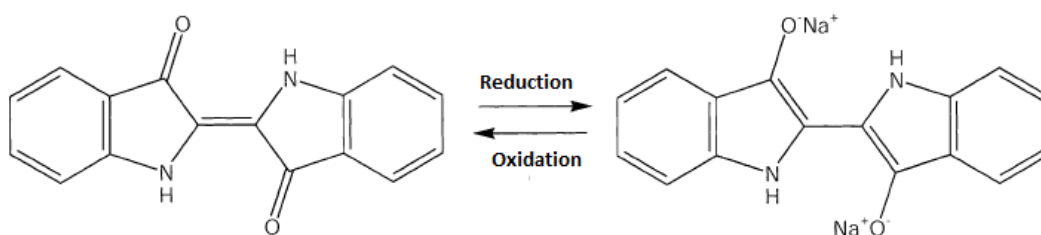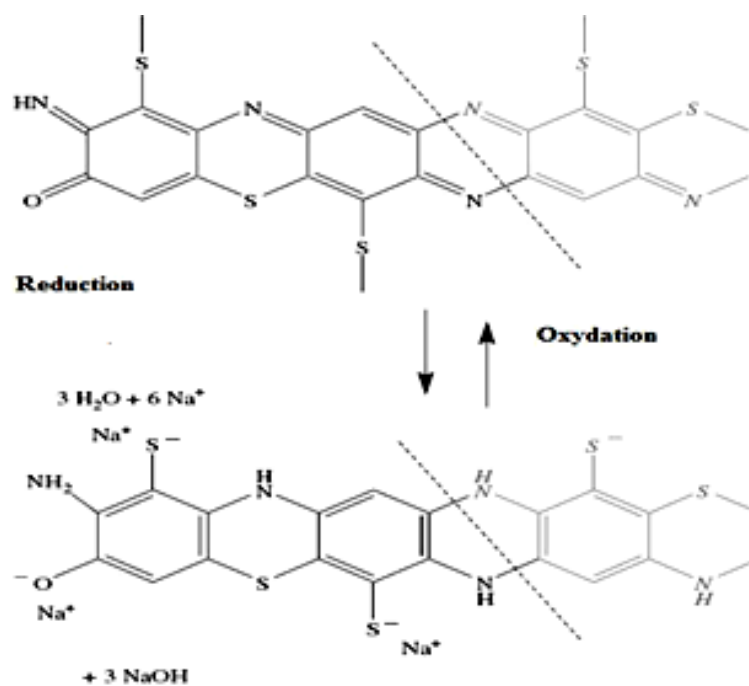

Figure 5: Reduction process of Vat Blue 1

Figure 6: Reduction process of Sulfur Black 1

According to Figure 4, the redox potential was stabilized at a plateau of -700 mV. In its oxidized state, Sulfur Black B1 is present in a quasi-polymer state repetitive molecular submits being bridged together by a disulfide bound (Bechtold et al., 2000). During reduction, these disulfide bounds are reduced to thiolate groups. Thus, average molecular size of the dyestuff decreases and consequently the affinity to the cellulosic substrate. However, when chemical reducing agents are applied for dyeing with Sulfur Black B1 the highest color depth was limited by the highest redox potential (from about -550 mV to -600 mV) (Bechtold et al., 1998). It is also the same phenomenon when Vat dyes are chemically reduced. As a consequence, the average molecular size is becoming changing and the affinity to the fiber will be modified too. This hypothesis will be confirmed in the following dyeing and fastness results.

3.3. Dyeing results

In order to obtain further information about the behavior of the tested dyes when using the electrochemical dyeing process, a series of dyeing experiments was performed using 3% dye (owf). The CIELab coordinates of the dyed samples were compared with the coordinates of samples dyed with sodium dithionite and sodium sulfur as reducing agents under the same experimental conditions. Table 2 shows the main results of the dyeing experiments.

Table 2: Comparison of color yield and color coordinates of conventional and electrochemical dyed samples by Vat Blue 1 and Sulfur Black 1

Dye	Reduction/ dyeing process	K/S	L*	a*	b*	ΔE
Vat Blue 1	Standard	18.5488	40.52	-2.66	-21.13	0.68
	Electrochemical	12.6212	40.26	-2.72	-21.76	
Sulfur Black B1	Standard	21.8626	23.47	-0.48	4.50	1.74
	Electrochemical	18.8988	25.15	-0.40	-4.01	

Equally for the Vat and the Sulfur tested dyes, the electrochemical dyeing results correspond well with the behavior when using conventional reducing agents. A minimum difference of CIELab coordinates determined by measuring the distance in color space ΔE was reached with relatively small distance in color space values (0.68 for Vat Blue 1 and 1.74 for Sulfur Black 1). The differences in color coordinates between the two reducing processes can be explained by the difference of ionic strength of the dye in the bulk solution. The observed maximum in color depth was reached at 200 mA current intensity. This can be attributed to an optimum state of reducing/ molecular weight ratio of the soluble reduced dyestuff. At higher current intensities and especially in the Sulfur Black case, smaller molecular units in a higher state of reduction with lower molecular weight and lowered affinity to the cellulosic fiber are present in the dye-bath. These differences seem also to point out that there are differences or several reactions pathways for the reduction of these dyes. This hypothesis is in accordance with previous studies (Bechtold et al., 1998, 2000; 2008; Miled et al., 2010). In addition, the high variability of Sulfur Black B1 and its bad known chemical structure gives supplementary limits since model dyeing are very sensitive to irreversible changes in the molecular structure. This would change the affinity and the shade of the dyeing, compared to reference dyeing (Bechtold et al., 1998). Comparing with Vat dyes where the affinity varies from dye to dye, the substantivity of electrochemically reduced Sulfur dyes is high partly and its color strengths are altered with the lower dye pick-up.

From the variation of K/S and CIELab coordinates for the both tested dyes, Table 2 shows also that the color depth and shade is lower with electrochemical dyeing process and did not show sufficient result of the dyeing pick up and the dyeing diffusion into the fiber. However, the color depth appears to be slightly better in the sulfur dye case. A marginal improvement in color depth of the dyed samples was showed when dyeing experiments where done with salt. In fact, the color depth and shade shows strong dependence on the salt concentration in the dyeing solution. This auxiliary agent is essential to the

conventional dyeing process. In our case, electrochemical dyeing experiments were done without adding salt in order to avoid interferences with the current efficiency evolution.

3.4. Fastness results

All the dyed samples with indirect electrochemical dyeing technique were tested for washing fastness, light fastness, wet and dry rubbing fastness. The results of fastness properties of samples dyed with 3% dye (owf) are shown in Table 3. All the fastness properties appear to be equivalent with the conventionally dyed samples obtained using sodium dithionite and sodium sulfide as reducing agents.

Table 3. Comparison of fastness properties of electrochemical and conventional dyeing

Dye	Reduction Process	Washing fastness	Rubbing fastness		Light fastness
			Wet	Dry	
Vat Blue 1	Standard	3/4	2/3	1	3/4
	Electrochemical	4	2/3	2	4
Sulfur Black 1	Standard	4	4/5	2/3	6
	Electrochemical	5	4/5	2/3	6

3.5. Generalisation and reproducibility

The considered process was also generalized for the other chemical classes of vat dyes (anthraquinonic and polycyclic ones)and other sulfur dyes in low medium and high dye concentrations (Miled et al., 2010). Although results were very encouraging in low and medium concentrations (1% and 3% respectively), an exception was noted for high concentrations. In this case, color depth and shade of electrochemically dyed samples appears to be poor. The fastness properties results were more encouraging. With the electrochemical dyeing procedure, the fastness of dyed samples were well relative with those obtained by conventional dyeing process.

Also, experimental results showed that the reproducibility of dyeing experiments is difficult especially when the commercial form of vat and sulfur dyes is used. The bad reproducibility was recognized to the bad stability of indigo and its leuco form. Sulfur dyes are also non stable, especially their leuco form which makes some differences in dyeing results. These limits are common either with the conventional dyeing procedure.

4. CONCLUSION

This study aims at investigating the electrochemical reduction of Vat Blue 1 and Sulfur Black 1 and gives insight comparison on the reduction mechanism of the tested dyes. Results show that although the technical common points, Vat and Sulfur dyes show basic differences when electrochemically reduced. We reported this to differences in the chemical structure of the tested dyes. In fact, Sulfur dye is made by sulfur linkage but Vat dye is made by ketone linkage. Thus, the electrochemical behavior is changed. The electrochemically reduced Sulfur dye have its own reduction power and the chemical structure of the dye is changed. For the Vat dye case, all the peripheral changes have leaved the main structure intact.
The dyeing behavior of the tested dyes is in general unchanged. The color depth of the dyed samples depends on the chemical structure of the dye and the current intensity value. While colorimetric results are very encouraging in the case of Vat Blue 1, the build-up of the shade and the penetration of the dye are less encouraging in the Sulfur Black 1 case. However, fastness properties appear to be equivalent with conventional dyeing technique with comparable light, washing and rubbing fastness for both tested dyes.

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