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New Prospects in the Electrochemical Dyeing of Indigo

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Abstract: Although they have been largely studied, electrochemical dyeing of vat dyes is still at its early stages of development. In this research, we conducted an experimental parameters optimization study to establish more suitable conditions for industrial use. Under these conditions, we tested the electrochemical reduction of Vat Blue 1 (indigoid dye) in lucid, average and dark shades. Furthermore we tested potentiometry at imposed low current as a new control means of the dyeing bath. The colour and fastness evaluations of the obtained samples indicated that the performances of the dyeing operation were similar to those obtained by the conventional method. This result offers new prospects for the electrochemical reduction of Indigo.

Key words: Electrochemical reduction, indirect electrolysis, Vat dyes, Vat Blue 1, potentiometry at imposed low current

INTRODUCTION

Vat dyes and especially indigo, play an important role in today's dyeing industry (Roessler and Crettenand, 2004). Their use involves a reduction step in order to obtain their water-soluble forms (leuco dye). In most industrial dyeing processes, vat dyes are reduced using mainly sodium dithionite (Bechtold *et al.*, 1996, 1997). Although this reducing agent has been used for more than a century, its use involves many economical, ecological and technical problems. For instance, sodium dithionite produces large amounts of sodium sulphate and sulphite as by-products which increase the cost of industrial wastewater treatment (Chavan and Chakraborty, 2001).

Solving these problems has been the main concern of numerous researches. So, many attempts have been made to replace sodium dithionite or even the chemical reduction. In this frame, electrochemistry, well-known as an environmentally friendly technique, presents an attractive alternative (Chavan and Chakraborty, 2001; Kulandainathan *et al.*, 2007a; Roessler and Jin, 2003).

In recent investigations, various electrochemical reducing methods have been used, such as direct (Roessler *et al.*, 2002; Roessler and Crettenand, 2004) or indirect electrochemical reduction (Bechtold *et al.*, 1993, 1994). Although they have been largely studied, the electrochemical reduction of vat dyes is still at its early stages of development. Inappropriate experimental

conditions decrease the chances of an industrial application of the process. These conditions are related to the temperature of the dye-bath, the electrodes choice... Indeed, all previous studies have copied some experimental conditions either from the conventional dyeing process, or from the electrochemical reduction, but without considering their prospective applications in industry. In fact, several works are confined to the literature and thus create further limitations in addition to the engineering challenge related to the use of the electrochemical techniques. For example, in the electrochemical reduction of vat dyes, heating is employed during electrolyses (Bechtold *et al.*, 1994; Bechtold, 2000), though there is no evidence that it is required under unconventional conditions. Besides many other conditions like material to liquor or mediator to dye ratios are fixed without any scientific justifications.

In this research we adopted a simplifying approach concerning experimental parameters. Thus, we omitted heating, considerably reduced material to liquor ratio, lightened electrical apparatus and used relatively cheap electrodes.

Under these conditions, we tested the electrochemical reduction of a commonly used dye, the Vat Blue 1 (indigoid dye), in lucid, average and dark shades. This study is aimed at showing that the electrochemical reduction of vat dyes remains a very promising technique to replace the use of sodium dithionite in vat dyeing process.

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MATERIALS AND METHODS

Mediator: The mediator solution was prepared by dissolution of the iron sulphate $\text{Fe}_2(\text{SO}_4)_3 \cdot 7-8 \text{H}_2\text{O}$ (RIELD OF HAËN) 4.7 g L^{-1} in distilled water. Then, triethanolamine TEA (ACROS) 20 g L^{-1} and the 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 cited chemicals were of laboratory grade

Auxiliaries: Hydrosulfite of sodium (BASF, 1996), the wetting agent (Subitol LS-N, BEZEMA) and the dispersing agent (Dispertagol SMS, BEZEMA) were of commercial grade.

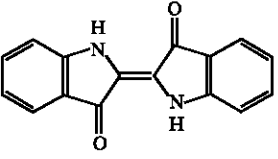
Dye: A commercial dye sample supplied by BASF was used. Its main features are given in Table 1 (BASF).

In earlier studies, this dye was mainly used in dark shades (Bechtold *et al.*, 1996, 1997). In this research, we varied dye concentration from 1 to 6% of weight of fabric (o.w.f), thus we varied the shades from lucid to dark.

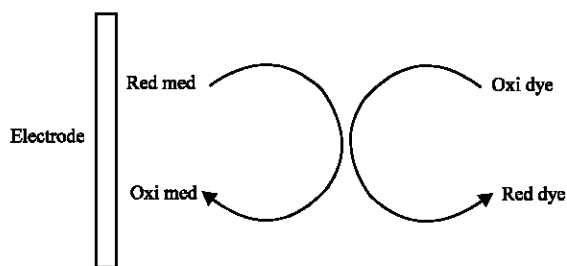
Support: Although knit and woven fabrics are the most commonly used materials in textile dyeing industry, most studies in the electrochemical field have been applied to yarns (Bechtold, 2000; Bechtold and Turcanu, 2002). In this research, we used a commercially bleached cotton fabric with the following features: surface weight ms 180 g m^{-2} ; warp count 35 and weft count 25.

Conventional dyeing: We prepared conventional vat dyed samples in the laboratory. Sodium dithionite and sodium hydroxide were used according to BASF technical instructions (Bechtold *et al.*, 1999; Bechtold and Turcanu, 2002; Kulandainathan *et al.*, 2007b).

Table 1: Technical features of Vat Blue 1

Technical feature	Vat dye
Structure	
Constitution number	CI.73000
Commercial dye house	BASF
Commercial name	Indigo
Chemical class	Indigoid
Molar mass (g mol^{-1})	262
λ_{max} (nm)	620
Dyeing process	IK
Reduction duration (min)	30
Reduction temperature ($^{\circ}\text{C}$)	60
Dyeing duration (min)	30-60
Dyeing temperature ($^{\circ}\text{C}$)	20-25

Electrochemical reduction and dyeing: In this study we used indirect electrochemical reduction. This method employs an electrochemical reversible system, called a redox mediator, as an electron carrier between electrodes and the dye (Bechtold *et al.*, 1993, 1999). At first, the mediator was introduced in the medium under its oxidized form. Once the mediator was reduced at the electrode, it would diffuse and exchange electrons with microcrystal of the dispersed dye pigment in solution. Then, the dye was reduced and the oxidized form of the mediator was regenerated (Scheme 1).



Scheme 1: Principle of the indirect electrolysis technique

Thus a loop of reactions was established. Thanks to this technique and since reduction occurs in a homogeneous phase, problems related to electrode surface could be avoided and reduction rate was enhanced (Bechtold *et al.*, 1993).

We used the iron-triethanolamine complex as a mediator system. This system is widely used in mediated electrochemical reduction of dyes. In previous works a very low mediator to dye ratio has been used (Cristea and Vilarem, 2006). This catalytic condition is generally necessary when the catalyst is very expensive or presents a limited solubility. This choice will require the use of a three-electrode system to ensure a good selectivity of the electrochemical reaction. In our case, since we operate in a closed system and the considered mediator does not represent any of the previous limitations, we can use a high mediator to dye ratio (around 10:1). Then simple galvanostatic electrolyses, more convenient for industrial applications, are needed to achieve reduction while ensuring a good faradic yield and stable reduction conditions.

The electrochemical dyeing involves the following steps: wetting (2 g L^{-1} of wetting agent, Rb 1: 40, T $20-25^{\circ}\text{C}$, during 30 sec), squeezing (60%), nitrogen splashing (15 min), electrochemical reduction, immersing the textile material in the dyeing bath, oxidation by air, finishing and finally, drying.

Design of the electrochemical cell: As shown in Fig. 1, the experimental mounting is composed of an

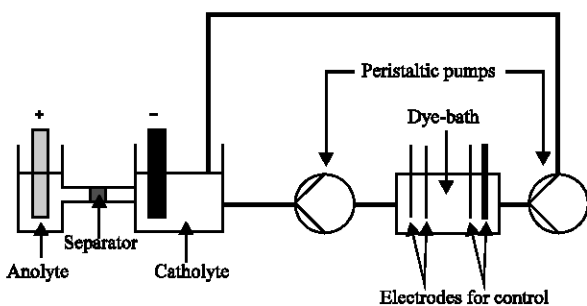


Fig. 1: Electro-reduction and dyeing apparatus

electrochemical cell and a dyeing cell ($V = 250 \text{ cm}^3$). A peristaltic pump of OSI type ($D = 145 \text{ mL min}^{-1}$) ensured the circulation and the homogenisation of the dye bath. The electrolysis cell was made up of a cathodic compartment ($V = 150 \text{ cm}^3$) and an anodic compartment ($V = 50 \text{ cm}^3$) separated by a number 3 glass frit ($\phi = 2 \text{ cm}$). As electrodes, we used a carbon cathode of 19 cm^2 and a stainless steel plate anode of 14 cm^2 . During the electrolyses the current was imposed by a generator of G ZIMMERMANN AG LUZERN type.

The use of the considered closed system extensively reduces water and chemical product consumption. Furthermore, it can be fed every time the ingredients are depleted.

Material to liquor ratio experiments: The experiments were carried out with 1:40 material to liquor ratio. The electrolysis cell was optimised with regard to a relatively short ratio compared with ratios described in previous studies (reaching 1:240) (Bechtold *et al.*, 1994; Kulandainathan *et al.*, 2007a, b). Our choice brings about considerable gain in water consumption. The employed ratio was imposed only by the design of the electrolysis cell, so it could be further lowered.

Dye bath analysis: Controlling the bath composition is of great interest. It allows us to avoid a useless prolongation of the reduction time and to prevent the phenomena of over or partial reduction which are frequent and difficult to control when reduction is carried out by dithionite (Bechtold *et al.*, 1997).

During electrolyses, we measured the redox potential (RP) between a platinum electrode and a saturated calomel electrode, both immersed in the cathodic compartment. The measured potential is sensitive to the solution's composition.

Furthermore, we were, to our knowledge, the first to apply potentiometry at an imposed low current as a control means of dye reduction. This technique consists in measuring the variation of potential $\Delta E/\text{mV}$ between

two platinum electrodes while a $1 \mu\text{A}$ current intensity is imposed between them. When the reduced and the oxidized 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, this technique will indicate the simultaneous presence of $\text{Fe}^{\text{III}}\text{-TEA}$ and $\text{Fe}^{\text{II}}\text{-TEA}$ in the solution. This condition is fulfilled only when the total amount of dye is reduced. In other words, a low value of ΔE is synonymous of a total dye reduction. For this purpose we used a pH-meter-millivoltmeter of Methrom Herisan Switzland 691 type endowed with the Ipol function.

The pH value is controlled by a pH-meter JENWAY. The current is measured by a Multimeter CA 406 of CHAUVINISTIC type ARNOUX.

Dyed sample evaluation: Results of the dyeing experiments were characterized by colour measurement in the form of K/S and CIELab coordinates. We used a colorimeter SPECTRAFLASH 300 (Datacolor International, 1994) interfaced to a PC using D65 light source and a viewing angle of 10° . The distance in colour space ΔE_{CMC} represents the difference between colours obtained by electrochemical dyeing and conventional dyeing. It is calculated using Eq. 1.

$$\Delta E_{\text{CMC}} = \sqrt{\Delta L^2 + \Delta a^2 + \Delta b^2} \quad (1)$$

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

RESULTS AND DISCUSSION

This study can be divided into two parts: A preliminary study intended to determine the optimum conditions for electrolyses and a comparative study between electrochemical and conventional dyeing processes.

In the preliminary study, electrolyses were carried out by varying the current intensity, dye concentration and immersion time.

Preliminary study

Effect of the current intensity: When operating with a galvanostatic mode, the current intensity is a crucial factor. Indeed, low current values will result in high selectivity of the electrochemical reaction but long lasting electrolyses. High current values will produce short experiments but a bad selectivity and a temperature increase due to joule effect.

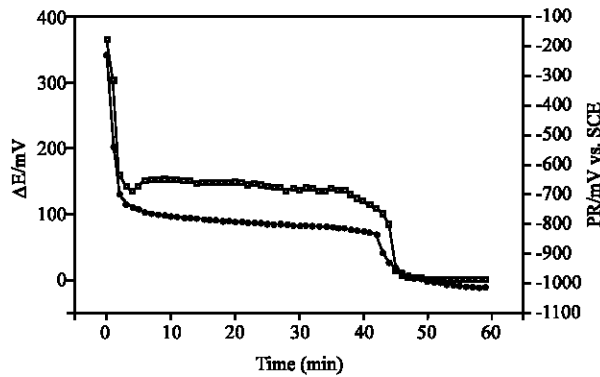


Fig. 2: PR and ΔE variation vs. time for 3% o.w.f Vat Bleu 1; electrochemical reduction at 100 mA

To investigate the effect of intensity of current I on the efficiency of reduction, we carried out the electrochemical reduction of Vat Blue 1 (3% o.w.f presenting a medium nuance) with I varying from 50 to 800 mA. For all experiments, we obtained similar evolutions of the RP and ΔE during the dye reduction. Figure 2 shows an example of evolution observed at $I = 100$ mA.

For all electrolyses we noted a good accordance between the values of the total reduction time obtained with both controlling methods. In both cases, this time is indicated by a sharp transition of RP or ΔE values. For RP evolution, values change from -800 mV, corresponding to the presence of Dye/leuco Dye couple, to -1000 mV, indicating the presence of the couple $Fe^{III}\text{-TEA}/Fe^{II}\text{-TEA}$. As for ΔE case, values fell to almost zero values when the total amount of dye is reduced.

The results of the current value optimisation study are shown in Table 2. For different intensities we give θ_{th} and θ_{ex} respectively, the theoretical and the experimental electrolysis time necessary for total dye reduction. We calculated θ_{th} from the Eq. 2 whereas we deduced θ_{ex} from the PR and ΔE variation.

$$\text{Faraday's law: } Q = \theta I_0 = n F n_0 \quad (2)$$

Where:

- Q : The charge used for total dye reduction
- θ : Electrolysis time for total dye reduction (sec)
- n : The number of electrons needed to reduce all ketonic groups (2 electrons for two ketonic groups)
- F : Faraday constant ($F = 96487 \text{ C mol}^{-1}$)
- n_0 : Amount of dye (moles)
- I_0 : Intensity of current (A)

Table 2: Influence of the amount of current on the faradic yield

I (mA)	θ_{th} (min)	θ_{ex} (min)	φ (%)
50	50.2	100.00	50
100	25.8	45.00	57
200	12.9	15.00	86
400	6.4	7.00	91
600	4.3	4.50	95
800	3.2	3.25	98

In the last entry of Table 2 we give the current efficiency (φ) calculated by Eq. 3.

$$\varphi = \frac{\theta_{ex}}{\theta_{th}} \times 100 \quad (3)$$

We note that the yield value increases with the current intensity and reaches an almost 100% value starting from 200 mA. The 100% value indicates that the two ketonic groups are well reduced to corresponding hydroxyl groups. This reduced form is not probably very stable and the reoxidation of the leuco form to initial form would cause a yield loss. This hypothesis explains the less important yields obtained with long time experiments at low current values (the first line of Table 2).

For high current values, the temperature increases both in the cathodic and anodic compartments by joule effect. In the latter, it reaches 80°C with $I = 600$ mA.

For the study continuity we adopted 200 mA as current intensity because it presented the best compromise between time of electrolysis and energetic efficiency.

Variation of the concentration of the dye: To extend the results of the previous section, we carried out indirect electrolyses for the selected dye at different concentrations. We observed the same aspect of variation of RP and ΔE for this series of electrolyses.

In Table 3 we compare the standard durations of reduction θ_s as fixed by the manufacture (BASF), to the empirical durations of the electrochemical reduction θ_e . Results show that the electrochemical reduction is faster than the standard technique, especially for clear and average shades.

Variation of the time of immersion: The optimal duration of dyeing is deduced by comparing colorimetric results obtained for different immersion times. An example of this study, carried out on a medium concentration (3% o.w.f), is given in Table 4.

We noted a meaningless colorimetric variation ΔE_{CMC} starting from 15 min of immersion. The electrochemical process reduces both the duration of reduction and that of dyeing, which presents an additional advantage for any industrial applications.

Table 3: Comparison of electrolysis and conventional reduction time for different concentrations of Vat Blue 1

Concentration (%)	1		3		6	
	θ_s (min)	θ_E (min)	θ_s (min)	θ_E (min)	θ_s (min)	θ_E (min)
Vat Blue 1	30	13.5	30	15	30	40

Table 4: Colour yield ($\lambda = 620$ nm) and colour coordinates of electrochemical dyeing with Vat Bleu 1 at varying time of immersion

Time of immersion (min)	K/S	L*	a*	b*	ΔE_{CMC}
5	3.5045	50.75	-4.25	-23.31	-
10	4.4401	49.34	-3.87	-22.55	1.64
15	5.6342	48.52	-3.51	-21.96	1.07
20	5.6552	48.16	-3.34	-21.64	0.51
30	5.7023	47.78	-3.18	-21.42	0.46

Table 5: Comparison of colour yield ($\lambda = 620$ nm) and colour coordinates of standard (S) and electrochemical (E) dyeing

Process	Dye (%)	K/S	L*	a*	b*
C	1	1.8767	57.61	-4.10	-19.08
E	1	1.1727	63.69	-4.91	-15.35
C	2	4.8704	44.83	-3.24	-23.19
E	2	5.2361	43.72	-2.70	-23.67
C	3	5.6342	41.45	-2.02	-23.31
E	3	5.9903	39.32	-1.81	-22.93
C	4	7.7244	37.62	-1.27	-23.44
E	4	7.5328	38.21	-1.32	-24.00
C	5	8.4427	36.65	-0.81	-24.43
E	5	7.7244	37.66	-0.96	-23.97
C	6	14.2600	28.24	0.00	-20.74
E	6	8.6229	36.27	-0.88	-24.12

Stability of electrolyses: It has been established that pH is an important parameter influencing the performance of vat dyes reduction (Etters and Hou, 1991). In conventional reduction, this parameter must be constantly controlled. The reaction below shows that the decomposition of dithionite generates a decrease of the pH values which can cause some disturbances (Francolor).



Previous studies have shown that the fall of pH below 13 units causes disturbances in the electrochemical reaction and the formed iron complex becomes unstable, which negatively affects the colour intensity (Bechtold *et al.*, 1993). In this study, we fixed the pH values around 13.

Figure 3 shows that pH was more stable in the electrochemical process than in the conventional one. Hence, there is no need for the addition of alkali during electrolyses.

Comparative study

Colour evaluations: We compared the electrochemical dyeing carried out earlier under the previously-fixed conditions, to conventional dyeing according to technical instructions. Table 5 gives coordinated CIELab and K/S value for all experiments. The electrochemical process is referred to as E whereas the conventional process is referred to as S. These results show that the colour depth and shade for a same dye concentration are not greatly different, especially for clear and average shades.

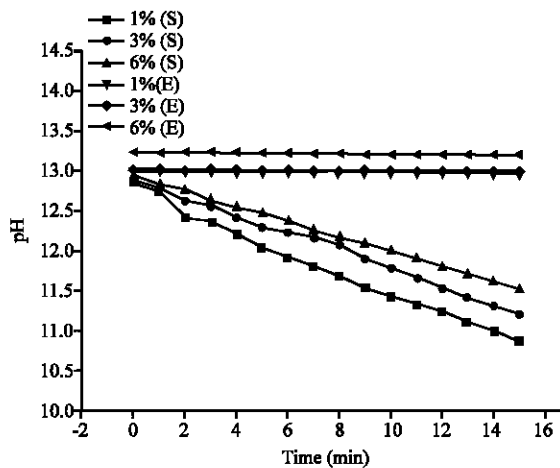


Fig. 3: Dye bath pH evolution with varying dye concentration and reduction process (Standard: S; electrochemical: E) with Vat Bleu 1

Fastness results: Indigo is known for a good level of fastness. The way of application of the dye and the presence of foreign substances (triethanolamine for example) can influence the quality of fastness (Francolor, 2006; Son *et al.*, 2004).

Samples dyed with the indirect electrochemical dyeing technique were tested for wet and dry rubbing fastness, washing fastness and light fastness. The results are shown in Table 6.

Compared to conventionally dyed samples obtained using sodium dithionite as a reducing agent, all the

Table 6: Comparison between electrochemical (E) and conventional (S) fastness properties

Process	Washing fastness	Rubbing fastness		
		Wet	Dry	Light fastness
E	3-4	1	2-3	3-4
S	4	2	2-3	4

fastness properties appear to be equal. These results show that the electrochemical technique does not deteriorate the intrinsic properties of indigo.

CONCLUSION

The main beneficial results of the above study can be summarized as follows:

- The iron TEA complex can be used in the alkaline solution to accomplish an indirect reduction of Vat Blue 1 under galvanostatic experiments.
- Electrolyses achieved with cheap electrodes and carried out at room temperature present good faradic yields.
- Potentiometry at an imposed current, tested for the first time, represents an efficient tool to control dye reduction.
- Dyed samples with an indirect electrochemical dyeing technique show dyeing results and fastness properties similar to those achieved with conventional dyeing.

These results offer new prospects for the electrochemical reduction of Indigo.

REFERENCES

BASF, 1976. Ratgeber Cellulosefasern, Ludwigshafen, Germany.

Bechtold, T., E. Burtscher, A. Amann and O. Bobleter, 1993. Alkali stable iron complexes as mediators for the electrochemical reduction of dispersed organic dyestuffs. *J. Chem. Soc. Faraday Trans.*, 89: 2451-2456.

Bechtold, T., E. Burtscher, A. Turcanu and O. Bobleter, 1994. The reduction of Vat dyes by indirect electrolysis. *J. Soc. Dyers Colour.*, 110: 14-18.

Bechtold, T., E. Burtscher, A. Turcanu and O. Bobleter, 1996. Indirect electrochemical reduction of dispersed indigo dyestuff. *J. Electrochem. Soc.*, 143: 2411.

Bechtold, T., E. Burtscher, A. Turcanu and O. Bobleter, 1997. Dyeing behaviour of Indigo reduced by indirect electrolysis. *Tex. Res. J.*, 67: 635-642.

Bechtold, T., E. Burtscher and A. Turcanu, 1999. Anthraquinones as mediators for the indirect cathodic reduction of dispersed organic dyestuffs. *J. Electroanal. Chem.*, 465: 80-87.

Bechtold, T., 2000. Réduction électrochimique dans les procédés tinctoriaux. *l'Industrie textile.*, 1322: 65-70.

Bechtold, T. and A. Turcanu, 2002. Electrochemical vat dyeing, combination of an electrolyzer with dyeing apparatus. *J. Electrochem. Soc.*, 149: D7-D14.

Chavan, R.B. and J.N. Chakraborty, 2001. Dyeing of cotton with indigo using iron (II) salt complexes. *Color Tech.*, 117: 88.

Cristea, D. and G. Vilarem, 2006. Improving light fastness of natural dyes on cotton yarn. *Dyes and Pigments*, 70: 238-245.

Etters, J.N. and M. Hou, 1991. Equilibrium sorption isotherms of indigo on cotton denim yarn: Effect of pH. *Text Res. J.*, 61: 773-776.

Francolor, 2006. Française des matières colorantes; Manuel d'application des matières colorants et produits spéciaux pour teinture et impression; La teinture du coton.

Kulandainathan, M.A., K. Patil, A. Muthukumar and R.B. Chavan, 2007a. Review of the process development aspects of electrochemical dyeing: Its impact and commercial applications. *Coloration Technol.*, 123: 143-151.

Kulandainathan, M.A., A. Muthukumar, K. Patil and R.B. Chavan, 2007b. Potentiostatic studies on indirect electrochemical reduction of vat dyes. *Dyes and Pigments*, 73: 47-54.

Roessler, A., D. Crettenand, O. Dossenbach, U. Meyer, W. Marte and P. Rys, 2002. Direct electrochemical reduction of indigo. *Electrochim. Acta*, 47: 1989-1995.

Roessler, A. and X. Jin, 2003. State of the art technologies and new electrochemical methods for the reduction of vat dyes. *Dyes and Pigments*, 59: 223-235.

Roessler, A. and D. Crettenand, 2004. Direct electrochemical reduction of vat dyes in a fixed bed of graphite granules. *Dyes and Pigments*, 63: 29-37.

Son, Y.A., J.P. Hong and T.K. Kim, 2004. An approach to the dyeing of polyester fiber using indigo and its extended wash fastness properties. *Dyes and Pigments*, 61: 263-272.