Potentiostatic studies on indirect electrochemical reduction of vat dyes

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Abstract

Dispersed vat dyestuffs can be electrochemically reduced by indirect electrolysis using iron−triethanolamine complex as a reducing agent. The application and mechanism of indirect electrolysis as a reduction technique are described in detail in this paper. Electrochemically reduced vat dye is tested on a laboratory scale in dyeing experiments, and the results of different reduction conditions are discussed. The influence of the concentration of the complex-system on the build-up of colour depth, shade and fastness is discussed and compared with samples of the standard dyeing procedure using sodium dithionite as the reducing agent. The new process offers environmental benefits as well as prospects for improved process stability, because the state of reduction in the dye-bath can be readily monitored by measuring the reduction potential.
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1. Introduction

Vat dye is most popular among dye classes used for coloration of cotton, particularly, when high fastness standards are required to light, washing and chlorine bleaching [1]. Also, from the commercial point of view, vat dyes (including indigo) have acquired a large share in the dyestuff market for the coloration of cellulosic fibres. The annual consumption of vat dyes including indigo is around 33,000 metric tons since 1992 and it holds 24% of cellulosic fibre dye market in value terms [2].

Vat dyes being water insoluble have to be first converted into water soluble form (leuco dye) by reduction with a strong reducing agent like sodium dithionate. In its reduced form, the vat dye has substantivity towards cellulosic fibres and, after absorption, is reoxidised to the original water-insoluble form in situ in the fibre [3,4]. The use of sodium dithionate is being criticized for the formation of non-environment friendly decomposition products such as sulphite, sulphate, thiosulphate and toxic sulphur [5,6].

Attempts are being made to replace the sodium dithionite by ecologically more attractive alternatives. In this connection

α-hydroxyketone which meets requirements in terms of reductive efficiency and biodegradability had been tried. However, such compounds are expensive and their use is restricted to closed systems due to the formation of strong smelling condensation products in an alkaline solution [7,8]. Some other sulphur containing compounds such as hydroxyalkyl sulphinate, thiourea, etc., have also been recommended [9,10]. These compounds have relatively low amount of sulphur content and also lower equivalent mass which leads to lower sulphur-based salt load in the wastewater. However, in these cases too, it is not possible to dispense with sulphur-based problems totally.

$Fe(OH)_2$ being a strong reducing agent in alkaline medium, the possibility of using it has also been explored for reducing organic dyestuffs. The reducing effect of $Fe(OH)_2$ increases with increase in pH. However, $Fe(OH)_2$ is poorly soluble in an alkaline solution and gets precipitated. It has to be complexed in order to hold it in solution [11]. A stable complex with good reducing power is obtained with weaker ligand, such as gluconic acid. Regarding eco-friendliness, gluconic acid can be eliminated in the sewage tank through neutralization with alkali; free $Fe(OH)_2$ can be aerated and converted to $Fe(OH)_3$ which acts as a flocculent and brings down wastewater load. Tartaric acid has also been tried as a ligand by Chakraborty for complexing $Fe(OH)_2$ in the presence of NaOH for

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reduction and dyeing of cotton with indigo and other vat dyes at room temperature [12]. Efforts have been made to complex $Fe(OH)_2$ with single and double ligand systems using tartaric acid, citric acid and gluconic acid which have shown encouraging results [13].

Electrochemical reduction of vat, indigo and sulphur dyes is also suggested as an alternative route for ecological and economic reasons. Electrochemical reduction can be achieved by direct and indirect electrochemical reduction. In direct electrochemical reduction chemical reducing agents are replaced by electrons from electric current, and effluent contaminating substances can be dispensed with altogether [14,15]. Although this technique is ideal, the stability of reduced dye species formed is poor thereby affecting the colour yield and the rate limiting step of electrochemical reduction is electron transfer from the cathode surface to the surface of the microcrystal of the dispersed dye pigment [16–20]. In indirect electrochemical reduction technique the reduction of dye is achieved through a redox mediator system [21,22]. This process is mediated by an electron carrier whereby reduction takes place between surfaces of the electrode and the dye pigment instead of direct contact between both surfaces. Among the various mediator systems suggested in the literature, iron–triethanolamine complex (iron–TEA) seems to be promising [23–29]. In order to meet all requirements in an economical way, a multi-cathode cell with a large number of cathodes, electrically connected with one or two anodes, has been suggested [30,31]. This configuration allows the operation of the cell with a maximum area cathode and minimum area anode [32–34]. Very recently, Bechtold et al. have demonstrated that mediator system obtainable by mixing one or more salts of a metal capable of forming a plurality of valence states with at least one amino-containing complexing agent and at least one hydroxyl-containing but amino-devoid complexing agent in an alkaline medium has the improved capacity to reduce the vat dyes [35,36].

Both the electrochemical reduction techniques are not yet commercialized and research and developmental efforts are in progress in this direction. Here, the most challenging engineering task is to achieve a dye reduction rate and a current efficiency, which are high enough to make electrochemical reaction industrially feasible.

In the present study attempts are being made to understand the fundamentals of indirect electrochemical reduction of selected vat dyes using iron–TEA complex as a mediator. Essential requirements for the design of electrochemical cell are suggested. Iron–TEA–NaOH molar ratio has been standardized to get the dyeing of cotton by indirect electrochemical reduction technique. Colour yields are compared with those of conventional sodium dithionate method. Repeated use of dye-bath after dye separation is also explored.

2. Experimental

2.1. Materials

The sodium dithionite and sodium hydroxide used for vat dyeing by conventional method were laboratory grade

chemicals. The mediator system necessary for indirect electrochemical reduction of vat dyes was prepared in an alkaline medium from triethanolamine and ferric sulphate, which were analytical grade chemicals. Potentiometric titrations were carried out to measure the dye reduction potential using $K_4Fe(CN)_6$ as an oxidizing agent which was also an analytical grade chemical. Dye systems investigated were commercial products from Atul Ltd.: Novatic Yellow 5G (CI Vat Yellow 2), Novinone Brown RRD (CI Vat Brown 5), Novinone Green FFB (CI Vat Green 1), Novinone Blue RSN (CI Vat Blue 4), Novinone Blue BO (CI Vat Blue 20), Novinone Brown BR (CI Vat Brown 1), Novinone Black BB (CI Vat Black 36), Novinone Brill. Violet RR (CI Vat Violet 1) and Novinone Black CH.

2.2. Dyeing procedure and process control

2.2.1. Conventional dyeing

Conventional vat dyed samples were prepared in the laboratory, with a standard procedure using sodium dithionite and sodium hydroxide as described elsewhere [13].

2.3. Electrochemical dyeing

2.3.1. Design of the electrochemical cell

The two-compartment electrochemical cell consists of a rectangular polyvinyl chloride vessel containing the capacity of 1 l catholyte and 0.1 l anolyte and the separator used was 423 Nafion membrane. The anode used was a thin stainless steel rod with the surface area of 6 cm². A three-dimensional copper wire electrode with a surface area of 500 cm² served as the cathode. The cathode compartment was thus providing porous flow through electrode filling the cathode compartment as coil. The catholyte was agitated by an analytical rotator at a constant speed to create homogeneous and stable conditions in the cathode chamber. The dye-bath of the dyeing apparatus was circulated through the electrochemical reactor for continuous renewal of the reducing capacity of the dye-bath.

A schematic drawing of the dye-bath circulation through the laboratory dyeing unit and the catholyte circulation through the electrochemical cell is given in Fig. 1.

2.3.2. Determination of reduction potential of vat dyes

Here, the reduction potential of the dye is referred as the potential developed on the bright platinum electrode vs the reference electrode when dipped in the dye-bath in which the dye gets just solubilised. In order to measure the reduction potential of vat dyes, a titration was carried out using bright platinum electrode with $Hg/HgO/OH^-$ as a reference electrode. A solution of 100 mg vat dye was prepared which was then reduced with 25 ml of 0.1 M NaOH and 100 mg $Na_2S_2O_4$. This solution was then diluted to 50 ml with distilled water and then titrated against 0.05 M $K_4[Fe(CN)_6]$. The $K_4[Fe(CN)_6]$ solution was added in the steps of 0.5 ml and the dye solution potential was measured at every step. The volume of 0.05 M $K_4[Fe(CN)_6]$ solution is then plotted against the dye solution potential in order to find out dye reduction potential.

Analytical rotator

Cu wire to measure solution potential w.r.t. Reference electrode
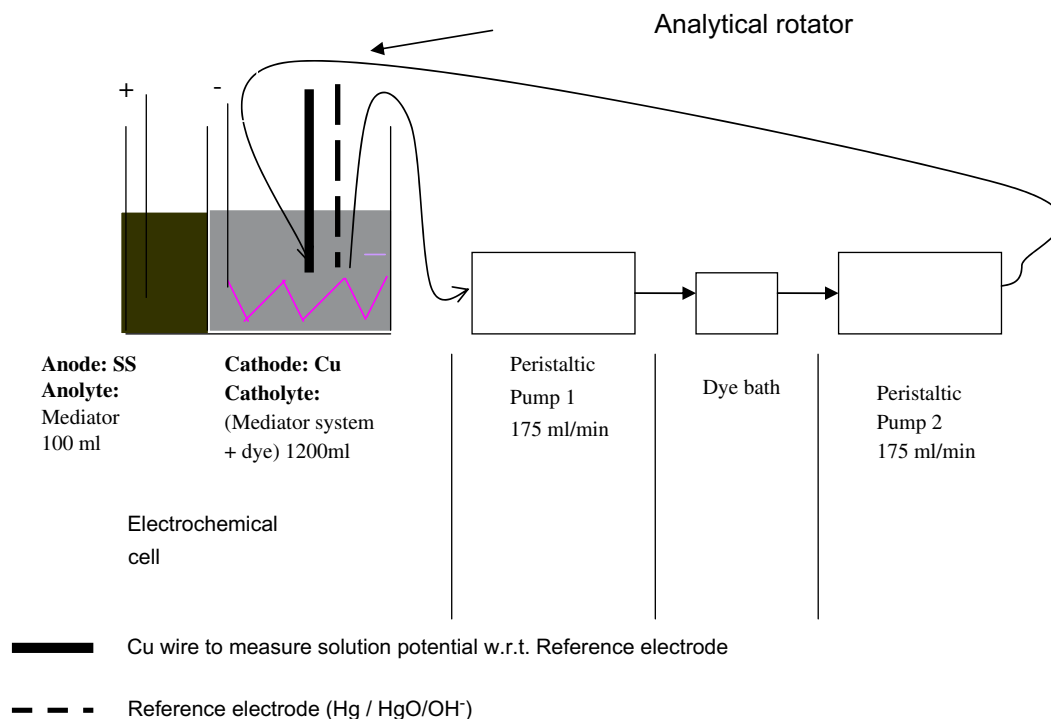
Reference electrode (Hg / HgO/OH⁻)

Fig. 1. Schematic representation of the electrochemical flow cell.

2.3.3. Dyeing procedure

Selected vat dyes were dyed under the standardized conditions of the mediator system as described in Section 3. While following the electrochemical dyeing technique, the dye-bath was circulated through the cathodic compartment of the electrolytic cell for continuous renewal of the reducing capacity. All the experiments were performed under potentiostatic conditions (-1050 mV vs Hg/HgO/OH$^-$) at room temperature. The catholyte was called as a mediator solution which comprised triethanolamine, ferric sulphate and sodium hydroxide. The potential prevailing in the catholyte, during electrolysis, was measured with a copper wire vs a reference electrode (Hg/HgO/OH$^-$). The catholyte was agitated in the catholyte compartment itself and was also circulated through the dye-bath continuously. When the potential achieved in the catholyte was equivalent to the reduction potential of the dyestuff, the dyestuff was introduced into the catholyte compartment. In all the experiments 2% of weight of fabric dye was used in the dyeing recipe. The fabric sample was introduced into the dye-bath after 10 min of introduction of dyestuff in order to allow reduction of the dyestuff. Experiments were carried out at a relatively large liquor ratio i.e. 240:1. The dyeing was continued in the dye-bath for 1 h with constant agitation of the fabric sample with glass rods, while electrolysis and circulation of the catholyte were in progress. After dyeing the sample was withdrawn from the dye-bath, air oxidized, cold rinsed, soaped at boil, cold rinsed and air dried.

2.3.4. Optimization of mediator solution

In order to make the indirect electrochemical dyeing technique eco-friendly and economical, the concentration of the mediator system should be made as low as possible. High concentrations of chemicals in the dye-bath enable more stable reduction conditions and prevent the oxidation of the reduced dyestuff. However, if we use the mediator solution towards its higher concentration end then there will be an eventual increase in the loss of chemicals in the recycling loop and also carried along the fabric at the end of dyeing operation. This makes the process uneconomical.

Table 1
Different composition of the mediator solutions used for dyeing experiments

Mediator solution	pH	Mediator solution composition		
		Fe$_2$(SO$_4$)$_3$ (M)	TEA (M)	NaOH (M)
Group I				
1.1	14	0.025	0.30	0.357
1.2	14	0.03	0.35	0.434
1.3	14	0.035	0.40	0.500
1.4	14	0.04	0.45	0.570
1.5	14	0.045	0.50	0.643
Group II				
2.1	10.5	0.03	0.35	0.185
2.2	12	0.03	0.35	0.225
2.3	13	0.03	0.35	0.275
2.4	14	0.03	0.35	0.315
2.5	14	0.03	0.35	0.375
2.6	14	0.03	0.35	0.429
2.7	14	0.03	0.35	0.480
Group III				
3.1	14	0.025	0.30	0.43
3.2	14	0.025	0.315	0.43
3.3	14	0.025	0.33	0.43
3.4	14	0.025	0.345	0.43
3.5	14	0.025	0.360	0.43

Table 2
Reduction potential of selected vat dyes

Dye	Reduction potential (V)	Dye	Reduction potential (V)	Dye	Reduction potential (V)
Novatic Yellow 5G	−0.818	Novinone Blue RSN	−0.880	Novinone Black BB	−0.952
Novinone Brown RRD	−0.841	Novinone Blue BO	−0.903	Novinone Brill. Violet RR	−0.953
Novinone Green FFB	−0.850	Novinone Brown RR	−0.935	Novinone Black CH	−0.964

Reduction potential (V vs Hg/HgO/OH⁻).

Indirect electrochemical dyeing was carried out with the selected dyestuffs at different mediator solution concentrations in three sets of mediator systems as shown in Table 1. In group I, the ferric sulphate to TEA and ferric sulphate to sodium hydroxide molar ratio was kept constant as 1:11.48 and 1:14.3, respectively as described elsewhere [13]. In group II, the ferric sulphate to TEA molar ratio was kept constant at 1:11.48 while the ferric sulphate to sodium hydroxide molar ratio was varied. Whereas in group III, the ferric sulphate to sodium hydroxide molar ratio was kept constant at 1:14.3 and the ferric sulphate to TEA molar ratio was varied.

The mediator solution was prepared according to the procedure described elsewhere [14]. Caustic soda was dissolved in a small amount of water in which TEA was added. Ferric sulphate was separately dissolved in a small amount of water and then added to the TEA/caustic soda mixture with continuous stirring with the magnetic stirrer. After the complete dissolution of the precipitated iron oxide, the solution was diluted to the full volume. The solution was subjected to constant stirring for 90 min.

2.3.5. Material to liquor ratio experiments

As the electrolysis cell was not optimized with regard to short liquor ratios, experiments were carried out at a relatively large material to liquor ratio i.e. 1:240. To understand the effect of the various materials to liquor ratios on the colour depth developed on the fabric samples by indirect electrochemical dyeing, experiments were also carried out with 1:120, 1:80 and 1:60 material to liquor ratios by making appropriate modifications in the system.

2.3.6. Recycling of mediator solution experiments

After completing the dyeing experiment, the remaining dye and reduced mediator were oxidized by bubbling air though the solution to form an insoluble dye.

The oxidized dye particles can be segregated out through the vacuum filtration using G3 type of porcelain membrane. The clear filtered out mediator solution was recycled further to carry out dyeing experiments.

2.3.7. Dyed samples evaluation

Results of the dyeing experiments were characterized by colour measurement in the form of *K/S* and CIELab coordinates with the help of spectrophotometer X4000 (Jaypak) using D65 light source, 10° viewing angle.

Dyed samples were also evaluated for wash fastness (SOURCES: IS 764; 1979), light fastness (SOURCE: IS 2454; 1985) and rubbing fastness (SOURCE: IS 766; 1988).

3. Results and discussion

3.1. Reduction potential of vat dyes

The reduction potential of vat dyes (Table 2) gives an idea about the level of difficulty involved in their reduction. Higher the reduction potential of the dye, higher is the reducing power required in the dye-bath for its reduction. Thus, from the reduction potential values, we can group the dyes under consideration in three groups viz. easy to reduce, normal to reduce and difficult to reduce.

While following the indirect electrochemical dyeing technique, three dyestuffs such as, Green FFB (an *easy to reduce* dye), Blue RSN (a *normal to reduce* dye) and Violet RR (a *hard to reduce* dye) were selected.

3.2. Dyeing results

The rates of potential development while carrying out potentiostatic electrolysis in the group I, II and III dyeing experiments with Violet RR dye only are shown in Figs. 2, 3 and 4, respectively. In each dyeing experiment, the dye was introduced in the cathodic chamber as soon as the reduction potential of Violet RR had reached i.e. −953 mV. The final dye-bath potential attained at the end of dyeing in few cases was lower than that attained during the course of dyeing, especially while dyeing with Green FFB and Blue RSN.
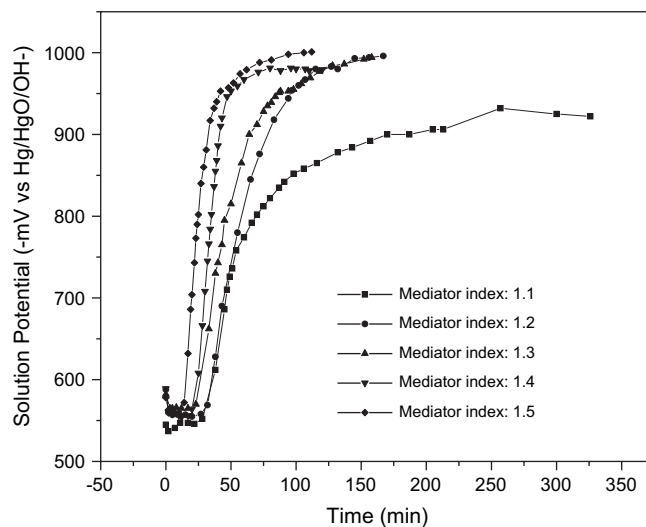

Fig. 2. Dye-bath potential development with varying ferric sulphate concentration (group I) electrolysis with Violet RR dye.
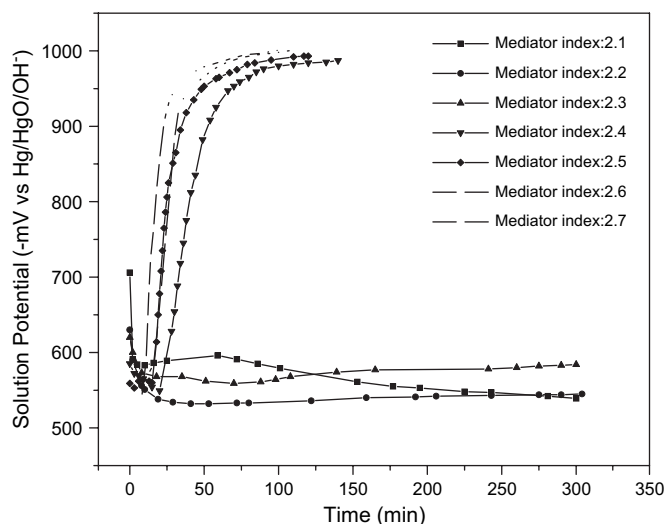
Fig. 3. Dye-bath potential development with varying sodium hydroxide concentration (group II) during electrolysis with Violet RR dye.

From the variation of the CIELab coordinates from the group I experiments as shown in Table 3, it becomes clear that the colour depth and shade did not show strong dependence on the iron salt concentration in the mediator solution. However, the depth appears to be good around 12–14 g/l ferric sulphate concentration. The potential development rate appears to be increasing with increase in ferric sulphate concentration as can be seen in Fig. 2.

In case of group II experiments, the solution potential could not be developed above −953 mV vs Hg/HgO/OH⁻ while working up to pH 13. Therefore dyeing was not possible during working with NaOH concentration below 11 g/l in the mediator solution. During electrolysis of the solution with pH below 13, the complex formed was found to be unstable and caused additional problems in the proper functioning of the electrochemical
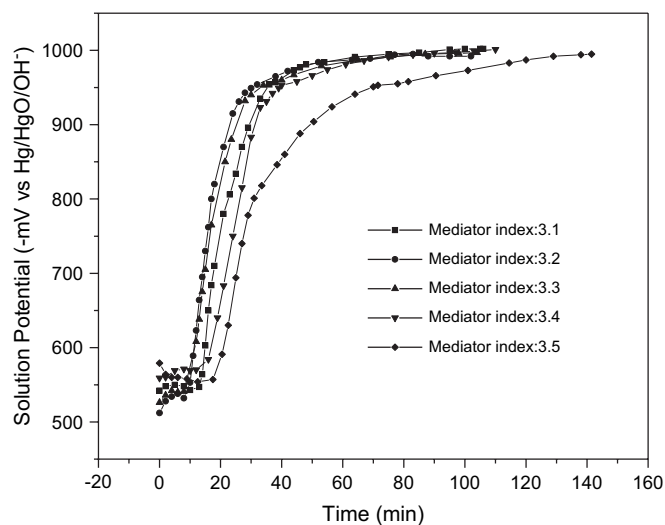

Fig. 4. Dye-bath potential development with varying TEA concentration (group III) during electrolysis with Violet RR dye.

Table 3
Comparison of colour yield and colour coordinates of conventional and electrochemical dyeing with Green FFB

Mediator solution index	Final dye-bath potential (V vs Hg/HgO/OH⁻)	K/S	L^*	a^*	b^*
With dithionite*		15.4626	35.44	−35.20	−0.98
1.1*	−0.860	5.1460	55.37	−39.92	−2.67
1.2*	−0.880	4.7258	53.39	−32.58	−6.24
1.3*	−0.870	5.6865	52.95	−38.25	−3.72
1.4*	−0.874	3.3465	58.97	−33.46	−4.71
1.5*	−0.996	4.1874	57.42	−36.84	−3.27

Initial dye-bath potential before starting the electrolysis in each case was −0.350 V vs Hg/HgO/OH⁻.

cell due to the deposition of a block material as a hard layer on the cathode. As can be seen from the corresponding K/S values in Table 4, the colour depth appears to be increasing with an increase in NaOH concentration above pH 13.

There is no effect of the TEA concentration variation in the mediator solution in the given range of group III experiments on the colour depth and shade which is shown in Table 5. Also the solution potential development rate is found to be unaffected (Fig. 4). However, at 44.75 g/l TEA, the iron complex becomes unstable and ferric hydroxide is found to be precipitating.

3.2.1. Influence of MLR on colour yield

All the dyeing experiments for mediator solution optimization were carried out at 1:240 material to liquor ratio. The depth of the dyed samples was very low as compared to the conventionally dyed samples which were dyed at 1:30 material to liquor ratio. In order to investigate the possibilities of improving the colour depth, dyeing experiments were carried out with Blue RSN dye at 1:240, 1:120, 1:80 and 1:60 material to liquor ratios using 1.2 mediator index solution.

Values of K/S and CIELab coordinates of dyeing experiments are given in Table 6 which show marginal improvement in colour depth of the dyed samples with shorter material to liquor ratios.

3.2.2. Recycling of mediator solution

Dyeing without effluent i.e. dye-bath recycling seems to be very attractive in the present environment conscious era.

Table 4
Comparison of colour yield and colour coordinates of conventional and electrochemical dyeing Blue RSN

Mediator solution index	Final dye-bath potential (V vs Hg/HgO/OH⁻)	K/S	L^*	a^*	b^*
With dithionite		9.1666	35.94	6.62	−38.03
1.1	−0.875	2.6641	52.92	−3.29	−27.93
1.2	−0.900	3.6045	48.44	0.58	−32.87
1.3	−0.890	2.2319	55.17	−2.25	−28.24
1.4	−0.905	2.5897	52.71	0.23	−31.25
1.5	−0.983	1.9702	56.10	−1.10	−27.58

Initial dye-bath potential before starting the electrolysis in each case was around −0.350 V vs Hg/HgO/OH⁻.

Table 5
Comparison of colour yield and colour coordinates of conventional and electrochemical dyeing with Violet RR

Mediator solution index	Final dye-bath potential (V vs Hg/HgO/OH⁻)	K/S	$L*$	$a*$	$b*$
With dithionite		15.73	23.10	16.93	−23.13
1.1	−0.922	0.2810	77.92	10.16	−9.76
1.2	−0.996	3.0499	47.82	22.82	−28.25
1.3	−0.994	3.2752	47.87	26.70	−30.07
1.4	−0.979	2.4236	52.75	26.42	−27.63
1.5	−0.1001	2.9228	49.78	26.78	−29.23
2.1	−0.539	Dyeing not possible			
2.2	−0.545	Dyeing not possible			
2.3	−0.584	Dyeing not possible			
2.4	−0.987	2.0706	54.97	25.45	−26.87
2.5	−0.993	2.2632	53.53	25.15	−26.66
2.6	−0.1001	3.1007	48.72	26.54	−30.03
2.7	−0.1001	4.4808	43.71	28.11	−30.84
3.1	−0.1002	2.8823	49.71	26.59	−30.50
3.2	−0.992	3.5124	47.04	27.51	−30.79
3.3	−0.997	3.9246	45.32	27.49	−31.02
3.4	−0.1001	3.0499	47.82	22.68	−28.25
3.5	−0.995	3.1660	48.79	26.99	−28.83

Initial dye-bath potential before starting the electrolysis in each case was around −0.350 V vs Hg/HgO/OH⁻.

Table 6
Effect of ML ratios on colour yield and CIELab coordinates

MLR	Final dye-bath potential (V vs Hg/HgO/OH⁻)	K/S	$L*$	$a*$	$b*$
1:240	−0.900	3.6045	48.44	0.58	−32.87
1:120	−0.958	2.9914	50.85	−0.72	−30.43
1:80	−0.950	3.0879	50.49	−1.65	−29.25
1:60	−0.965	4.0401	46.55	−1.01	−29.91

Table 7
Regeneration of mediator solution

Recycling step	Fresh solution added[a] (ml)	Absorbance	
		Before oxidation and filtration	After filtration
Original	0	1.384	0.072
1	30	1.533	0.027
2	41	1.403	0.050
3	28	1.417	0.079
4	42	1.420	0.070

[a] Fresh solution was added to make the total volume to 1 l before starting each experiment.

Table 8
Colour yield and CIELab coordinates for repeated dyeing with regenerated mediator solution

Recycling step	Final dye-bath potential (V vs Hg/HgO/OH⁻)	K/S	$L*$	$a*$	$b*$
Original	−0.995	2.4954	52.95	0.62	−31.06
1	−0.965	2.3803	53.82	−0.97	−29.35
2	−0.950	2.8766	51.25	−0.55	−30.31
3	−0.958	2.6414	52.39	−0.39	−29.67
4	−0.953	3.0783	50.65	−1.09	−30.50

Table 9
Comparison of fastness properties of electrochemical and conventional dyeing

Reduction/mediator system	Washing fastness	Light fastness	Rubbing fastness	
			Wet	Dry
With dithionite[a]	4–5	5	4	5
With dithionite[b]	4–5	5	4	5
With dithionite[c]	4–5	5	4	4–5
0.025 M Fe₂(SO₄)₃ + 0.345 M TEA + 0.45 M NaOH (MLR 1:240)[a]	4–5	4–5	4–5	5
0.025 M Fe₂(SO₄)₃ + 0.345 M TEA + 0.45 M NaOH (MLR 1:240)[b]	4	4–5	4	4–5
0.025 M Fe₂(SO₄)₃ + 0.345 M TEA + 0.45 M NaOH (MLR 1:240)[c]	4–5	5	4	4–5
0.025 M Fe₂(SO₄)₃ + 0.345 M TEA + 0.45 M NaOH (MLR 1:60)[a]	4	4–5	4–5	5
0.025 M Fe₂(SO₄)₃ + 0.345 M TEA + 0.45 M NaOH (MLR 1:60)[b]	4	4–5	4–5	5
0.025 M Fe₂(SO₄)₃ + 0.345 M TEA + 0.45 M NaOH (MLR 1:60)[c]	4	4–5	4–5	5

[a] With Green FFB.
[b] With Blue RSN.
[c] With Violet RR.

Fig. 5. Effect of mediator recycling on the dye-bath potential development.

In order to reuse the mediator solution with different dyes, the residual dye has to be removed from the dye liquor. However, this is very straightforward especially in case of vat dyes which become insoluble in the dye-bath on oxidation. In the

laboratory dyeing experiments, this can be achieved by bubbling air through the dye-bath. Insoluble oxidized dye particles were removed by vacuum filtration with G3 porcelain filter.

The mediator solution used for the recycling experiments was composed of 0.025 M $Fe_2(SO_4)_3$ + 0.345 M TEA + 0.45 M NaOH (1.2 index mediator solution). Table 7 shows the absorbance of the dye-bath before oxidation and the filtered mediator solution after oxidized dye-bath at 620 nm. The difference in the absorbance shows a high degree of dye removal. The filtered mediator solution was again used for the next dyeing experiment. However, there was a loss of 4—5% of the mediator solution throughout the process which had to be replenished with fresh mediator solution which is also given in Table 7. Thus the dye-bath was recycled four times. Blue RSN dye was used during each dyeing experiment.

The CIElab coordinates of the dyed samples (Table 8) for four recycling dyeing experiments, carried out under similar experimental conditions show no effect on the colour depth and shade. There was also no effect on the rate of

development of the solution potential as shown by curves in Fig. 5. Thus, reproducibility of the dyeing results was confirmed along with the electrochemical regeneration of the reducing agent.

3.2.3. Fastness results

A few selected dyed samples with indirect electrochemical dyeing technique were tested for washing fastness, light fastness, wet and dry rubbing fastness. The results are shown in Table 9. All the fastness properties appear to be equivalent with the conventionally dyed samples obtained using sodium dithionite as a reducing agent.

3.2.4. Indirect electrochemical reduction mechanism

A general reaction for indirect electrochemical dyeing process using Fe(II)—TEA complex is established [26,37] as follows.
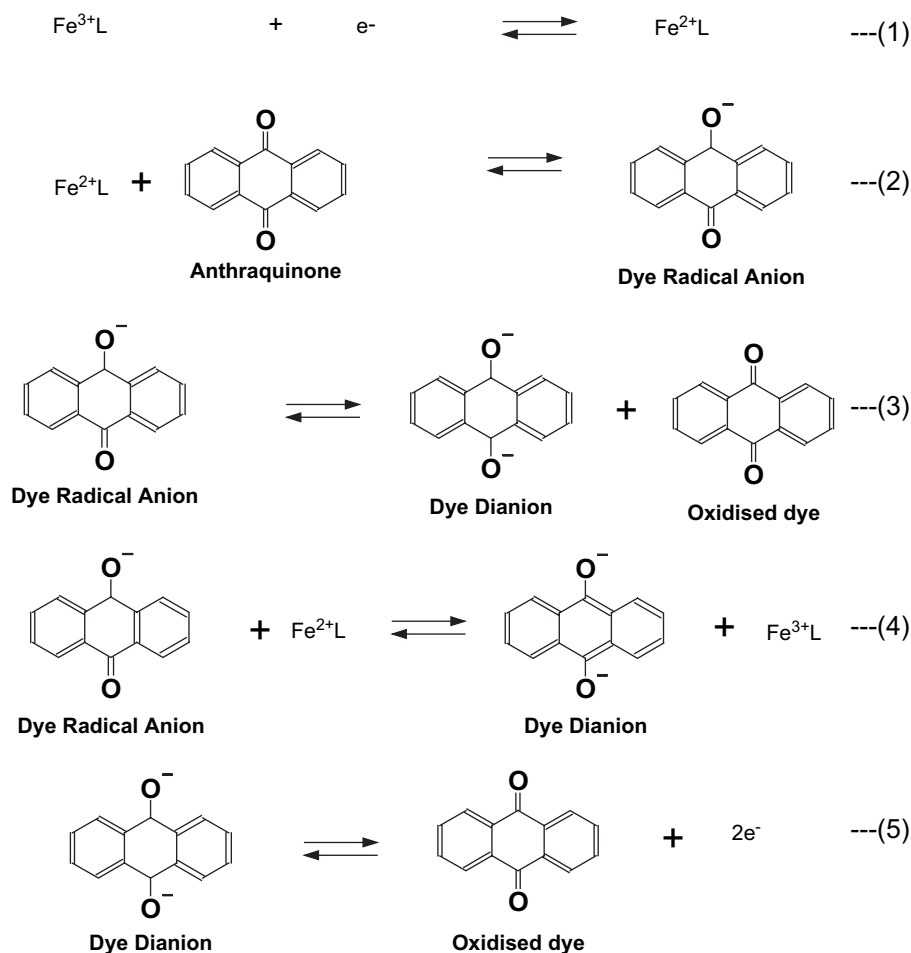
General Reaction Scheme of Dye Reduction by Fe(II) complex
system `L` denotes the associated TEA ligand

4. Conclusions

The above study has resulted in the following conclusions.

(1) Potentiostatic experiments revealed that iron–TEA complexes show a sufficiently negative redox potential in the alkaline solution, which is sufficient for indirect electrochemical reduction of vat dyes.
(2) The continuous regeneration of the reducing agent is possible by cathodic reduction. However, colour depth appears to be poor with the implemented electrochemical system as compared to the conventional vatting technique using sodium dithionite as a reducing agent. Better results may be possible with sophisticated electrochemical systems and optimization of the mediator system.
(3) Experiments with shorter material to liquor ratios have shown better colour depths.
(4) Fastness properties appear to be equivalent with the conventional dyeing technique with good light, washing and rubbing fastnesses.
(5) Iron–TEA complex regenerable reducing system allows reuse of the dye-bath chemicals after replenishing it with the lost amount of chemicals during the oxidation and filtration stage of indirect electrochemical dyeing. Thus the system offers enormous ecological advantages.
(6) Recycling experiments also show the capability of reproducing the same depth and shade while working with the same dye.

The main advantages of this present work are:

1. Design of suitable electrochemical cell for electrochemical dyeing of cotton with dyes on laboratory scale is suggested.
2. Molar concentrations of mediator system were optimized for development of reduction potential suitable for reduction of vat dyes.
3. It was possible to get the electrochemical dyeing of cotton with selected vat dyes under optimized conditions. However, the depth of dyeing is much weaker compared to conventional dyeing with sodium dithionate as reducing agent.
4. It was possible to regenerate the mediator system and its repeated use for dyeing.
5. Further work is essential to improve the dye uptake and establish the economic and environment benefits of the electrochemical dyeing system.

References

[1] Phillips D. J Soc Dyers Colour 1996;12:183.
[2] Roessler A, Jin X. Dyes Pigments 2003;59:223.
[3] Baumgarte U. Melliand Textilber 1987;68:189–276.
[4] Baumgarte U. Rev Prog Color 1987;17:29.
[5] Cegarra J, Puente P, Valldeperas J. The dyeing of textile material. Italy: Texilia; 1992. p. 355.
[6] Aspland JR. Text Chem Color 1992;22:24.
[7] Jermini M. Ph.D dissertation, ETH Zurich; 1997.
[8] Federer-Lerch S. Ph.D dissertation, ETH Zurich; 1997.
[9] Makarov SV. Russ Chem Rev 2002;70:885.
[10] Marte E. Text Praxis Int 1989;44(7):737.
[11] Somet B. Melliand Textilber 1995;76:161.
[12] Chavan RB, Chakraborthy JN. Indian J Fibre Text Res 2000;25:130.
[13] Chakraborty J.N. Ph.D thesis, Indian Institute of Technology, New Delhi; 2002.
[14] Schrott W. ITB International Textile Bulletin May 2000.
[15] Bechtold T. US Patent No. US 5244549; 1993-09-14.
[16] Roessler A, Crettenand D. Dyes Pigments 2004;63:29.
[17] Roessler A, Crettenand D, Dossenbach O, Rys P. J Appl Electrochem 2003;33:901.
[18] Roessler A, Dossenbach O, Rys P. J Electrochem Soc 2003;150:D1.
[19] Roessler A, Dossenbach O, Marte W, Rys P. J Appl Electrochem 2002; 32:647.
[20] Roessler A, Crettenand D, Dossenbach O, Meyer U, Marte W, Rys P. Electrochim Acta 2002;47:1989.
[21] Ibanez JG, Chai C-S, Bedeer RS. J Electrochem Soc 1987;134:3083.
[22] Betchtold T, Burkscher E, Gmeiner D, Bobleter O. J Electroanal Chem 1991;306:169.
[23] Betchtold T, Burtscher E, Kuhnel G, Bobleter O. J Soc Dyers Colour 1997;113:135.
[24] Bechtold T, Burtscher E, Amann A, Bobleter O. J Chem Soc Faraday Trans 1993;89:2451.
[25] Bechtold T, Burtscher E, Turcanu A, Bobleter O. J Soc Dyers Colour 1994;110:14.
[26] Bechtold T, Burtscher E, Turcanu A, Bobleter O. J Electrochem Soc 1996;143:2411.
[27] Bechtold T, Burtscher E, Turcanu A, Bobleter O. Text Res J 1997; 67:635.
[28] Bechtold T, Berktold F, Bobleter O. J Soc Dyers Colour 2000;116:215.
[29] Bechtold T, Turcanu A. J Electrochem Soc 2002;149:D7.
[30] Herhardt W, Gehlert W, Gluck E. US Patent 4,786,384; 1988.
[31] Bechtold T, Burtscher E, Turcanu A, Bobleter O. J Appl Electrochem 1997;27:1021.
[32] Mohr S, Bechtold T. J Appl Electrochem 2001;31:363.
[33] Blatt W, Schneider L. Textilveredelung 2002;37:10.
[34] Trauer J. Melliand Int 1999;80:240.
[35] Bechtold T, Stefan M, Wolfgang S, Norbert G, Wolfgang H. US Patent 6,814,763; 09-11-2004.
[36] Bechtold T, Edward S, Wolfgang S, Norbert G, Peter M, Georg S, et al. US Patent 6,790,241; 14-09-2004.
[37] Bechtold T, Burtscher E, Turcanu A. J Electroanal Chem 1999; 465:80.