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ORIGINAL PAPER

Electrochemical reduction of CI sulphur black 1—correlation between electrochemical parameters and colour depth in exhaust dyeing

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Abstract Direct cathodic reduction of oxidised CI Sulphur Black 1 was achieved by means of a multi-cathode electrolyser at cell currents of 0.9–1.5 A. The redox potential in the catholyte decreased from initially −250 to −533 mV as a function of charge flow. The catholyte also served as dyebath for cotton fabric samples. Colour depth was characterised by Kubelka–Munk value K/S and CIELab-coordinates and was studied as function of charge flow and redox potential in the catholyte. Direct correlation between redox potential and colour depth of the dyed samples was observed. Electrochemical reduction permits steering of catholyte/dyebath potential by adjustment of cell current and thus permits direct control of the dyeing process by electrochemical methods.

Keywords Sulphur dye · CI Sulphur Black 1 · Cathodic reduction · Dyeing · Multi-cathode electrolyser · Dyestuff

1 Introduction

With an annual production of more than 80,000 t/year, CI Sulphur Black 1 probably represents the textile dyestuff produced in largest amount world wide. Major fields of application are dyeing of black denim and garment dyed black cotton textiles [1, 2]. From the synthesis of the dye the crude CI Sulphur Black 1 is released as an oxidised water insoluble filter cake. To formulate the commercial liquid form of CI Sulphur Black 1 the dyestuff is reduced into its alkali soluble leuco form, which readily dissolves in aqueous alkali solution [3]. Suited reducing agents should establish a reduction potential of −600 mV (vs. Ag/AgCl, 3 M KCl); important representatives are sodium sulfide, glucose or hydroxyacetone [4–6]. The same reducing agents are applied in the textile dyeing operation to stabilise the reduced form of the dyestuff during dyeing procedures and to avoid uncontrolled re-oxidation of the dyestuff by atmospheric oxygen [3, 7, 8].

Chemical reducing agents used at present cannot be regenerated, thus, besides costs for the chemicals, environmental problems, e.g. due to toxicity or high chemical oxygen demand in the waste-water are increasingly important [6, 9].

An interesting alternative route to reduce the dyestuff could be direct cathodic reduction of the oxidised pigment. Promising results were achieved in the seventies by Frind et al. [10]. More detailed studies to reduce crude filter cake of CI Sulphur Black 1 electrochemically proved the principle of reducing the dye by cathodic reduction and applying the product in continuous dyeing operations [11–13].

CI Sulphur Black 1 is synthesised as bake Sulphur dye so that the technical product is not very well defined. Proposed chemical structures show the oxidised dyestuff as a polymeric compound consisting of various chemically similar subunits, which are bridged together by disulfidic groups. Scheme 1 gives a representation of the proposed structure and also indicates where reduction can occur.

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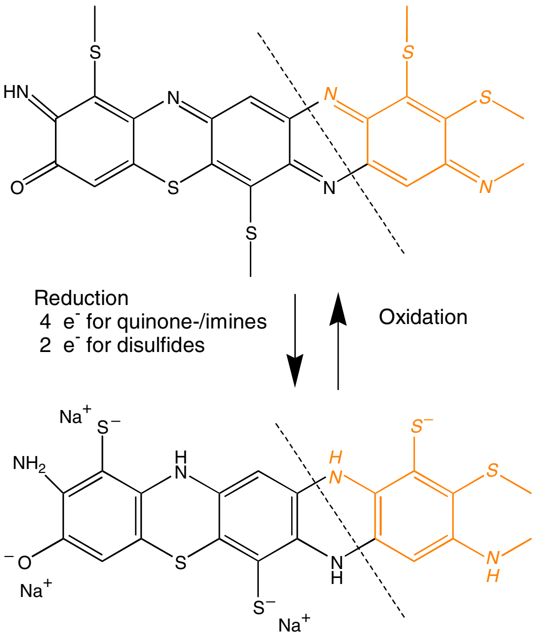

Scheme 1 Reaction model for reduction of CI Sulphur Black 1

Disulfidic bonds are cleaved and the oxidised polymer form is reduced to lower molecular weight units [8].

The high variability of CI Sulphur Black 1 makes use of analytical methods difficult and at present only sum-parameters, like titration with $K_3(Fe(CN)_4]$ and model dyeing results have been used to confirm that cathodic reduction does not destroy the dyestuff irreversibly [10–13]. Model dyeings are very sensitive to irreversible changes in the molecular structure, which would change affinity and shade of the dyeing, compared to reference dyeings [11–13].

For exhaust dyeing operations the application of indirect cathodic reduction with use of mediator systems also has been investigated [14]. The redox behaviour of CI Sulphur Black 1, which can undergo several reduction/oxidation steps in solution, could form the basis for use of the dyestuff both as colorant and mediator to stabilise the reduction conditions in the dyebath [8].

In the literature the application of cathodically reduced CI Sulphur Balck 1 for pad-steam dyeing epxeriments has been shown [12, 13]. However these processes were based on a two-step process, the first step being cathodic reduction, the following step being the dyeing procedure. This separation permits application of dyeing conditions (100 °C, saturated steam atmosphere), which would not be applicable in the electrolyser. For exhaust dyeing a direct coupling between electrolyser and dyebath is required and the cell has to operate at much lower concentrations of SB1 than in case of continuous dyeing operations.

In this paper, laboratory experiments are presented in which coupling between electrolyser and dyebath was realised for electrochemical dyeing experiments. Crude filter cake CI Sulphur Black 1 was reduced by direct cathodic reduction. The catholyte also served as dyebath. Samples of cotton fabric were dyed and colour depth was analysed as a function of the electrochemical parameters.

2 Experimental details

2.1 Construction of the electrochemical cell

A multi-cathode cell was used for dyestuff/dyebath reduction [15, 16]. A scheme of the cell including dyebath circulation is given in Fig. 1. Three cathodes were driven by separately adjustable electric power supplies connected to a common anode. Catholyte and anolyte were separated by a cation exchange membrane (Nafion®). A solution of 1 mol L^{-1} NaOH was used as anolyte and a stainless steel electrode (front area 100 cm^2, V4A-stainless steel) served as anode. The cathodes were three dimensional electrodes manufactured from stainless steel fabric (steel 1.4404, aperture size 0.325 mm, wire diameter. 0.2 mm, open area 37%; Haver and Boecker, Oelde, Germany), each cathode unit exhibiting a front area of 100 cm^2 and surface area of 1,440 cm^2, thus giving a full cathode area of 4,320 cm^2. The cathode units were insulated from each other by three layers of PE fabric. A multi-cathode cell constructed in similar manner is described in more detail elsewhere [15, 16]. The catholyte circulation through the electrode was driven by a peristaltic pump, which was adjusted at

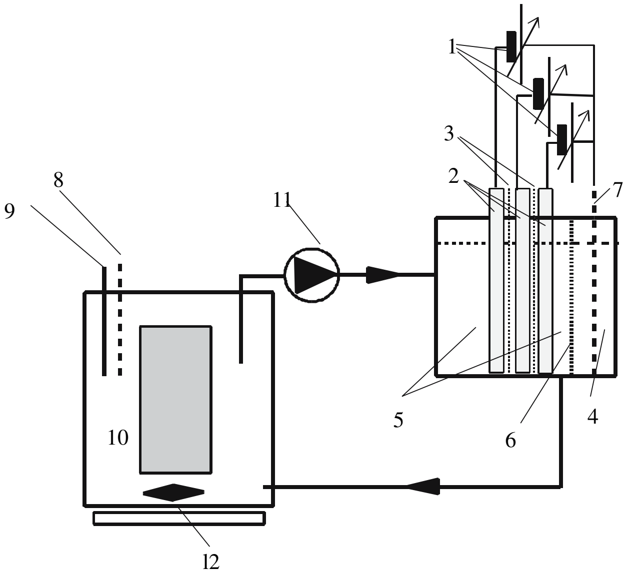

Fig. 1 Scheme of the multi-cathode electrolyser, coupled to the dyebath. Key: (1) current supply, (2) cathode unit, (3) porous insulator, (4) anolyte, (5) catholyte/dyebath (6) separator, (7) anode, (8) redox electrode, (9) thermometer, (10) material sample, (11) catholyte circulation, (12) magnetic stirrer/heater

150 mL min^{-1}. Assuming an equal flow and a porosity of about 40% in the cathodes, the average catholyte velocity through the electrodes can be calculated as 0.06 cm s^{-1}.

In contrast to previous work, electrolysis was directly coupled to the dyeing process, which was performed in an open beaker [12, 13]. In the dyebath bleached cotton knitted fabric (6.8–6.9 g) with a mass per area of 270 g m^{-2} was used as sample material. The catholyte circulation also served as a circulation between cell and dyeing vessel, which was agitated and heated by means of a hot-plate magnetic stirrer. Two L dyebath were used for dyeing of 6.8–6.9 g fabric which resulted in a liquor ratio of 1:290–295 (mass of fabric in g : volume of dyebath in mL). Temperature and redox potential were measured in the dyebath (Metrohm pH meter 654, Metrohm, Herisau, Switzerland) and controlled manually. All potential values given are related to the (Ag/AgCl, 3 M KCl) reference electrode.

To simulate technical conditions the experiments were not performed under inert atmosphere.

2.2 Chemicals

Technical grade NaOH, H_2O_2, acetic acid were used for preparation of the ground electrolyte and dyeing procedure. Crude filter cake CI Sulphur Black 1 (Carbon CMR, DyStar Frankfurt a.M., Germany) was used as delivered.

2.3 Dyeing procedure

The dyeing procedure was performed as an exhaust process with parallel electrochemical reduction of the dyestuff. Dyebath temperature is given in Table 1 and kept within ±8 °C for a given experiment. Detailed conditions are shown in the respective Table 1.

A volume of 2 L catholyte respectively dyebath circulated between cell and dye vessel. A solution of 0.075 mol L^{-1} NaOH and 0.5–0.6 g L^{-1} wetting agent (Primasol NF® BASF, Ludwigshafen a.R., Germany) served as catholyte. A concentration of 10.0 –10.5 g L^{-1} crude CI Sulphur Black 1 was used in the dyeing experiments. This corresponds to a colour depth of 150% (mass of dyestuff per mass of fabric); thus the amount of actually exhausted dyestuff can be neglected when consecutive dyeings were performed in the same dyebath. Cathodic reduction was started when dyeing temperature had been reached.

Following to the dyeing step the fabric samples were rinsed with cold water and oxidised in a separate bath containing 1.0 ml L^{-1} H_2O_2 (35% w/w) and 0.7 ml L^{-1} acetic acid for 20 min at 50 °C. The samples then were rinsed in cold water and dried at room temperature.

CIE-Lab values of the dyeings were measured with a tristimulus colorimeter (Minolta Chroma-Meter CR 210, sample diameter 50 mm, measuring geometry d/0°). Colours are given in CIE-Lab coordinates, L* 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 (diffuse reflectance sphere 8°/d, one-beam spectrophotometer Specord 50, Analytik Jena, Germany).

Table 1 Charge-flow Q, cell current I, redox potential E measured at the end of the dyeing step, dyeing time, temperature, diffuse reflectance R% (580 nm), K/S-value and CIELab coordinates of dyed samples

Sample	Q (A min)	I (A)	E (mV)	Dyeing time (min)	Temp. (°C)	$R\%$		K/S		L*		a*		b*	
						/%	Average		Average		Average		Average		Average
blank	–	–	–	–	–	80.9		0.023		91.66		−2.57		+0.64	
						83.4	82.14	0.017	0.02	91.56	91.61	¯2.55	−2.56	+0.55	0.60
A	129.0	1.2–1.5	−415.5	100	57–73	9.3		4.43		42.25		+0.57		−2.78	
						11.7	10.50	3.33	3.88	45.34	43.80	+0.57	+0.57	−3.38	−3.08
B	157.5	0.9	−440.1	175	60–64	6.6		6.60		33.04		−3.48		−6.05	
						8.6	7.63	4.83	5.71	39.93	36.49	¯3.38	−3.43	−5.72	−5.89
C	229.5	0.9	−431.1	80	62–64	5.6		7.98		29.41		−3.35		−5.75	
						5.5	5.53	8.15	8.06	28.92	29.17	¯3.18	−3.27	−5.59	−5.67
D	177.3	0.9	−498.6	197	60–73	4.5		10.24		24.11		−4.65		−6.37	
						4.1	4.28	11.24	10.74	22.61	23.36	+0.58	−2.04	−3.4	−4.89
E	204.3	0.9	−544.8	30	70–71	3.0		15.66		20.72		−4.03		−6.4	
						3.0	3.01	15.63	15.64	19.92	20.32	¯3.83	−3.93	−6.28	−6.34

Colour related values given as results measured on both sides of the sample and average values

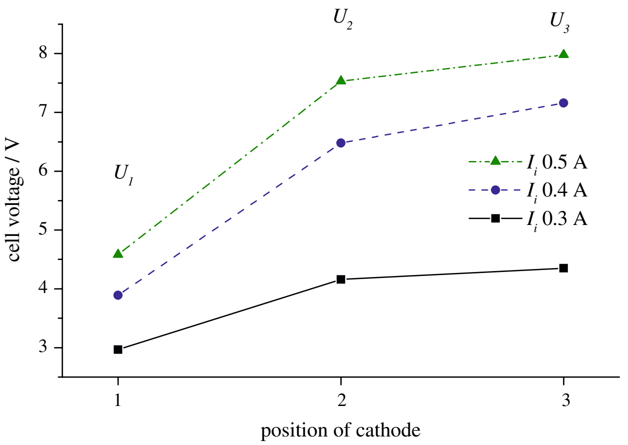

Fig. 2 Cell voltage of cathode units 1–3 as function of current per cathode unit (position 1 cathode nearest to anode). (▲) I_i = 0.5 A per cathode unite, I = 1.5 A cell current; (●)I_i = 0.4 A per cathode unit, I = 1.2 A cell current; (■) I_i = 0.3 A per cathode unit, I = 0.9 A cell current

CIELab-values and diffuse reflectance for calculation of K/S were measured on both sides of the fabric, single values and average are given.

3 Results and discussion

A total cell current of I = 0.9–1.5 A was used in the reduction experiments. This corresponds to a current per cathode unit (I_i) of 0.3–0.5 A, and a cathodic current density of 0.21–0.35 mA cm^{-2}. The cell voltages of the multi-cathode electrolyser as a function of applied current are given in Fig. 2.

Dependent on the applied current, voltage increases from U_1 = 3 V for the front cathode at I_1 = 0.3 A current per cathode unit (total 0.9 A cell current) to U_3 = 4.58 V at I_1 = 0.5 A current per cathode unit (total cell current I = 1.5 A). As expected for multi–cathode cells, the increase in cell voltage decreases with cathode to anode distance. This is due to the lower current transported in the electrolyte through the porous electrodes, which are positioned at greater distance to the anode. Thus the voltage drop in the electrolyte decreases for a particular cathode in the multi-cathode stack with distance to the anode [16]. Limitations in cell current are defined by the dyestuff concentration in the catholyte, the conductivity of the catholyte, the construction of the electrode and by economic considerations due to the strong increase in cell voltage with higher total cell current [16].

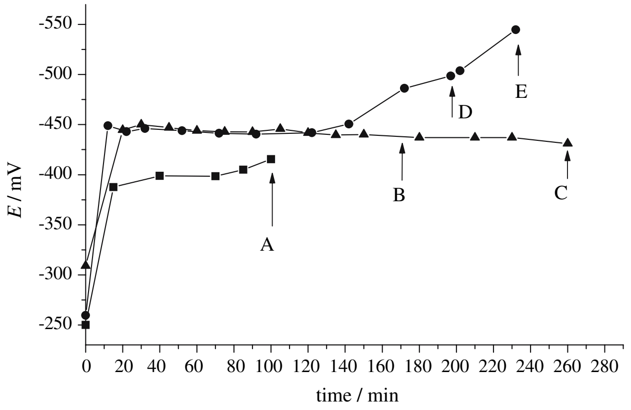

Fig. 3 Redox potential E (vs. Ag/AgCl, 3 M KCl) measured in the dyebath during dyestuff reduction as function of electrolysis time. Arrows A–C indicate time of experiment when dyed specimen was removed from the dyebath.). (■) Experiment A; (▲) experiment B and C; (●) experiment D and E in Table 1

The experiments were performed as galvanostatic electrolyses. A defined equal current I_1–I_3 was fed into the three cathode units. Reduction was monitored by redox potential E in the catholyte. Oxidised crude CI Sulphur Black 1 was used for the reduction experiments. As a result of the cathodic dyestuff reduction, redox potential in the catholyte fell from −250 to −300 mV at the beginning of the experiment, from −400 to −550 mV at the end of electrolysis. Temperature was adjusted in the range of 60–75 °C. Redox potential observed during the electrolysis/dyeing as function of time is given in Fig. 3.

After a defined dyeing time the first sample was removed and was replaced by a second undyed specimen which was added to the dyebath. To complete the dyeing procedure, the dyed samples M1–M5 were rinsed, oxidised and dried and characterised by K/S at 580 nm and CIELab-coordinates.

During a reduction/dyeing experiment redox potential stabilises at a plateau of −450 mV while cathodic dyestuff reduction proceeds. In the oxidised state CI Sulphur Black 1 is present in a quasi-polymer state, repetitive molecular subunits being bridged together by disulfide bonds [8]. During reduction these disulfide bonds are reduced to thiolate groups. Thus average molecular size of the dyestuff decreases and affinity to the cellulosic substrate increases. When chemical reducing agents are applied for dyeing with CI Sulphur Black 1 a redox potential of −550 to −600 mV was found to yield the highest colour depth [8]. Thus the colour depth of dyed samples was expected to increase with applied charge flow and more negative redox potential measured in the catholyte.

In Table 1, charge flow, redox potential in catholyte, K/S-values and CIELab-coordinates of the dyed samples are summarised. Results in Table 1 have been sorted by increasing K/S values, which can serve as a direct measure of fixed dyestuff.

CIELab-coordinates and K/S values were measured on both sides of each specimen. From Table 1 it can be seen that lighter samples show higher differences in colour between the two sides of the fabric. As long as the dyestuff is present in partially reduced form the flow conditions in the dyebath influence the dyeing result considerably (samples A and B). When dyestuff reduction is more complete, a reduced influence of streaming conditions in the dyebath on the colour depth of a sample is observed (samples C–E).

Due to the experimental procedure of dyestuff reduction, dyeing times of samples differ; however dyeing time was sufficient to be of minor relevance for the observed variation in colour depth. For example sample E is darkest after the shortest dyeing period of 30 min, which supports this assumption.

Reduction of the CI Sulphur Black 1 can be monitored by the redox potential *E* in the electrolyte, which also is dependent on the charge flow *Q* applied during electrolysis.

In Figs. 4 and 5 the colour of the sample as K/S-value and L*-value are shown as a function of charge flow *Q* (Fig. 4) or redox potential *E* (Fig. 5) measured in the dyebath at the end of the dyeing.

Both parameters K/S and L* show the expected dependence on applied charge flow *Q*, however sample C dyed at a quite high charge flow of 230 A min shows insufficient colour depth. As can be seen from Fig. 3, the reduction potential slightly decreased during the dyeing of sample C, which indicates incomplete dyestuff reduction. Using the charge flow *Q* as a measure to predict the colour depth and the reduction state of the dyeing, the full efficiency of the system has to be considered. For example the actual cell current efficiency and the overall reduction efficiency of the installation, including possible re-oxidation by uptake of atmospheric oxygen will determine the reduction state in a dyebath at given charge flow.

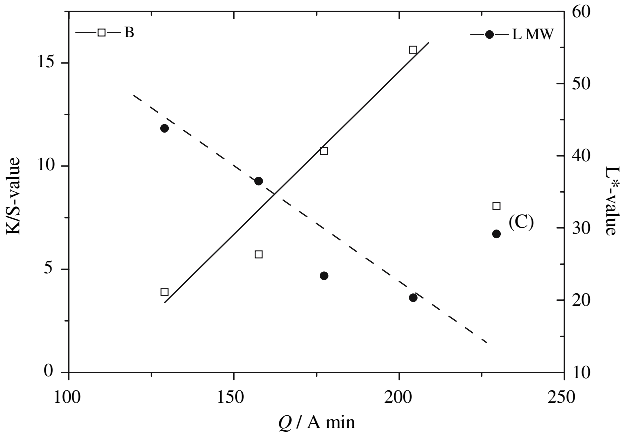

Fig. 4 (□) K/S-values (580 nm) and (●) L*-coordinate of dyed samples as function of charge applied for reduction of the dyestuff

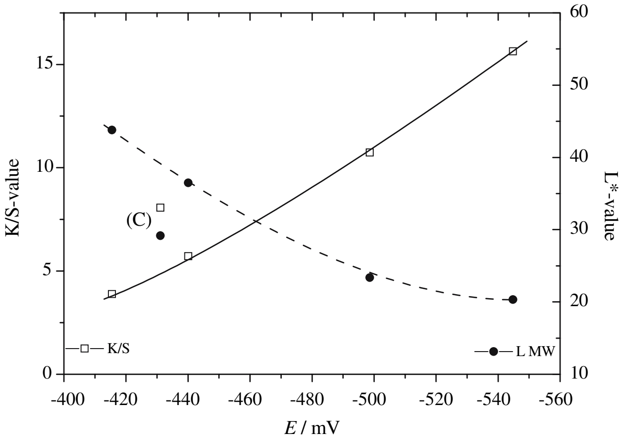

Fig. 5 (□) K/S-values (580 nm) and (●) L*-coordinate of dyed samples as function of redox potential measured in catholyte/dyebath

The correlation between K/S and L* and redox potential measured in the dyebath at the end of the dyeing step is shown in Fig. 5. As expected K/S increases and L-value decrease with more negative redox potential in the electrolyte. K/S increases with the amount of dyestuff fixed on the sample. Under the experimental conditions applied an almost linear relation was found between redox potential in the dyebath and the amount of dyestuff fixed on the sample.

In Fig. 6 the decrease in redox potential as function of charge flow is shown. Similar to the redox titration curves published in previous papers the redox potential in the dyebath decreases with charge flow [8,12,13]. Again experiment C shows deviations form the general trend, and the measured redox potential is more positive than expected from the applied charge flow. This can be explained by the higher oxidative load which reduces the overall efficiency of the reduction process in case of sample C.

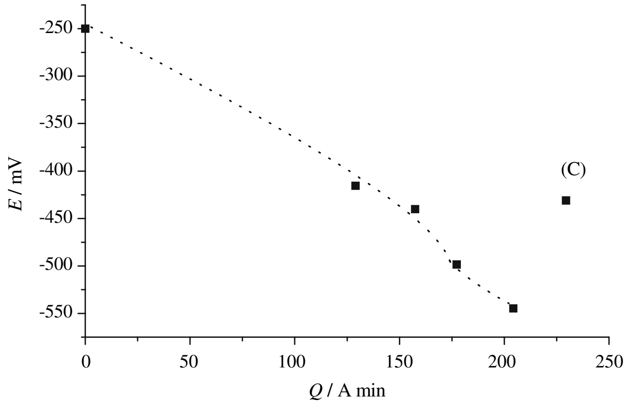

Fig. 6 Redox potential *E* (mV) in the dyebath as function of charge flow *Q* (A min)

The electrochemical measures thus go parallel with the experimentally observed colour depth.

Cathodic reduction of CI Sulphur Black 1 permits establishment of defined dyeing conditions at temperatures from ambient to 70 °C, the upper limit being defined by the construction of the electrolyser. Within this temperature range reproducible conditions cannot be established when sugar type reducing agents are used [9]. Comparable conditions for reference dyeings were thus not available.

From the experiments energy consumption of the reduction process can be estimated. To obtain the reduced form of CI Sulphur Black 1 in experiment E a charge flow of 204 A min was required with an average cell voltage of 5.5 V (U_1–U_3 = 4–7 V). In a volume of 2 L catholyte containing 20 g L^{-1} Sulphur Black 1 an amount of 40 g could be reduced with 18.7 Wh. This corresponds to an energy consumption of 0.935 kWh/kg crude CI Sulphur Black 1. For chemical reduction of 1 kg commercial Sulphur Black 1 300 g glucose and 25 g $Na_2S_2O_4$ are required [13].

4 Conclusions

Direct cathodic dyestuff reduction of CI Sulphur Black 1 can be used to substitute non-regenerable reducing agents in dyeing processes. The direct coupling of a multi-cathode electrolyser to a dyeing unit permits immediate preparation of the reduced dyebath and steering of the dyeing conditions by measurement of the cell current and redox potential of the dyebath. Analysis of the colour depth by measurement of K/S and CIELab-coordinates indicates that, at the experimental conditions chosen, the colour depth of the dyeings depends on the redox potential in the dyebath. These results are in agreement with the behaviour of CI Sulphur Black 1 in the presence of reducing sugars as reducing chemicals published by Blackburn and Harvey [9].

Charge flow applied to reduce a dyebath could be used as a measure to predict colour depth; however, cell efficiency and dyestuff re-oxidation due to air-oxidation have to be considered and kept constant. Only identical experimental conditions will permit reproducible dyestuff reduction at given charge flow.

For a technical application thus both redox potential measurement and applied charge flow form useful measures to achieve reproducible dyeing conditions.

While the redox potential will be more important to describe the dyestuff reduction, charge flow measurement and achieved redox potential will be helpful to characterise the efficiency of the electrochemical installation.

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