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# Pilot-scale electrolyser for the cathodic reduction of oxidised C.I. Sulphur Black 1

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**Abstract**

A multi-cathode electrolyser was used for the direct cathodic reduction of oxidised, dispersed C.I. Sulphur Black 1. Crude C.I. Sulphur Black 1 at concentrations of 80 g $L^{-1}$ and 131 g $L^{-1}$ could be reduced using a cathodic current density of 5.3 mA $cm^{-2}$. During reduction at pH 12.2–12.6 the redox potential fell from −270 mV to between −550 mV and −600 mV. As crude C.I. Sulphur Black 1 contains considerable amounts of reductants, the current yield was >100% of theoretical value. Energy consumption for the reduction of 1 kg of crude C.I. Sulphur Black was ∼1.1 kW h $kg^{-1}$. The reduced C.I. Sulphur Black 1 was directly used for laboratory dyeing of cotton yarn. Kubelka–Munk values and CIELab coordinates of dyeings using cathodically or chemically reduced dyestuff showed only small differences, indicating similar dyeing behaviour of the reduced dye, independent of the reduction technique.

*Keywords:* Sulphur dye; C.I. Sulphur Black 1; Cathodic reduction; Black denim; Multi-cathode electrolyser; Cotton

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## 1. Introduction

A considerable amount of the annual production of more than 80,000 tons of C.I. Sulphur Black 1 (SB1) is used for dyeing of black denim (jeans) [1,2]. These dyeings are made on slasher- or rope-type dyeing machines, where only the warp yarn is dyed before the fabric is weaved. During the synthesis, C.I. Sulphur Black 1 is released as an oxidised water insoluble filter cake, which then has to be reduced by alkaline solutions, mainly of sodium sulphide or glucose [3–6]. Commercial liquid preparations of C.I. Sulphur Black 1 contain the dyestuff in its reduced form, which is soluble in alkali. The same reducing agents may also be used in the dyeing process to stabilise the reduced form of the dyestuff during the dyeing procedure, and to inhibit uncontrolled re-oxidation of the dyestuff by atmospheric oxygen [3,7–9].

A reduction potential of −600 mV is required for optimal dyeing results [8,9], which at present is achieved predominantly by the use of chemical reducing agents. These reagents cannot be regenerated, and hence present dyeing techniques suffer from the disadvantages of significant chemical costs as well as the associated environmental costs of high toxicity and high chemical oxygen demand of the waste water [6].

A promising strategy to replace chemical reducing agents is direct cathodic reduction of the dyestuff [10]. Previous studies to reduce crude filter cake of C.I. Sulphur Black 1 by electrochemical methods have successfully demonstrated the viability of direct cathodic dyestuff reduction and application of the reduced dye in continuous pad-steam dyeing processes [11–13]. For exhaust dyeing operations, where only low concentrations of dye are used in the dyebath, the application of indirect cathodic reduction with use of mediator systems has also been proposed [14].

C.I. Sulphur Black 1 can undergo several reduction/oxidation steps in solution, which is the electrochemical basis to use the dyestuff both as colourant and as a mediator. A reduced

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dyestuff molecule is able to transport a reduction capacity of up to six equivalents from the cathode into the dyebath and thus can also act as a redox mediator [8].

The concentration of dye in baths is dictated by the colour depth to be achieved in dyeing. As the current density is limited in exhaust baths of low dyestuff concentrations, there is a need for flexible cells capable of operation at low current densities. In multi-cathode electrolysers a number of cathodes, which operate at low current density, are combined with a common anode. Thus a high overall cell current can be achieved even when the applied cathodic current density remains low [15].

In this paper we describe the use of a pilot-scale multi-cathode electrolyser to prepare 12 L volume of dyebath for black denim dyeing. Reduced C.I. Sulphur Black 1 was prepared by direct cathodic reduction of dispersed oxidised C.I. Sulphur Black 1. The catholyte then was used for dyeing experiments. Black denim dyeing was simulated on a Mini-loop laboratory dyeing unit which simulates the slasher-type denim process. Colour depth was analysed as a function of the reduction state, bath temperature and dip time. For comparisons, standard dyeings with use of glucose/dithionite as reducing agent were prepared.

## 2. Experimental details

### 2.1. Chemicals

Crude filter cake C.I. Sulphur Black 1 (water containing solid, dye content 50% by mass, DyStar Frankfurt a. M., Germany) was used as delivered. The concentrations cited for the dyestuff are of the crude product.

*Primasol*® *NF* (BASF AG, Ludwigshafen a. R., Germany) was used as a wetting agent.

Analytical grade $K_3[Fe(CN_6)]$ and NaOH were used for the determination of reducing equivalents in the catholyte.

For the reference dyeings technical grade glucose (*Reductor D*, Clariant, Basel, Switzerland), sodium dithionite and NaOH were used. Technical grade NaOH was used for the preparation of ground electrolyte.

### 2.2. Laboratory scale multi-cathode electrolyser

A multi-cathode flow-through electrolyser with three-dimensional cathodes was used for the reduction experiments. The cathode stack was built up of 10 isolated cathode units which were connected to independently adjustable power supply units. All cathode units were connected to the common anode. Anolyte and catholyte were separated by a cation exchange membrane (Thomapor MC-3470). The catholyte flow was parallel to current flow through the porous cathode stack.

The redox potential in the catholyte was measured with a Pt electrode vs. an Ag/AgCl, 3 M KCl reference (potentiometer Metrohm 654 pH-meter, Herisau, Switzerland). A general scheme of the electrolyser is given in Fig. 1.

### 2.3. Determination of current yield

Current yield was calculated from analytical determination of reducing equivalents formed in solution as a function of electrolysis. Catholyte of 1.25 ml was added to a warm mixture of 30 ml distilled water and 6 ml 1 M NaOH maintained at 50–60 °C. Redox titration with 0.1 M $K_3[Fe(CN)_6]$ was performed under an inert gas atmosphere at 50–60 °C. Potentiometric titration was performed using a titroprocessor equipped with a Pt redox electrode and an Ag/AgCl, 3 M KCl reference (Orion 960 autochemistry system, Boston, MA).

The experiments were structured in two parts:

- phasewise electrochemical reduction of SB1 (phases I–VI) and

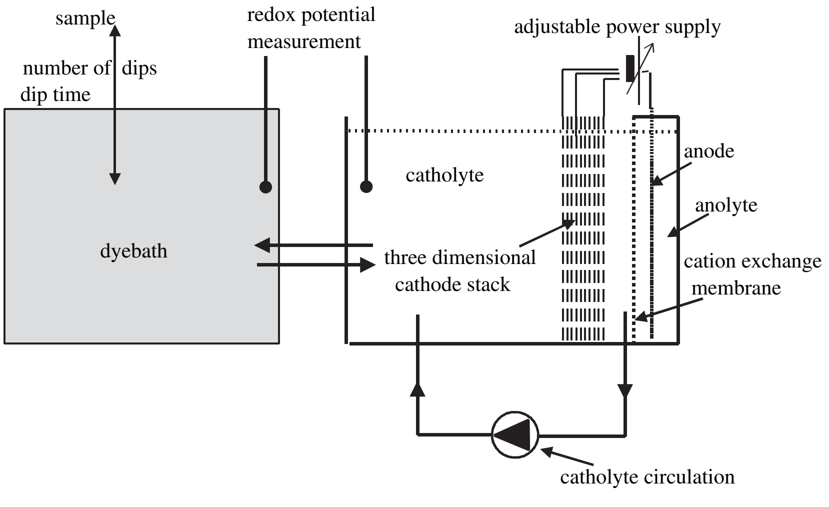

Fig. 1. Scheme of the multi-cathode electrolyser. It consists of three-dimensional cathode stack 20 × 20 $cm^2$, 10 stainless steel cathodes each 0.19 $m^2$ area, total area of cathode stack 1.9 $m^2$, catholyte volume 12 L, circulation 20 L $min^{-1}$, Pt-mixed oxide coated titan anode 400 $cm^2$, anolyte 1.9–2 L 1 M NaOH, cathodic current density 0.5–5 A $m^{-2}$, cell current 1–10 A.