

# Cathodic decolourization of textile dyebaths: Tests with full scale plant

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## Abstract

Direct cathodic reduction of azo dyes permits decolourization of intensively coloured textile wastewater without addition of chemicals or formation of sludge. The technique is of particular interest for the treatment of concentrated dyebaths from pad batch-dyeing with reactive dyes which contain on average about 50 g  $L^{-1}$  of dyestuff. On the basis of laboratory scale experiments with model dyebaths and dyebath samples from technical application a scale-up was performed. A multicathode electrolyser for a maximum cell current of 150 A successfully was tested in a dyehouse. The treatment capacity of the installed electrolyser was 1 m<sup>3</sup> of used concentrated dyebath per day. This corresponds to the full amount of such concentrates which have to be treated in a medium sized dyehouse. By cathodic decolourization the absorbance of the concentrated dyebaths was lowered to approximately 20% of the initial value with an energy consumption of 20–25 kWh m<sup>-3</sup>.

#### 1. Introduction

A large amount of coloured wastewater containing unfixed dyestuff is released from dyehouses as a byproduct from textile dyeing operations. As a result legal limits for the absorbance of wastewater released from textile dyehouses have been defined in many countries [1]. To solve the problem of highly coloured wastewater numerous attempts to decolourize textile effluents have been proposed, for example, by oxidative destruction [2], biological treatment [3], adsorption and precipitation [4, 5] and reductive treatment [6]. For all the proposed techniques great care has to be taken to keep the costs of such processes at reasonable levels and to avoid the formation of byproducts which cause additional costs for secondary treatment or disposal (e.g., formation of AOX, disposal of sludge).

In pad-batch dyeing of cellulose textiles with reactive dyes at the end of the impregnation process the residual filling of the padder and a certain surplus of dyestuff solution required to finish the process at defined conditions has to be withdrawn and is released into the wastewater. Depending on the demands of fashion and on the textile material processed in a dyehouse an average concentration of 50 g L<sup>-1</sup> dyestuff is quite common [7]. Such dyebaths cannot be regenerated and a volume of 30–50 L of dyebath is released at the end of each impregnation process. Depending on technical parameters (e.g., the average length of a lot to be dyed) a total volume of 500–1000 L of highly coloured dyebaths

has to be treated per day in a medium sized dyehouse (average production length of dyed material 10–20 million square metres per year).

As the main part of textile dyes contains azo groups in the chromogene, the direct cathodic reduction to the corresponding amines could be an interesting process for the decolourization of highly coloured concentrated dyestuff solutions [8, 9]. Results of experiments performed at laboratory scale, indicate that the cathodic decolourization of azo groups in textile dyes is a useful technique particularly for the treatment of concentrated dyestuff solutions [9, 10]. As in European dyehouses the use of azo dyes which can release carcinogenic amines properties has been banned for several years, only products with low toxic potential are released from reductive processes. A comparable pattern of products is formed during the reductive treatment of reactive dyes in standard processes, for example, reductive discharge printing.

As a result of the promising laboratory-scale experiments, a full-scale test with plant dimensions in a dyehouse was planned and carried out. In this paper the scale-up and the results obtained during the test run at technical scale are presented. As a first step the experimental basis was evaluated in the laboratory experiments using model recipes. Then the decolourization of dyebaths from real processes was investigated. Based on these results a modification of the cathodes of a standard multicathode batch electrolyser was performed to meet the technical demands of the decolourization process. To check the modified technical scale cell, decolourization experiments with selected model dyes were performed and a full scale optimization in a textile dyehouse was also performed. Results describing the performance of the cell for cathodic dyestuff decolourization are presented.

## 2. Experimental details

### 2.1. Materials

All chemicals used were technical grade products. With regard to the amount of dyestuff required for the scaleup experiments, commercial products were used for all experiments. In many cases neither chemical structures nor Colour Index numbers (C.I.) are available from the dyestuff supplier, thus in this paper the technical product name and the name of the supplier are presented to define the type of dyestuff used (Table 1). In the full scale tests in the textile dyehouse a mixture of 8–10 different dyebaths was used as catholyte. Such mixtures contained various dyes and chemicals, so these solutions only were characterized by measurement of the absorbance at four selected wavelengths (445, 520, 620 and 660 nm) [1].

#### 2.2. Apparatus and procedures

## 2.2.1. Laboratory scale multicathode electrolyser

A multicathode flow-through electrolyser with three dimensional cathodes was used for the reduction experiments. The cell is described in more detail in [11]. Anolyte and catholyte were separated by a cation exchange membrane (Nafion<sup>®</sup>). Important data for the cell are given in Table 2. The catholyte flow was parallel to the current flow through the porous cathode stack.

Each cathode unit was connected to a separately adjustable current supply, which was connected to a common anode. The redox potential in the catholyte was measured with a Pt electrode vs an Ag/AgCl, 3 M KCl reference.

## 2.2.2. Pilot scale multicathode electrolyser

A De Nora multicathode electrolyser constructed for the recovery of heavy metals from wastewater was modified for this application. Instead of cathodes made from

*Table 2.* Geometric data and general experimental conditions used in the laboratory decolourization experiments

	Experimental parameter	
Cathode	stainless steel fabric, front area 3	$10 \text{ cm} \times 10 \text{ cm}, 100 \text{ cm}^2$
	isolated cathode units, each	1440 cm <sup>2</sup>
	total area	$4320 \text{ cm}^2$
Catholyte	volume composition catholyte flow flow in the cathode temperature	700–750 ml alkaline dyestuff solution 140–150 ml min <sup>-1</sup> 0.06 cm s <sup>-1</sup> 22–28 °C
Anode	stainless steel plate, front area	$10 \text{ cm} \times 10 \text{ cm}, 100 \text{ cm}^2$
Anolyte	volume composition	300–350 ml 0.5–1.0 м NaOH
Cell current	per cathode unit total	0.5 A 1.5 A

copper foil, stainless steel fabric was mounted into the cathode frames because all previous laboratory and full scale electrolysis tests were performed with this material [9-13]. The used type of stainless steel fabric offers good mechanical stability, high porosity and surface area at moderate costs.

A schematic presentation of the electrolyser is given in Figure 1. The cell was built up as a divided cell with two anodes and 24 cathodes. The distance between two cathode units was about 3 cm thus no isolator was required between the cathode units. Each cathode unit had a geometric area of  $3573 \text{ cm}^2$  corresponding to a surface area of  $8580 \text{ cm}^2$ . According to Figure 1, 20 cathode units were connected to the power supply. The catholyte circulation was perpendicular to the current direction.

An adjustable power supply was used to supply the cathodes with similar current density. The current fed into the different cathodes was adjusted by adjustment of the voltage of the power supply. The relationship of the various cell voltages was fixed by the construction of the transformer; thus only part of the cathodes could be connected to the power supply to achieve a relatively uniform current distribution on the connected cathodes. Thus, instead of a maximum of 24 cathodes only 20 cathodes were connected to the power supply. The

Table 1. Dyestuffs used in model experiments (laboratory scale and full technical scale)

Symbol	Dyestuff	C.I.	Supplier
RB	Remazol Black B Plv. 133%	React. Black 1	DyStar, Frankfurt, Germany
DR	Drimaren Brillant Red K-4BL		Clariant, Basel, Switzerland
DY	Drimaren Brillant Yellow K-3GL		Clariant, Basel, Switzerland
СО	Cibachron Orange C-3R		CIBA Spezialitätenchemie, Lampertheim, Germany
LM	Levafix Marine CA		DyStar, Frankfurt, Germany
СВ	Cibachron Blue C-R		CIBA Spezialitätenchemie, Lampertheim, Germany



*Fig. 1.* Scheme of the technical scale batch electrolyser, a1 and a1', a5 and a5', a7 and a7', cathode units in position 1, 5, 7; b and b' anodes, c and c' cation exchange membrane, d1, d5 and d7 power supply, e catholyte, f and f' anolyte compartment, g catholyte circulation, h drain.

*Table 3.* Geometric data and general experimental conditions of the technical scale electrolyser

	Experimental parameter	
Cathode	stainless steel fabric 20 cathode units, area each total area	0.8580 m <sup>2</sup> 17.16 m <sup>2</sup>
Catholyte	volume composition catholyte flow temperature	400 L alkaline dyestuff solution $140-150 \text{ Lmin}^{-1}$ ambient temperature
Anodes	Pt-mixed oxide coated titan geometric area each	0.39 m <sup>2</sup>
Anolyte	total volume composition (in model expts. additional)	116 L 0.32 M NaOH, (2 g $L^{-1}$ complexing agent, phosponate)
Cell current	total current cathodic current density	150 A 8.7 A m <sup>-2</sup>

maximum cell current was defined as 150 A and as 10 A for a cathode unit; the corresponding current density was  $11.7 \text{ A m}^{-2}$ .

The power supply permitted only the adjustment of the cell voltage, thus the cell current was held within a defined range (e.g., 110–130 A) by manual adjustment of the cell voltage.

## 2.3. Photometrical determination of the decolourization

In the laboratory experiments the decrease in absorbance was registered photometrically using a diode array spectrophotometer with a 0.1 mm path length cuvette (Zeiss CLH 500/MCS 521 UV–VIS, Carl Zeiss Jena, Germany). The decolourization in the full scale tests was observed by means of a transportable onebeam filter photometer (Merck SQ 300, Merck, Darmstadt, Germany) equipped with a 0.1 mm path length cuvette. The wavelengths for measurement of the absorbance were selected according to the standard procedure for the determination of the absorbance in effluents [14].

## 3. Results and discussion

## 3.1. Laboratory scale experiments

The overall reaction scheme for the cathodic reduction of azo groups is shown in Equations 1 and 2. For complete dyestuff reduction to the corresponding amines  $4 e^-$  are consumed per azo group.

As a result of the ion-transport through the cation exchange membrane, NaOH is formed in the catholyte when a solution of NaOH is used as anolyte, while  $H_2O$  is formed in the catholyte in case of an acidic anolyte.

$$-N = N - + 2e^{-} + 2H^{+} = -NH - NH - (1)$$

$$-\mathbf{NH}-\mathbf{NH}-+2\mathbf{e}^{-}+2\mathbf{H}^{+} = -\mathbf{NH}_{2}+\mathbf{H}_{2}\mathbf{N}-$$
(2)

The laboratory scale experiments were performed to obtain data for the dimensions of the pilot scale electrolyser. Corresponding to the planned application the cathodic reduction of model solutions was performed first, then technical recipes were tested in the multicathode electrolyser. The experiments were performed at room temperature.

Important cell data are presented in Table 4 and results describing the decolourization are given in Table 5 and Figures 2 and 3.

In the model experiments no ground electrolyte was added to the catholyte; thus the cell voltage decreased during the electrolysis experiments from more than 10 V at the beginning of the experiment to an average value of 4-5 V. The cell voltage at the beginning of the experiments is mainly dependent on the concentration of dyestuff present in the dyebath/catholyte. As 0.5 M NaOH solution was used as anolyte, NaOH was formed in the catholyte during the reduction process and the cell voltage decreased with electrolysis time. 50% NaOH was added to the anolyte to maintain the caustic soda concentration in the anolyte constant. The added amount of NaOH was calculated on the basis of the transported charge, according Faraday's law. In the case of laboratory experiments at a total cell current of 1.5 A, 3.0 ml of 19.2 M NaOH were added to the anolyte per hour of electrolysis.

A technical dyeing recipe contains NaOH, sodium metasilicate, soda and other conducting electrolytes in such concentration that low cell voltages are measured at the beginning of the process. In the test with technical recipes the composition of the ground electrolyte was determined by the dyeing recipe and no adjustment of

Table 4. Cell data describing laboratory scale experiments

Expt.	Dye	Current /A	E /mV	U1 /V	U2 /V	U3 /V	Temp. /°C
1	RB	$3 \times 0.5$	-450	14.1–4.2	17.5-5.0	18.5-5.1	22–26
2	DR	$3 \times 0.5$	-206	7.7-5.3	10.2-5.6	10.8 - 5.9	23-28
3	DY	$3 \times 0.5$	-28	12.9-5.0	15.1-6.3	16.0-6.5	23-27
4	LM	$3 \times 0.5$	-13	13.7-5.6	16.9-10.0	17.6-12.0	23-29
5	techn.	$3 \times 0.5$	-637	3.1-3.5	3.3-4.1	3.3-4.4	22-26
6	techn.	$3 \times 0.5$	-802	3.5–3.3	3.7–5.8	3.8-6.4	23–27

Table 5. Experimental data describing the laboratory scale experiments with model dyes and technical dyebath formulations (tech.)

Expt.	Dye	Catholyte conc. dye /g $L^{-1}$	Wetting agent /g L <sup>-1</sup>	Anolyte NaOH /M	Final decolourization %, (wavelength)	Charge, Q /Ah L <sup>-1</sup>	Energy consumption /kWh m <sup>-3</sup>	80% decolourizaiton Charge, $Q$ /Ah L <sup>-1</sup>	80% deco- louriztion Energy con- sumption /kWh m <sup>-3</sup>
1	RB	1.0	0.5	0.5	85.7, (599 nm)	16.8	134	14.6	117
2	DR	10.0	0.5	0.5	91.1, (545 nm)	11.1	89	9.8	78.6
3	DY	10.0	0.5	0.5	<5, (399 nm)	5.9	47	-	-
4	LM	10.0	0.5	0.5	<15, (575 nm)	3.9	31	-	-
5	techn.	$\sim 25$	1.0	1.0	84, (416 nm)	5.0	25	2.0	10
6	techn.	$\sim 50$	1.0	1.0.	<10, (625 nm)	5.0	27.5	_	-



Fig. 2. Decolourization of a technical dyebath in laboratory scale as function of electrolysis time (expt. 5,  $\sim$  25 g  $L^{-1}$  dyestuff).

the concentration of the ground electrolyte was possible with regard to the cost of the process.

The decolourization as function of electrolysis time for experiment 5 (technical dyebath) is shown in Figure 2. The decrease in absorbance for experiments 1-6 measured at the wavelength of maximum absorbance is shown in Figure 3. In Table 5 the composition of the model solutions, the final decolourization obtained and the energy consumption are summarized. The energy consumption for a lowering of the absorbance to 20% (80% decolourization) is also given.



*Fig. 3.* Decolourization of dyes in laboratory scale experiments 1–6, observed at wavelength of maximum absorption 1 (599 nm), 2 (545 nm), 3 (399 nm), 4 (575 nm), 5 (416 nm), 6 (625 nm). Experiments: ( $\blacksquare$ ) 1, ( $\bullet$ ) 2, ( $\blacktriangle$ ) 3, ( $\bigtriangledown$ ) 4, ( $\diamondsuit$ ) 5 and ( $\Box$ ) 6.

In experiments 3 and 4, performed with Drimaren Brillant Yellow K-3GL (DY) and Levafix Marine CA (LM), only minimal decolourization (<5 and <15%) was observed, indicating that not all individual types of dye will be decolourized successfully (e.g., anthrachinoid dyes, phthalocyanine dyes). V5 and V6 show results obtained with technical formulations of dyebaths. In V5 all dyes were azo dyes so intensive decolourization could be obtained, while in V6 the main component was a blue–green phthalocyanine dye which was found to be resistant to the cathodic treatment.

During electrolysis the redox potential in the catholyte changes to more negative values. As the redox potential in the catholyte is determined by the reduced products

946

formed, the potential is dependent on the composition of the dyebath to be decolourized. Thus, in technical processes the redox potential will be a rather complex parameter, which will be of low practical importance, so these values are given for the model electrolysis experiments only. The values given in Table 4 were registered at the end of the electrolysis process.

From the charge passed and an average value of the cell voltage an estimation of the electric energy consumption for the decolourization of 1 m<sup>3</sup> of dyebath can be performed. Besides the NaOH consumption in the anolyte, which has to be compensated for by the addition of NaOH, the consumption of electric energy will form the major part of the process costs. The data for the energy consumption given in Table 5 indicate that on the basis of the laboratory scale experiments the electrical energy consumption ranges from more than 100 kWh m<sup>-3</sup>, in the case of model experiments with low concentration of conducting electrolytes, to 25 kWh m<sup>-3</sup> in the case of technical recipes containing considerable concentrations of salt and alkali.

In technical dyebaths dyestuff concentrations usually range from 10 to 50 g L<sup>-1</sup> and, according to the dyestuff manufacturers recommendations, 10–20 ml L<sup>-1</sup> NaOH 50% (0.187–0.375 M NaOH) or other basic compounds, for example, sodium metasilicate are added to obtain dyestuff fixation. In the case of high dyestuff concentration, up to 100 g L<sup>-1</sup> urea is added as hydrotrope [7].

From the values obtained from laboratory scale experiments with concentrations of dyestuff of 10 g  $L^{-1}$  an average consumption of electrical energy of about 25 kWh m<sup>-3</sup> was expected for a full scale process.

### 3.2. Technical scale dyebath decolourization

For a general system check the electrolyser was tested with model dyebaths of known composition before installation in the dyehouse. In the dyehouse a 1000 L container was installed to collect the used dyebath. From this storage vessel 400 L were treated in the electrolyser in batch processes. The standard procedure was as follows: (i) filling of the cathode compartment of the cell with used dyebath, (ii) start of anolyte circulation and catholyte circulation, (iii) turn on of power supply and adjustment of cell voltage to achieve a cell current of about 120–130 A, (iv) decolourization of batch, addition of NaOH to anolyte according to Faraday's law, (v) observation of decolourization, cell voltage and cell current, and (vi) release of decolourized batch after defined duration of electrolysis (e.g., 8 h, 16 h).

The composition of the model dyebaths and the results of the electrolysis tests are given in Table 6. Results of the technical test runs describing the change in absorbance at selected wavelengths, transported charge and the energy consumption per  $m^3$  are given in Table 7. From the duration of the experiments and the applied cell current the average charge flow per 1 L of dyebath and for the 75% decolouration of 1  $m^3$  dyebath was calculated. In Figure 4 the cell voltage and the current of the cathode units for experiments 7 and T1 are shown. The energy consumption of the process was calculated on the basis of an average value for the cell voltage of 9 V (expt. 7) and 8 V (expt. T1).

In the tests with model dyebaths a charge flow of about 1400 Ah and an energy consumption of 14 kWh was required to reach 75% decolourization of 400 L dyebath, so the corresponding values for the technical test run were expected to be about 30 kWh m<sup>-3</sup>.

In the case of technically used dyebaths the conductivity of the catholyte will vary depending on the dyeing recipe, which mainly is determined by type and concentration of the dyestuff used. At normal conditions of operation a residual volume of about 40–50 L is released at the end of a dyeing batch; thus 8–10 different dyebaths had to be collected to obtain a total volume of 400 L, which was required as catholyte filling.

In Figures 5 and 6 the decolourization as function of time is shown for experiments T4 and T9 as typical representation for the decolourization experiments. As can be seen from the curves and the data shown in Table 7, an electrolysis time of 8 h was sufficient to achieve the main part of the decolourization (Figure 6). After 16 h electrolysis the consumption of electrical energy per  $m^3$  was doubled, but only low additional decolourization was observed (Figure 5).

At the end of the test period no deposition of organic matter was observed on the cathodes and no irreversible membrane fouling was observed. Cleaning of the cell by a soft water jet was sufficient to remove any residue.

Table 6. Experimental data describing the technical scale experiments with model dyes (average cell voltage 9 V)

Expt.	Dye	Catholyte conc. dye /g $L^{-1}$	Wetting agent $/g L^{-1}$	NaOH /M	Cell current /A	Duration of electrolysis /h	Final de- colourization %, (wave- length)	Charge, $Q$ /Ah L <sup>-1</sup>	Energy consumption /kWh m <sup>-3</sup>	75% De- colourization Charge, $Q$ /Ah L <sup>-1</sup>	75% Deco- lourization Energy con- sumption /kWh m <sup>-3</sup>
7	RB	10.0	0.5	0.19	130-140	10.5	86.0, (620 nm)	3.54	31.9	3.38	30.4
8	DR	10.0	0.5	0.19	110-140	10.0	97.8, (540 nm)	3.13	28.2	1.17	10.5
	DY	5.0					36.6, (405 nm)				
9	CO CB	15.0 12.5	0.5	0.19	110-130	9.0	76.9, (445 nm) 75.6, (620 nm)	2.7	24.3	2.70	24.3

Anolyte composition: 0.3 M NaOH.

n	1	0
9	4	0

Table 7. Experimental data describing the technical scale experiments using technical process dyebaths (anolyte  $\sim 0.3$  M NaOH, average cell voltage 8 V)

Expt.	Absorbance start	Absorbance end	Decolouri- zation /%	Cell current /A	Time of electrolysis /h	Charge, Q /Ah	Energy consumption /kWh	Energy consumption /kWh m <sup>-3</sup>
T1	2.987 (445)	0.390 (445)	86.9 89.8	110–140	12.4	1550	12.4	31.1
	3.901 (620)	0.885 (620)	77.3					
	2,276 (660)	0.305(660)	86.6					
T2	1.250 (445)	0.083 (445)	93.4	120-140	16.0	2080	16.6	41.6
	1.201 (520)	0.019 (520)	98.4					
	0.716 (620)	0.029 (620)	96.0					
	0.442 (660)	0.000 (660)	100					
T3	1.027 (445)	0.075 (445)	92.7	120-130	16.0	2000	16.0	40.0
	1.084 (520)	0.039 (520)	96.4					
	0.683 (620)	0.118 (620)	82.7					
	0.397 (660)	0.027 (660)	93.2					
T4	1.642 (445)	0.390 (445)	84.9	110-120	16.0	1840	14.8	36.9
	2.281 (520)	0.389 (520)	89.7					
	2.17 (620)	0.885 (620)	71.9					
	0.942 (660)	0.305 (660)	78.7					
T5	1.61 (445)	0.430 (445)	73.3	110-120	8.0	920	7.4	18.4
	2.22 (520)	0.364 (520)	83.6					
	2.106 (620)	0.756 (620)	64.1					
	0.908 (660)	0.279 (660)	69.3					
T6	2.794 (445)	1.012 (445)	63.8	100-120	10	1100	8.8	22.0
	3.701 (520)	1.060 (520)	71.4					
	3.713 (620)	1.181 (620)	68.2					
	2.065 (660)	0.484 (660)	71.7					
T7	2.420 (445)	0.512 (445)	78.8	110-120	16	1840	14.8	36.9
	3.330 (520)	0.522 (520)	84.3					
	3.768 (620)	1.376 (620)	63.5					
	2.221 (660)	0.484 (660)	78.2					
T8	1.444 (445)	0.386 (445)	73.3	100-120	8.0	880	7.0	17.5
	1.939 (520)	0.422 (520)	78.2					
	2.262 (620)	1.108 (620)	51.0					
	1.050 (660)	0.394 (660)	62.5					
T9	2.281 (445)	0.602 (445)	73.6	110-120	8.0	920	7.4	18.4
	2.925 (520)	0.835 (520)	71.5					
	3.724 (620)	1.427 (620)	61.7					
	2.137 (660)	0.550 (660)	74.3					
T10	0.868 (445)	0.179 (445)	79.4	100-120	8.0	880	7.0	17.6
	0.975 (520)	0.084 (520)	91.4					
	0.309 (620)	0.131 (620)	57.6					
	0.138 (660)	0.043 (660)	68.8					

Wavelength corresponding to the absorbance values is given in parentheses.

### 4. Conclusions

The cathodic decolourization of azo dyes permits a lowering of the absorbance of highly coloured wastewater from textile dyehouses. The method is particularly suited to the treatment of highly coloured dyestuff solutions which are typically of pad-batch dyeing with reactive dyes. As a result of the treatment intensive decolourization is obtained, while the follow-up mineralization of the amino products has to be performed in the wastewater treatment plant. Such a strategy is favourable because the contribution of dyes in used dyebaths to the total chemical oxygen demand of textile effluents is low compared to the total load released from other textile treatment steps (e.g., scouring and bleaching). As the dyebaths contain chlorides the use of a divided cell is of particular importance to avoid formation of chlorine and chlorinated products.

Basing on results obtained from laboratory scale experiments a technical scale electrolyser with a capacity of 1 m<sup>3</sup> per day was constructed and tested in full scale operation for treatment of solutions containing 10–50 g  $L^{-3}$  reactive dye. The multicathode electrolyser was designed for a maximum cell current of 150 A. The planned capacity of 1 m<sup>3</sup> per day corresponds to the full volume flow of such concentrates released from a medium size dyehouse.

During the test run an average decolourization of 80.0% at 445 nm, 85.5% at 520 nm, 69.4% at 620 nm and 78.3% at 660 nm was realized. The lower degree of decolourization at 620 nm is due to the presence of stable blue–green dyestuffs, which contain phthalocya-



*Fig.* 4. Cell voltage U (circles) and current (squares) of the cathode units for exp. 7 (t = 410 min) ( $\bigcirc$ ,  $\Box$  respectively) and exp. T1 (t = 265 min) ( $\bigcirc$ ,  $\blacksquare$  respectively).



*Fig.* 5. Decrease of extinction as function of electrolysis time for experiment T4 at different wavelengths. Key: ( $\Box$ ) 445, ( $\bullet$ ) 520, ( $\triangle$ ) 620 and ( $\nabla$ ) 660 nm.



*Fig. 6.* Decrease of extinction as function of electrolysis time for experiment T9 at different wavelengths. Key:  $(\Box)$  445,  $(\bullet)$  520,  $(\triangle)$  620 and  $(\mathbf{\nabla})$  660 nm.

nine or anthraquinoide groups in their chromophoric system.

The average energy consumption was found to be near 20 kWh m<sup>-3</sup>. A further lowering of the electrical energy consumption is expected to result from optimisation of the cell geometry, for example, by decreasing the interelectrode gap. Experiments at elevated temperatures were not performed because even a small increase in temperature (e.g., from 20 °C to 40 °C) will consume 23 kWh m<sup>-3</sup> and will double the overall energy consumption [9,10]. At a cell current of 130 A the consumption of NaOH in the anolyte was 0.25 L of 50% NaOH solution per hour.

Assuming an average concentration of 50 g  $L^{-1}$ dyestuff about 20 kg of dyestuff were decolourized per batch and an overall amount of 200 kg dyestuff were treated during the technical test period. On the basis of an average charge flow of 200-300 As  $g^{-1}$  of technical dyestuff [9,10] and a dyestuff concentration of 50 g  $L^{-1}$ , a charge of  $(4-6) \times 10^6$  C can be estimated for full dyestuff decolourization. During the technical tests about 70-80% decolourization was obtained with a transported charge of  $(3.5-7.9) \times 10^6$  C. From these data a current efficiency better than 50% can be estimated for the technical process [9,10]. In the literature at similar apparative conditions for a dyestuff concentration of 0.5 g  $L^{-1}$  a current efficiency of about 3% was determined so the value of about 50% current efficiency for a dyestuff concentration of 50 g  $L^{-1}$  lies within the expected range.

The cathodic decolourization of azo dyes has been shown to be a useful method for decolourizing highly concentrated textile wastes without addition of chemicals and without formation of precipitates and sludge, which would have additional disposal costs.

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#### References

- Regulation of the Austrian Ministry of Agriculture, 'Limitation of the emission released from textile finishing and textile treatment plants', Austrian BGBL, 207 Vienna, Austria (1992).
- W.S. Perkins, W.K. Walsh, I.E. Reed and C.G. Namboodi, *Text. Chem. Color.* 28 (1995) 31.

950

- 3. A.A. Oxspring, G. McMullan, W.F. Smyth and R. Marchant, *Biotechnol. Lett.* 18 (1996) 527.
- 4. A. Wilcock, M. Brewster and W. Tincher, Am. Dyestuff Rep. 81 (1992) 15.
- 5. K.R. Ramakrishna and T. Viraraghavan, Am. Dyestuff Rep. 85 (1996) 28.
- J. Tokuda, R. Ohura, T. Iwasaki, Y. Takeuchi, A. Kawashida and M. Nango, *Text. Res. J.* 69 (1999) 956.
- 7. DyStar, Levafix<sup>®</sup> and Remazol<sup>®</sup>, High Performance Reactive Dyes for all Requirements and Processes, 0.1010-00(E/D), 6/1999, DyStar, Frankfurt, Germany.
- 8. E. Burtscher, T. Bechtold, A. Amann, A. Turcanu and C. Schramm, *Melliand Textilber*. **74** (1993) 903.

- 9. T. Bechtold, E. Burtscher and A. Turcanu, *Tex. Res. J.* **71** (2001) 870.
- T. Bechtold, E. Burtscher and A. Turcanu, J. Chem. Technol. Biotechnol. 76 (2001) 303.
- T. Bechtold, E. Burtscher and A. Turcanu, J. Appl. Electrochem. 28 (1998) 1243.
- T. Bechtold, E. Burtscher, O. Bobleter, W. Blatt and L. Schneider, Chem. Eng. Technol. 21 (1998) 877.
- 13. W. Blatt and L. Schneider, Melliand Textilber. 80 (1999) 624.
- Deutsche Einheitsverfahren zur Wasser-, Abwasser und Schlammuntersuchung, EN ISO 7887:1994, C1 Wasserbeschaffenheit – Untersuchung und Bestimmung der Färbung (Wiley-VCH, Weinheim, 1994).