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Cathodic decolourisation of dyes in concentrates from nanofiltration and printing pastes

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Abstract

Direct cathodic reduction of dyes which contain an azo-goup in the chromophore was successfully used for decolourisation of intensively coloured concentrates from Nanofiltration treatment of textile effluents. Based on laboratory scale experiments, a technical multi-cathode electrolyser was applied for full scale decolourisation experiments at cell currents from 40 to 80 A. The absorbance of the treated wastes decreased from 60 to 80% of the initial value at an energy consumption of 2–8 kWh m^{-3}. Experiments with addition of redox mediator indicate a significant increase in decolourisation rate; however chemical consumption is increased for 0.5–1.5 kg m^{-3} of waste. The decolourisation of reactive dye containing printing pastes was also achieved at the laboratory scale, where decolourisation of 60–80% was achieved.

1. Introduction

Dyes are released during dyeing and printing operations and can be attributed to the following main sources:

- in continuous pad-batch dyeing the released residual filling of padder contains high concentrations of dyestuff [1, 2];
- in exhaust dyeing hydrolysed dyes are released with the spent dyebath;
- residual printing pastes contain a high amount of reactive dyes [3];
- washing processes following to the dyestuff application lead to the formation of a huge amount of diluted coloured waste water.

When modern formulations of dyes are used the toxicity of the dyes in the waste water is a minor problem, however the limited biodegradation of the dyes in communal waste water treatment plants has led to definition of limits for absorbance of coloured wastes [4].

The treatment of mixed waste water collected from various sources in a dye house has been the usual technique for waste water treatment for a long time [5].

Nowadays the strategy has changed towards identification and separation of waste water streams which contain a distinct chemical content and thus need further treatment [5]. As a result in many cases much lower volumes of waste water are treated using specialised techniques. The specific costs per m^3 for such treatments might be higher than for an unspecific treatment of high amounts of mixed wastes; however, the overall costs decrease while the efficiency of the treatments increase [5, 6].

The cathodic reduction of azo-group containing waste water from reactive dyeing is a suitable process for decolourisation of concentrated wastes from pad-batch reactive dyeing [1, 2]. Basic investigations and successful scale-up trials have been described [1, 2, 7, 8]. At present a full scale electrolyser for the cathodic treatment of such wastes has started operation in a textile dyehouse (cell current approx. 120–150 A).

A detailed analysis of the sources for coloured waste water released by a dyehouse indicated that 15–30% of the applied dyestuff are released into the waste water. The main part, corresponding to 50–80% of this amount, results from washing/rinsing steps and thus has been diluted to an average concentrations of 1–2 g l^{-1}.

To achieve efficient treatment of such wastes a removal and reconcentration of the dyestuff is performed by means of nanofiltration (NF) which permits a removal and reconcentration of the dyestuff to concentrates with approximately 5 g l^{-1} dyestuff [9–13]. For the treatment of such concentrates research is needed to establish suited processes. Due to the reconcentration and the volume reduction cathodic dyestuff destruction could be an interesting procedure for the treatment of NF-concentrates.

Another source for dyestuff containing wastes is found in textile printing operations [14]. The residual printing pastes and the washing water from cleaning of screens and printing equipment contain high concentrations of dyes but additional problems result from the presence of thickeners to increase viscosity and auxiliaries [3, 14–16].

In the present scientific and technical study cathodic dyestuff reduction was applied to the decolourisation of

- dyestuff containing baths from reactive dyeing (exhaust dyeing) and washing operations (continuous and exhaust dyeing) which were reconcentrated by Nanofiltration [17];
- printing pastes from reactive dye printing. These mixtures contain thickener, auxiliaries and weak oxidising agents (e.g. m-nitro-benzene-sulphonic acid sodium salt) [3].

The results were obtained by use of a laboratory multi-cathode electrolyser. Part of the results were measured in full scale operation of a technical electrolyser installed in a textile dyehouse. The data shown form a basis for the evaluation and optimisation of the cathodic dyestuff cleavage in complex systems and indicate strategies for an extension of the technique to treatment of reconcentrated dyestuff solutions and printing pastes.

2. Experimental details

2.1. *Materials*

The decolourisation experiments were performed with wastes collected from full scale technical processes. NF-concentrates used were produced by reconcentration of diluted waste water from reactive dyeing (Riedel and Tietz textile dyehouse, Limbach-Oberfrohna, manufacturer of NF-unit: Junghans, Germany).

Residual printing pastes were collected from reactive printing (Mascioni, textile printing company, Varese, Italy). The mixtures contained various dyes and chemicals, thus the samples were characterised by measurement of the absorbance at selected wavelengths.

All chemicals used were technical grade ($FeCl_3$, triethanolamine (TEA), NaOH, sodium D-gluconate (DGL)).

Addition of redox mediator was made in the form of a stock solution which was added to the catholyte. Two concentrations of mediator were tested in the catholyte 0.001 and 0.003 M (related to c($FeCl_3$)). The composition is given in Table 3 in more detail.

2.2. *Laboratory scale multi-cathode electrolyser*

A multi-cathode flow-through electrolyser with three dimensional cathodes was used for the reduction experiments. The cell is described in detail in [1]. Anolyte and catholyte were separated by a cation exchange membrane (Thomapor MC-3470). Relevant data of the cell are given in Table 1. The catholyte flow through the porous cathode stack was parallel to the current flow.

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

Table 1. Geometric data of the laboratory scale electrolyser and general experimental conditions

	Experimental parameter	
Cathode	Stainless steel fabric	20 × 20 cm
	10 cathode units, area each	0.19 m^2
	Total area	1.9 m^2
Catholyte	Volume	5–10 l
	Composition	Alkaline dyestuff solution
	Catholyte flow	20 l min^{-1}
	Temperature	Ambient temperature
Anode	Pt-mixed oxide coated titan	
	Geometric area	0.04 m^2
Anolyte	Total volume	1.5 l
	Composition	1 M NaOH
Cell current	Total current	1–6 A
	Cathodic current density	0.5–3.2 A m^{-2}

2.3. *Pilot scale multi-cathode electrolyser*

A technical scale DE NORA multi-cathode electrolyser HKE-M-60/250/S (DE NORA Deutschland, Rodenbach, Germany) designed for decolourisation of residual padder fillings was used for the technical scale tests (max. cell current 250 A). The electrolyser contained two symmetric units each unit consisting of a centre anode and 5 stainless steel cathodes on both sides of an anode. The catholyte circulation was perpendicular to the current direction. Adjustable power supplies were connected to the cathodes to permit equal current density at each cathode. The installation was fully automated thus filling, electrolysis, drain of catholyte were steered by a micro-computer.

2.4. *Determination of decolourisation*

The decolourisation was observed by means of a transportable one-beam filter photometer (Merck SQ 300, Merck, Darmstadt, Germany) equipped with a 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 [18]. The absorbance of the concentrates used for the laboratory experiments is given in Table 2.

Table 2. Absorbance of the NF concentrates used in laboratory experiments (1 mm path length)

Concentrate	Absorbance		
	445 nm	520 nm	620 nm
A	1.450	2.781	0.376
B	1.258	1.616	0.391

Table 3. Experimental conditions and concentration of mediator used in laboratory scale experiments (p_L = redox potential in solution at the start of experiment and after 60 min electrolysis, U_1 = cell voltage cathode unit 1, U_{10} = cell voltage cathode unit 10, cell voltages measured at the beginning of the electrolysis)

Expt.	Concen-trate	c(NaOH) (M)	c($FeCl_3$) (M)	c(TEA) (M)	c(DGL) (M)	pH	p_L start (mV)	p_L 60 min (mV)	I (A)	U_1 (V)	U_{10} (V)
1	A	0.094	–	–	–	12.61	+172	−436	1	2.25	2.44
2	A	0.094	0.001	0.001	0.001	12.75	+31	−449	1	2.50	2.59
3	A	0.094	0.003	0.003	0.003	12.55	+132	−457	1	2.48	2.65
4	A	0.094	0.001	0.001	0.001	12.71	+159	−491	3	4.42	5.45
5	A	0.094	0.003	0.003	0.003	12.53	+202	−507	3–2.6	4.79	5.89
6	B	0.094	–	–	–	10.18	+206	−377	1	2.91	3.39
7	B	0.094	0.001	0.001	0.001	10.13	+32	−429	1	2.64	2.99
8	B	0.094	0.003	0.003	0.003	10.22	+199	−587	1	2.75	3.41
9	B	0.094	0.001	0.001	0.001	10.20	+31	−302	3	5.69	7.24

3. Results and discussion

3.1. *Decolourisation of NF-concentrates*

Laboratory electrolysis experiments were performed with two different NF-concentrates (A and B). A volume of 5 l of concentrate was treated in the electrolyser for each experiment. The experimental conditions and the composition of added mediator are shown in Table 3.

The redox potential measured in the NF-concentrate can be used to describe the initial conditions in the catholyte. However due to the low concentration of redox active species the measured potential values are not very stable. During the electrolysis the redox potential changes towards negative values; the most negative potentials were measured in the presence of mediator (expts. 2–5, 7 and 8).

During the membrane concentration the major part of the salt and alkali passes through the filter thus a basic stock of NaOH (0.094 M, 5 ml l^{-1} of 50% NaOH solution) was added to the catholyte to increase conductivity. For concentrate A for a cell current of 1 A a cell voltage between 2.3 and 2.7 V was observed (expts. 1–3), which increased to 4.4–5.9 V for 3 A cell current (expts. 4 and 5). For concentrate B a lower pH value of 10.2 was measured in the catholyte, thus higher cell voltages were observed. With 1 A cell current cell voltage ranged from 2.6 to 3.4 V (expts. 6–8), for 3 A cell voltage was measured between 5.7 and 7.2 V (expt. 9).

In technical scale experiments the conductivity was increased by mixing the NF-retentate with alkali containing residual fillings of padders from pad batch dyeing.

Table 4 presents results and electrochemical parameters describing the performance of the laboratory scale electrolyser. The energy consumption of the process in Ah m^{-3} to achieve 50% decolourisation at a wavelength of 520 nm, the consumption of NaOH, $FeCl_3$, TEA and DGL in kg m^{-3} of treated concentrate also are given. In absence of mediator concentrate A can be decolourised to 50% of the initial absorbance with an energy consumption of 0.92 kWh m^{-3} (expt. 1). The addition of mediator increases the efficiency of the electrolysis; thus energy consumption lowers to 0.44–0.55 kWh m^{-3} (expts. 2 and 3). Increase of cell current does not result in a distinct shortening of electrolysis time but raises energy consumption to 3.2–6.4 kWh m^{-3} (expts. 4 and 5). Comparable results were obtained with concentrate B. Due to the lower pH in the catholyte cell voltage and energy consumption are higher.

Figure 1 shows the decrease of the absorbance of retentate A during experiment 1 (no redox mediator added). Intensive decolourisation was observed in both

Table 4. Results and electrochemical parameters describing the performance of the laboratory scale electrolyser: maximum decolourisation and energy consumption in kWh m^{-3} to achieve 50% decolourisation, consumption of NaOH, $FeCl_3$, TEA and DGL kg m^{-3} of concentrate

Expt.	Concen-trate	Duration (min)	Max. decolour. (%)			Time 50% decol. (520 nm) (min)	Energy consumpt. (kWh m^{-3})	Consumption of chemicals			
			(445 nm)	(520 nm)	(620 nm)			NaOH (kg m^{-3})	$FeCl_3$ (kg m^{-3})	TEA (kg m^{-3})	DGL (kg m^{-3})
1	A	165	53	69	75	90	0.92	3.76	–	–	–
2	A	150	78	96	92	55	0.55	3.76	0.16	0.15	0.22
3	A	90	74	96	92	45	0.44	3.76	0.49	0.45	0.66
4	A	300	70	89	83	80	6.4	3.76	0.16	0.15	0.22
5	A	302	75	94	83	40	3.2	3.76	0.49	0.45	0.66
6	B	135	29	60	67	100	1.3	3.76	–	–	–
7	B	110	47	80	77	60	0.8	3.76	0.16	0.15	0.22
8	B	137	38	84	81	60	0.9	3.76	0.49	0.45	0.66
9	B	120	51	81	76	30	3.1	3.76	0.16	0.15	0.22

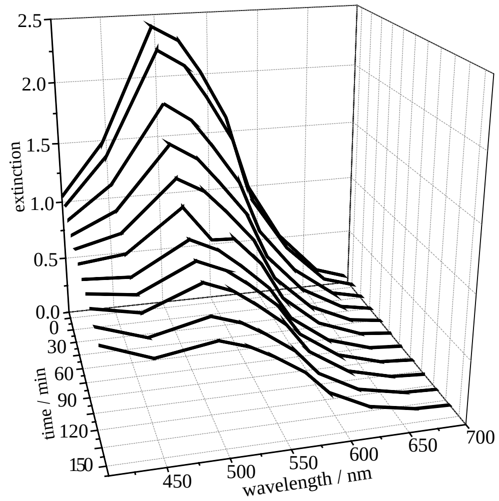

Fig. 1. Decolourisation as function of electrolysis time. Solution A, experiment 1, cell current 1 A.

experiments; however, the higher reaction rate is observed in the presence of 0.001 M redox mediator. Assuming a molar mass of 1000 g mol^{-1} for the dyestuff, an average concentration of 5 g l^{-1} dyestuff in the concentrate corresponds to a concentration of 0.005 M which continuously decreases during electrolysis. Addition of Fe(III)-complexes increases the concentration of redox-active species and thus an increased rate of decolourisation is observed; however, additional costs for chemical consumption have to be considered. Even in the case of a low mediator concentration of 0.001 M, 0.53 kg of chemicals are spent per each m^3 of electrolysed waste.

The effect of added mediator can be demonstrated by comparison of experiments 1–5. The decolourisation as a function of time recorded at 445, 520 and 620 nm for experiments 1–5 is shown in Figure 2. Compared with the results at a cell current of 1 A an increase of cell current to 3 A does not result in a distinct improvement of the decolourisation effect. The disappointing performance of the cell in experiment 4 can be explained with the beginning of bipolar effects of the cathode stack at relative high cell current of 3 A. Similar effects are observed in experiment 9 (3 A, 0.001 M mediator).

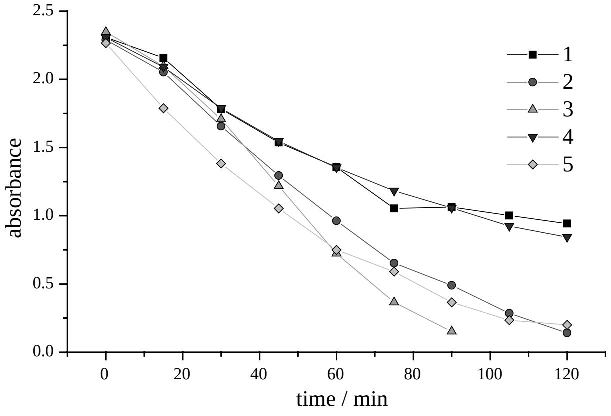

Fig. 2. Decolourisation as function of electrolysis time at selected wavelength of 445, 520, 620 nm for experiments 1–5.

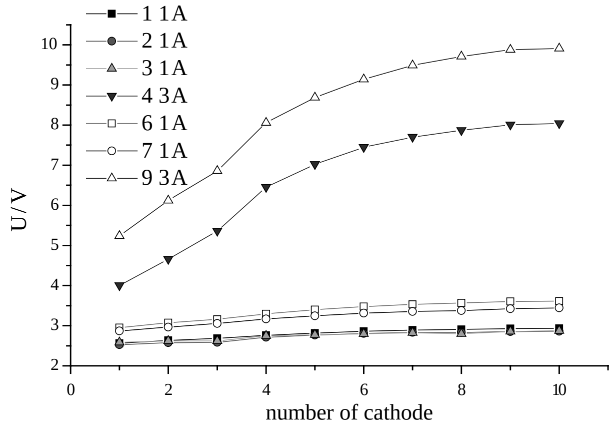

Fig. 3. Cell voltage of the cathode units as function of the number of the cathode for experiments 1, 2, 3, 4 (concentrate A) and experiments 6, 7, 9 (concentrate B). Distance between cathode units approximately 2 mm.

The cell voltage measured at the separated cathode units in the cathode stack for experiments 1–4 (solution A) and experiments 6, 7 and 9 (solution B) are shown in Figure 3.

The increase in cell voltage in the experiments at 3 A cell current explains the increase in energy consumption (Table 4). The formation of Fe(II)-complexes due to the reduction of the Fe(III)-complex can be observed at a more negative redox potential. Figure 4 shows the change of the redox potential in the experiments 1–5.

3.2. *Decolourisation of NF-concentrates in technical scale*

On the basis of the experiments given above technical scale electrolysis test were performed using a DE NORA

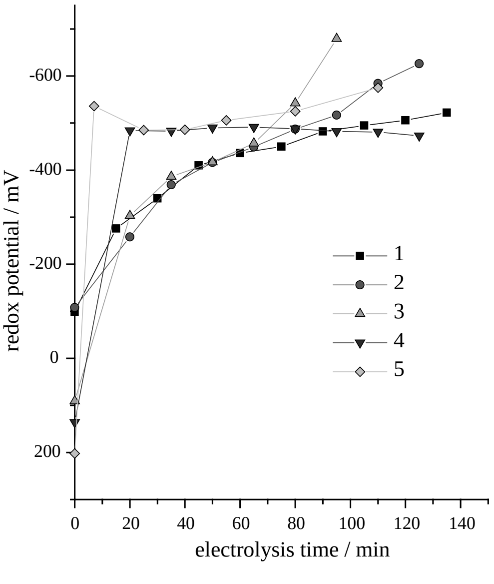

Fig. 4. Redox potential measured in the catholyte as function of electrolysis time for experiments 1–5.

multi-cathode electrolyser, installed for the cathodic decolourisation of concentrated dyestuff containing solutions from padding processes [1].

The laboratory experiments indicated that two strategies could be followed to minimise total costs:

- direct electrolysis with minimum chemical costs but larger cathode areas and thus higher cell costs;
- indirect cathodic reduction with addition of mediator chemicals and thus higher chemical consumption, but lower invest for the electrolysis cell due to the higher efficiency.

To minimise chemical consumption and total chemical load released into the effluents, direct cathodic reduction was favoured for decolourisation.

In the technical experiments both types of waste (concentrates from padding which contain NaOH) and reconcentrated solutions were mixed; thus addition of NaOH to increase conductivity was necessary. A mixture of 1 part of padder filling and 10 parts (per volume) of NF-concentrate served as catholyte. Complete filling of the cell required 580 l mixture consisting of approx. 53 l of padder filling and 530 l NF-concentrate. 1 M NaOH was used as anolyte.

Representative chemical data of the NF-concentrates, padder filling and the catholyte are given in Tables 5 and 6. A set of experiments with different cell current was performed to obtain data describing the decolourisation of the catholyte. In Table 5 results of a series of experiments with 40, 60 and 80 A are given. In Table 6 detailed data for the run of a decolourisation experiment at 40 A cell current are given.

Depending on the conditions applied 60–80% decolourisation was found at an average energy consumption of 2–8 kWh m^{-3}.

The results indicate a much lower consumption of electrical energy, which is considerably less than the values expected from previous data with 20–25 kWh m^{-3} [1]. Due to the smaller distance between the electrodes in the technical electrolyser cell voltage is lower and thus total energy consumption is smaller. In

Table 5. Experimental results of full scale decolourisation experiments

Expt.	Current (A)	Duration (h)	Decolourisation (%)			Energy consumpt. (kWh m^{-3})
			445 nm	520 nm	620 nm	
10	40	8	60	70	68	2.26
			436 nm	525 nm	620 nm	
11	40	8	56	66	61	2.25
12	60	8	62	68	58	4.55
13	80	8	67	79	67	7.85

Table 6. Experiment 10: Conditions and representative chemical data of the wastes (NF-concentrate, filling of padder), the mixture used as catholyte and results of the decolourisation process (pathlength of cuvette 0.1 mm)

		NF-concentrate	Padder filling	Mixture
Volume	(L)	530	50	580
pH		9.65	12.21	10.27
p_L	(mV)	−109	−215	−125
Temp	(°C)	RT	RT	RT
Conduct.	(mS)	5.4	30.3	8.4
Cell current	(A)			40
U_1	(V)			3.12
U_5	(V)			4.09
Start				
Absorb. 445 nm		0.088	2.474	0.367
Absorb. 520 nm		0.098	3.018	0.419
Absorb. 620 nm		0.059	3.200	0.362
Decolourisation 8 h				
Absorb. 445 nm	(%)			60
Absorb. 520 nm	(%)			70
Absorb. 620 nm	(%)			68
Energy consumption	(kWh m^{-3})			2.26
Decolourisation 10 h				
Absorb. 445 nm	(%)			67
Absorb. 520 nm	(%)			79
Absorb. 620 nm	(%)			89
Energy consumption	(kWh m^{-3})			2.82

addition the extrapolation given in [1] based on the treatment of concentrates of padders which contained high concentration of dyes.

In a full operation cycle of 8–10 h a volume of 580 l of coloured concentrate can be treated. The fully automatic installation thus reaches a capacity of approx. 1.5 m^3; of concentrated waste water per day. In the examples given in Tables 5 and 6 this volume is split into 150 l of concentrated padder filling and 1.35 m^3 of NF-concentrate.

Typical cell voltages of the cathode units as a function of the cell current are shown in Figure 5. On the basis of these results the energy consumption per m^3 of treated waste can be calculated as 2.3–7.8 kWh m^{-3} (Table 5).

Figure 6 shows the decolourisation of coloured wastes in the full scale electrolyser as a function of electrolysis time.

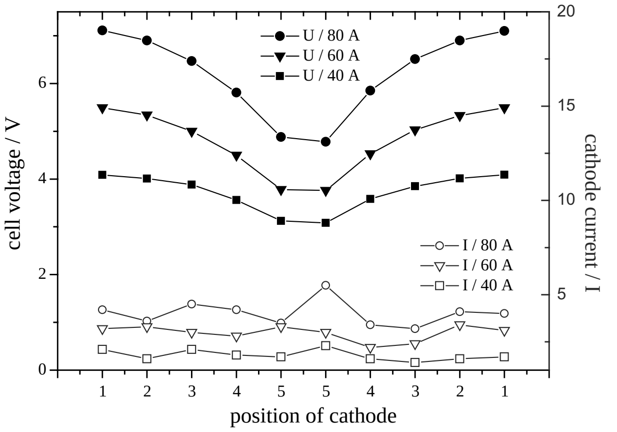

Fig. 5. Cell voltages of the cathode units at different total cell current (40, 60, 80 A) and current fed into the cathode units.

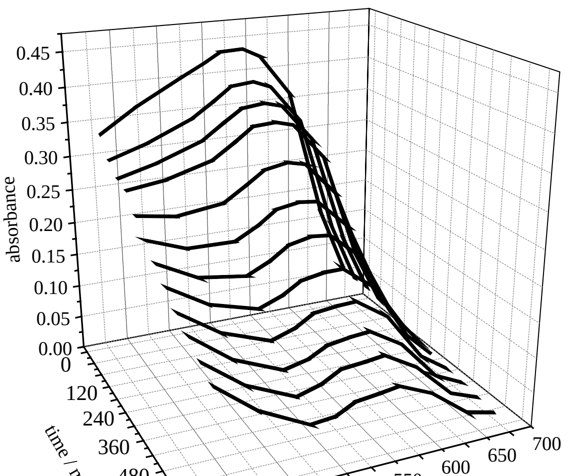

Fig. 6. Decolourisation during experiment 10 as function of electrolysis time (40 A cell current), experimental conditions in Table 6.

3.3 *Decolourisation of printing pastes*

In reactive printing the residual printing pastes contain thickener on basis of alginates, considerable amounts of a weak oxidising agent (e.g. m-nitro-benzene-sulfonic-acid Na-salt) and dyestuff concentrations up to 100 g kg^{-1} [3]. The addition of oxidising agent is required to prevent reductive cleavage of the dyestuff during drying/steaming steps.

The reductive decolourisation process has to consider the following aspects:

- lowering of viscosity;
- increased time of electrolysis or increased charge flow to reduce the added oxidising agent;
- low conductivity. In the case of technical processes NaOH containing waste e.g. fillings of padders have to be added.

The laboratory scale experiments were performed under conditions similar to the experiments described with the NF-concentrates (Table 7).

The decolourisation as a function of electrolysis time is shown in Figure 7. For comparison of the effects the amount of printing paste used has to be considered. The decolourisation in the presence of added mediator (expt. 22) is more rapid than in the same experiment at 3 A current (expt. 20). The decolourisation at 6 A (expt. 21) increased but energy consumption was very high. At 6 A 634 kWh were consumed per ton of paste while in experiment 22 an amount of 282 kWh t^{-1} were required to reach comparable decolourisation. In experiment 20 the electrolysis time had to be prolonged to approximately 14 h; thus energy consumption can be estimated as 376 kWh t^{-1}.

An experimental problem is observed in electrolysis experiment 22 (Figure 7). During the first hour of electrolysis the absorbance seems to increase, in fact dissolution of the thickened paste was not complete at the begin of the electrolysis so dyestuff was still released from

Table 7. Decolourisation of printing pastes: Experimental conditions and results

		Experiment number		
		20	21	22
m(paste)	(g)	503	530	355
V(H_2O)	(l)	5.0	5.0	5.1
pH		12.40	12.73	12.72
T	(°C)	22–28	24–28	22–24
v(NaOH)	(ml l^{-1})	5	5	5
c($FeCl_3$)	(M)	–	–	0.001
c(TEA)	(M)	–	–	0.001
c(DGL)	(M)	–	–	0.001
I	(A)	3	6	3
Decol. 445 nm	(%)	28	62	73
Decol. 520 nm	(%)	26	70	89
Decol. 620 nm	(%)	58	78	72
U_1	(V)	3.58	4.65	3.64
U_{10}	(V)	4.50	8.02	4.76
Energy cons.	(kWh t^{-1})	188	634	282

Decolourisation and energy consumption per ton of paste calculated for 7 h electrolysis time.

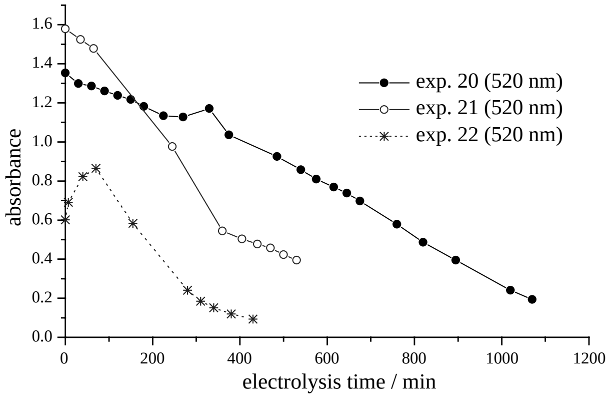

Fig 7. Decolourisation of printing pastes experiments 20, 21, 22 as function of electrolysis time at 520 nm.

small particles of paste present in the catholyte. In experiment 20 sufficient time for mixing of the paste in the catholyte before electrolysis was given; thus a decrease in absorbance is observed at the beginning of electrolysis.

An important problem to be considered in the discussion of a treatment of printing pastes is the content of heavy metals in the paste, which will not be lowered to a remarkable extent by cathodic reduction.

Generally, the cathodic decolourisation of intensively coloured wastes will not lower TOC or COD remarkably; thus the process has to be understood as a selective pretreatment of heavily coloured wastes to meet the legal limits before further release to a (communal) waste water treatment plant.

4. Conclusions

The results demonstrate the successful use of the direct cathodic decolourisation process for the treatment of both concentrates obtained from NF-treatment of diluted waste water from reactive dyeing and printing pastes from textile printing with reactive dyes.

A technical concept for the treatment of coloured wastes from dyehouses and textile printing considers all three sources of waste which can be treated in the same electrolysis cell as long as the ratio of the different wastes can be kept within certain limits:

- residual fillings of padders (volume should exceed 10% of total volume in catholyte);
- NF-concentrates (volume should not exceed 90% of total volume in catholyte);
- printing pastes (maximum addition is limited by viscosity of catholyte).

Figure 8 shows a concept for the cathodic treatment of coloured wastes from textile dyeing and printing processes and also indicates limits for the maximum volume fed into the catholyte.

In full scale operation an energy consumption between 2 and 8 kWh m^{-3} was found for the treatment of concentrates. During the cathodic treatment a decolourisation of 60–80% of the initial absorbance was observed after a charge flow of 550–1100 Ah m^{-3}.

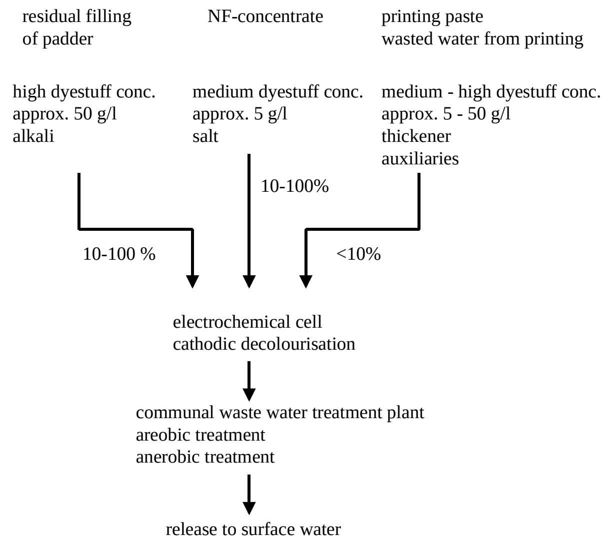

Fig. 8. Scheme for the decolourisation of coloured wastes from textile dyehouses.

The capacity of the apparatus in full scale operation was

- 1–1.5 m^3 per day of residual padder filling when a cell current of 120 A is used or
- 1–1.5 m^3 per day of NF-concentrates at a cell current of 40–80 A.

The addition of soluble mediator systems can be applied to lower the size of electrochemical cells considerably but also the released chemical load will be increased.

The decolourisation of printing pastes by cathodic reduction was achieved at laboratory scale with relatively high energy consumption (approx. 300–650 kWh t^{-1} of waste).

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