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On-site formation of hypochlorite for indigo oxidation – Scale-up and full scale operation of an electrolyser for denim bleach processes

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Abstract

On-site production of hypochlorite for denim bleach was investigated using undivided unipolar electrolysers. The current efficiency of the electrolysis process was studied at laboratory scale with up to 20 A cell current and at the technical scale using a 1200 A electrolyser. NaCl solutions in the concentration range 0.236–0.944 M NaCl (13.8–55.2 g l^{-1}) were used. Anodic current densities up to 400 A m^{-2} were used. Hypochlorite solutions with active chlorine concentration $c(\mathrm{Cl}) = 0.10$–0.12 M were obtained with current efficiency of 58–70%. For denim bleach processes a concentration of active chlorine up to $c(\mathrm{Cl}) = 0.12$ M is required. This corresponds to approximately 30 ml l^{-1} of commercial hypochlorite solution. Electrical energy consumption calculated per kg of active chlorine formed ranges from 5.7 to 8.6 kWh kg^{-1}. By coupling the electrolyser to a commercial 30 kg capacity drum washing machine the electrochemically prepared oxidant was successfully used in bleach processes. The technique overcomes problems of insufficient reproducibility of bleach, chemical costs and released wasted water due to the use of commercial NaOCl solution.

List of symbols

I	cell current, A	$\eta_{1,2}$	current efficiency, %
i_d	current density, A m^{-2}	Q	charge flow, Ah
U_z	cell voltage, V	n_{th}	mol Cl theoretically formed, mol
T	electrolyte temperature, °C		
$t_{1,2}$	duration of experiment, min	c_{exp}	analytically determined conc. of chlorine, M

1. Introduction

The production of indigo dyed textiles for Denim (jeans) holds an almost unique position in the worldwide textile market. The annual production is in the magnitude of approximately 2.0 billion m^2 of denim fabric, mainly dyed with indigo. The indigo dyestuff production can be estimated at more than 30,000 t per year.

A central step in the processing of indigo dyed textiles is the wash/bleach process of the garments to obtain the final wash down effect. To remove/destroy the ring dyed indigo dyestuff a combination of both mechanical agitation in drum washing machines and addition of chemicals to oxidize/reduce the dyestuff are used at present [1, 2].

Table 1 gives an overview on relevant processes and bleach chemicals in denim wash-down.

As can be seen, use of oxidising agents forms the chemical basis of the main part of treatments applied. Within these sodium hypochlorite is used in more than 80% of the bleach processes. NaOCl offers a broad variety of bleach effects, simple handling and relative low costs and thus still forms the chemical basis of the standard processes in denim bleach. However, problems can arise from insufficient chemical stability during storage of NaOCl particularly at higher temperatures which results in unsatisfactory reproducibility of bleach effects. Further, total costs for chemicals and transportation of the hazardous material are considerable.

In other textile bleach processes hypochlorite has been replaced by other chemicals because of the AOX released in the waste water (AOX adsorbable halogenated organic compounds).

In the last decade substantial research has been done to investigate electrochemical processes for reduction of indigo and vat dyes in textile dyeing processes [3–5]; however, recently use of anodic processes for oxidative bleach processes has been studied more intensively.

DyStar Textilfarben GmbH&Co Deutschland KG and the Institute for Textile Chemistry and Textile Physics of the University of Innsbruck, Austria have been working together for many years on the development of electrochemical processes for the textile industry which they aim to commercialise. The main focus of this work is on electrochemical dyeing but also includes decolouration of textile effluent and bleaching of textiles.

Processes for electrochemical production of bleach chemicals have been studied for delignification of pulp and for textile bleach processes [6–13]. The electrochemical formation of hydrogen-peroxide on-site has been investigated [14, 15]. The use of electrochemical methods to form organic oxidizing agents for denim bleach has been described [13]. Limited scientific information is available about the electrochemical *in-situ* formation of hypo-halogenites for bleach operations [9, 10, 16, 17]. The in-house preparation of NaOCl also has been described, however the efficiency of the bleach process has been described as rather low [12].

The use of electrochemical processes for on-site or *in-situ* formation of oxidizing agents e.g. hypochlorite, offers interesting new aspects for denim bleach:

- improved process control, better reproducibility leading to processing cost reduction
- higher reproducibility of bleach result
- lowered total costs for chemicals
- regeneration of used bleach baths improves the ecological profile.

The chemical reaction of the bleach process can be formulated according to Equations (1)–(3). Figure 1 shows a general scheme for the oxidation reaction of indigo in presence of hypochlorite [18, 19].

$$2\,H_2O + 2\,e^- \leftrightarrows 2OH^- + H_2 \text{ cathode} \qquad (1)$$

$$Cl^- + H_2O \leftrightarrows OCl^- + 2H^+ + 2e^- \text{ anode} \qquad (2)$$

$$2OCl^- + \text{indigo} \leftrightarrows 2Cl^- + \text{isatin solution} \qquad (3)$$

In this work results from laboratory experiments to design a simple and robust electrolyser for anodic formation of hypochlorite for denim bleach are presented and the scale-up to full technical operation is described. Performance tests of the technical scale hypochlorite electrolyser are presented and data from tests in full operation of the 1200 A cell current electrolyser are presented. The coupling of an electrolyser to a 30 kg drum washing machine is discussed in detail. Current efficiency for hypochlorite formation and results from full scale tests are summarised.

Table 1. Relevant processes in denim wash-down

Chemical	Formula	Reaction	Market share/%
Hypochlorite	NaOCl	Oxidative	> 85
Persulphate	$K_2/Na_2S_2O_8$	Oxidative	< 5
Permanganate	$K/NaMnO_4$	Oxidative	< 2
Enzymes	Oxidoreductases	Oxidative	< 2
Ozone	O_3	Oxidative	No relevance
Peroxocompounds	··–O–O–··	Oxidative	No relevance
Glucose	$C_6H_{12}O_6$	Reductive	< 5
Sulfinic acids	R–S(O)OH	Reductive	< 1

2. Experimental

2.1. *Chemicals*

NaCl used as electrolyte was technical grade quality. Chemicals used for the analytical determination of the NaOCl content were analytical grade chemicals.

2.2. *Laboratory scale experiments*

An undivided monopolar cell was used for the electrolysis experiments. A Pt-mixed oxide coated titanium

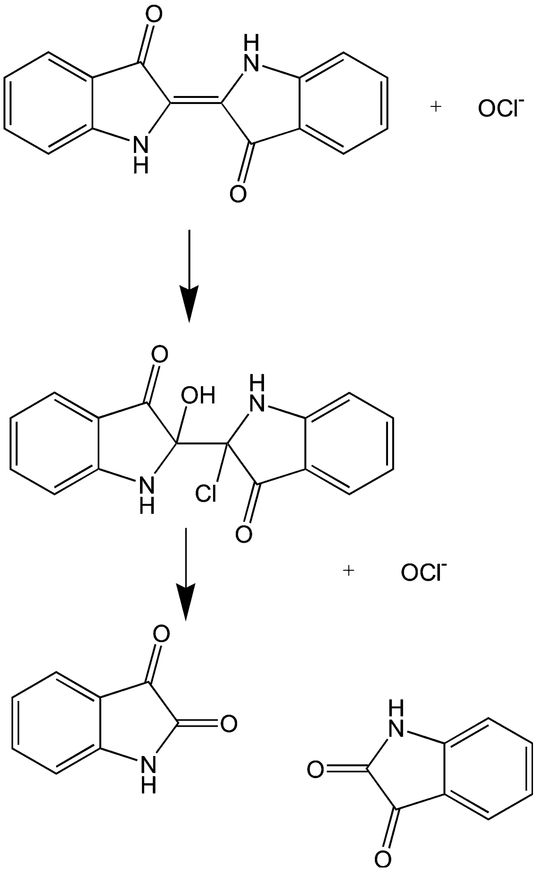

Fig. 1. Scheme for the oxidation of indigo by hypochlorite to yield isatin [18, 19].

electrode (DE NORA, Rodenbach, Germany) was used as anode and a stainless steel fabric served as cathode. Dimensions are given in Table 2.

The redox potential of the electrolyte was measured with a Pt-electrode vs. a (Ag/AgCl, 3 M KCl) reference. The pH of electrolyte was measured with a glass electrode (Hamilton-flush-trode, Orion 720 A, Orion Research Inc. Boston, MA). The electrolyte flow was parallel to the direction of the current flow (20 l min^{-1}, flow approx. 0.8 cm s^{-1}).

Experiments were performed in galvanostatic batch electrolysis mode. Samples of the bleach solution were analysed for hypochlorite as function of electrolysis time by redox titration with sodium thiosulphate. 5 ml of 10% KI solution and 10 ml of 10% HCl were added to a volume of 50 ml of electrolyte and titration was performed with 0.1 M $Na_2S_2O_3$ by means of a titroprocessor (Orion Autochemistry System 960, Orion, Boston, MA).

2.3. *Technical scale process*

For full scale tests a undivided cell manufactured by DE NORA Elektrochemie (HKE-4-H, DE NORA Deutschland, Rodenbach, Germany) was used. The cell was a monopolar cell and equipped with parallel electrodes (5 cathodes and 4 anodes). Titanium anodes coated with Pt-mixed oxide were used. Titanium cathodes were used for initial tests, and were later replaced by stainless steel electrodes due to severe corrosion of the titanium.

For full scale operation tests a Tonello G1 150 drum washing machine with a load capacity of 30 kg textiles and a fill of 300 l of bleach bath was coupled to the cell (Tonello, Sarcedo, Italy).

A scheme of the installation is given in Figure 2. The operation cycle of the unit was as following

- filling of electrolyser with NaCl solution
- electrochemical formation of NaOCl bleach solution
- pumping of bleach solution into washing machine
- wash/bleach process.

For the electrolysis a volume of 145 l of electrolyte was filled in the cell and electrolysed at constant current. Both, formation of oxidant in the bleach solution and decrease of NaOCl concentration during bleach process in the washing machine, were monitored by redox titration with $Na_2S_2O_3$.

After a defined concentration of oxidant had been formed in the electrolyte, the bleach bath was pumped into the washing machine for processing the garment. Indigo dyed jeans were used for the full scale bleach experiments.

The result of the bleach step was evaluated visually and by measuring CIELab-coordinates. The colours are described in CIELab-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). Details for the bleach effect are given elsewhere [11, 20].

For comparison and standardisation reference wash-down procedures were performed with 24.4–28.2 mM NaOCl (addition of 13–15 ml l^{-1} of commercial 1.88 M NaOCl).

3. Results and discussion

3.1. *Laboratory scale electrolysis*

In discussions with denim experts a concentration of 0.86 M NaCl (50 g l^{-1}) had been evaluated as the upper limit for NaCl concentration acceptable for the technical process. To keep the number of variations limited this concentration was used in the electrolyte and the formation of hypochlorite was studied in galvanostatic batch electrolysis experiments.

Experimental conditions and results of the turnover experiments in laboratory scale are given in Table 3.

Electrolysis was performed with an anodic current density of 64–500 A m^{-2}. The total duration of a batch

Table 2. Geometric data of the laboratory scale electrolyser and general experimental conditions

	Experimental parameter	Laboratory scale	Technical scale
Anode	Material	1 Electrode Pt-mixed oxide coated titan expanded mesh	4 Electrodes 0.4 m^2 Pt-mixed oxide coated titan expanded mesh
	Geometric area (both sides considered)	400 cm^2	$4\times0.4\ \mathrm{m}^2 = 1.6\ \mathrm{m}^2$ $2\times4\times0.4\ \mathrm{m}^2 = 3.2\ \mathrm{m}^2$
Cell current	Total current	5–20 A	250–1200 A
	Anodic current density	12.5–50 mA cm^{-2} 125–500 A m^{-2}	7.8–37.5 mA m^{-2} 78–375 A m^{-2}
Cathode	Material	1 Electrode Stainless steel fabric	5 Electrodes 0.4 m^2 Stainless steel expanded mesh
	Geometric area	360 cm^2	$5\times0.4\ \mathrm{m}^2 = 2.0\ \mathrm{m}^2$
	Cathodic current density (both sides considered)	140–560 A m^{-2}	125–600 A m^{-2} 62.5–375 A m^{-2}
Distance	Anode/cathode	12 cm	2.5 cm
Electrolyte	Volume	11 l	160 l

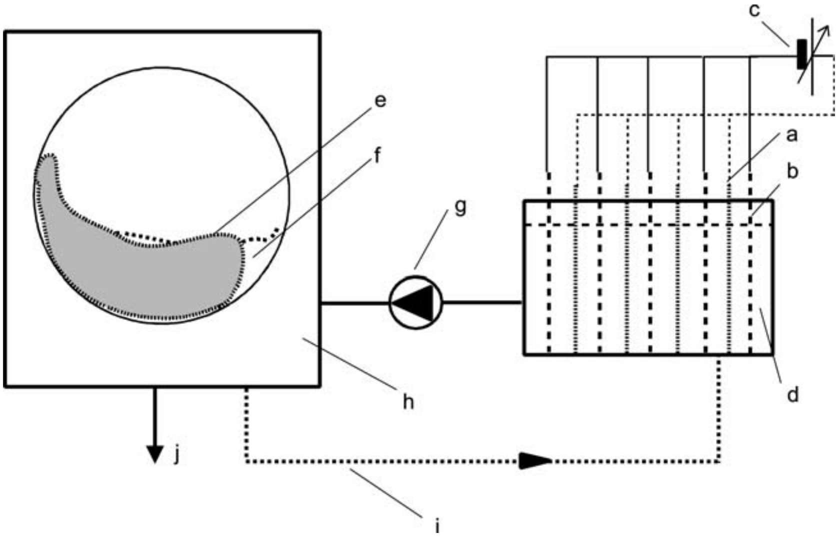

Fig. 2. Scheme of the coupling between electrolyser and drum washing machine: a anode, b cathode, c power supply, d electrolyte, e denim fabric, f bleach bath, g filling pump, h drum washing machine, i bleach bath regeneration, j drain.

electrolysis was fixed at approx. 150 min. Within this time an average current efficiency of 56–67% was determined. A current efficiency of apparently more than 100% is observed at the beginning of the experiment which can be explained by the influence of small experimental errors causing considerable effects particularly at the initial phase of the experiment. As a function of cell current the applied cell voltage, U_z , ranged from 3.7 to 13.4 V. The rather high cell voltage was caused by the considerable geometric distance of 12 cm between anode and cathode. Experiments were started at room temperature. During electrolysis the temperature of the electrolyte increased to values near 40 °C. The final temperature reached was dependent on the cell current. pH values typically remained below pH of 9, e.g. at the end of experiment (8) a final pH value of 8.9 was measured in the electrolyte. The formation of the oxidant, current efficiency and electrolyte temperature as function of time for experiment (8) are shown in Figure 3.

The highest concentration of active chlorine c(Cl) was observed in experiment (8) with $c(\mathrm{Cl}) = 0.0914$ M; this corresponds to 24 ml l^{-1} commercial NaOCl solution ($c(\mathrm{NaOCl}) = 1.88$ M). A concentration of 0.1 M NaOCl can be seen as upper limit for a technical bleach process. Thus NaOCl solutions with sufficient concentration to be applicable for denim bleach operations can be produced in the cell.

3.2. *Technical scale process*

The size of the electrolyser was defined by the technical requirement to produce the chlorine bleach within the cycle time of a bleach in the drum washer. Assuming a current efficiency of 50% a cell current of 1210 A was calculated to deliver 22.6 mol of oxidant within 60 min. This amount corresponds to 200 l 56.4 mM NaOCl, equivalent to 30 ml l^{-1} commercial 1.88 M NaOCl solution.

Before the electrolyser was coupled to the drum washer a set of batch experiments was performed to characterise the performance of the cell (c(NaCl) = 0.86 M, 50 g l^{-1}). The formation of hypochlorite as function of electrolysis time and the corresponding current efficiencies were determined. Figure 4 shows the concentration of oxidizing equivalents formed and the current efficiency measured at cell currents of 250, 500 and 750 A. At the begin of the tests high current efficiency of 80–100% is observed, which decreases with increased concentration of oxidant. An increase in

Table 3. Experimental conditions and results of the electrochemical bleach experiments in laboratory scale: Composition of electrolyte 0.86 M NaCl (50 g l^{-1}), volume electrolyte 11 l, distance anode–cathode 12 cm

Expt. No.	I/A	i_d/A m^{-2}	U_z/V	T/°C	Flow/l min^{-1}	t_1/min	η_1/%	t_2/min	Q/Ah	n_{th}(Cl)/mol	c_{exp}(Cl)/M	η_2/%
1	2.6	64	3.7–3.6	20.6–24.8	20	60	77.3	150	6.4	0.239	0.014	62.4
2	5.0	125	4.8–4.7	20.7–25.9	20	60	79.7	150	12.5	0.466	0.029	67.6
3	5.5	138	5.0–4.8	18.7–23.9	4	60	69.5	140	11.7	0.435	0.027	67.3
4	7.0	175	5.8–5.6	20.9–26.8	20	60	87.0	135	15.8	0.588	0.040	63.5
5	10	250	6.9–6.6	20.8–28.9	20	50	73.5	155	25.8	0.964	0.057	64.4
6	15	375	10.1–8.6	19.3–33.4	20	50	76.9	135	33.8	1.259	0.074	64.6
7	15	375	10.7–9.0	21.3–34.1	20	45	72.3	–	33.8	1.259	–	–
8	20	500	13.4–10.3	19.0–41.1	20	45	77.9	143	47.7	1.778	0.091	56.5

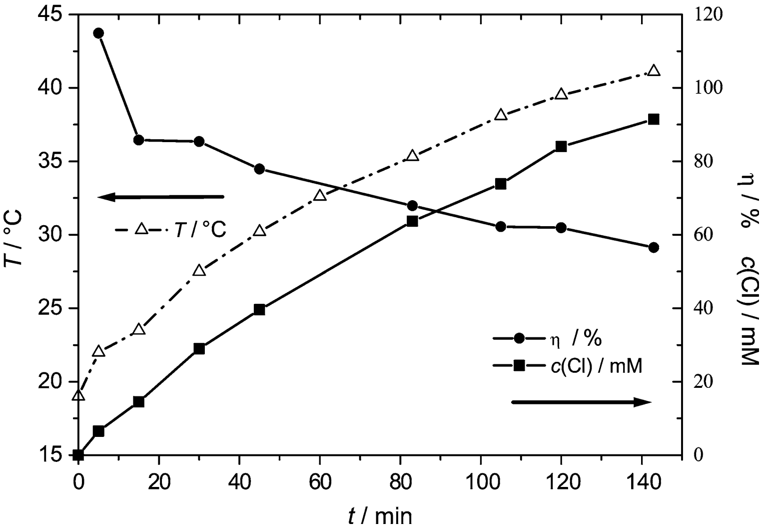

Fig. 3. (Left scale:) (△) temperature T and (right scale:) (●) current efficiency η, (■) concentration of oxidant c(Cl) as function of electrolysis time t for experiment (8) (cell current I 20 A).

current efficiency from 74 to 86% was observed with increase of anodic current density from 156 to 468 A m^{-2} . The upper value corresponds to 750 A cell current.

A considerable decrease of current density is observed at rather low concentrations of hypochlorite of $c(\mathrm{Cl}) = 0.015$ M which corresponds to a turn-over of less than 2% of the NaCl present in the electrolyte.

The cell voltage U_z increased from 2.75 V at 100 A to 4.12 V at 600 A and 5.2 V at a cell current of 1200 A. A linear correlation between U_z and I was observed in the 100–1200 A range.

3.3. *Preparation of denim bleach solution*

For full scale tests the cell was coupled to a 30 kg capacity drum washer which, technically, is used for

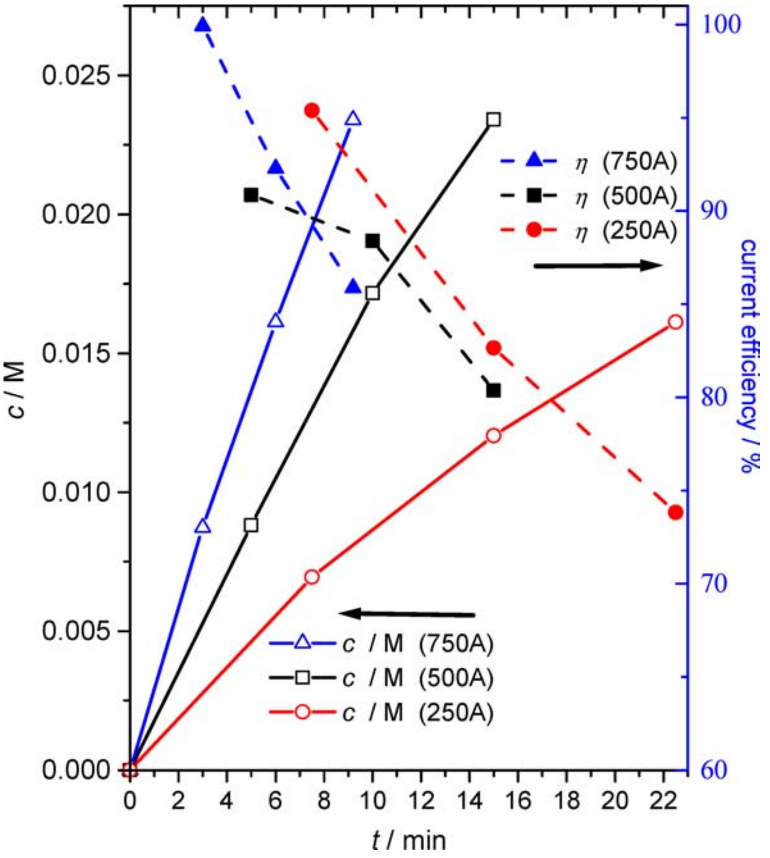

Fig. 4. Current efficiency η and concentration of equivalents of oxidant c(Cl) formed in galvanostatic tests as function of electrolysis time t, cell current of 250, 500 and 750 A.

Table 4. Experimental conditions and results of the electrochemical bleach experiments in technical scale: volume electrolyte 145 l

Expt. No.	c (NaCl)/M	c (NaCl)/g l^{-1}	I/A	U_z/V	t/min	η/%	Q/Ah	n_{th}/mol	c_{th}/M	c_{exp}/M
9	0.236	13.79	1000	6.8	40	57.7	667	28.9	0.172	0.10
10	0.354	20.69	1000	6.1	40	57.7	667	28.9	0.172	0.10
11	0.472	27.59	1000	5.4	41	69.5	683	25.5	0.176	0.12
12	0.708	41.38	800	4.5	85	45.7	1138	42.3	0.292	0.13
13	0.944	55.17	1000	4.5	55	48.9	917	34.2	0.236	0.12
14	0.944	55.17	1000	4.5	54	51.1	900	33.6	0.232	0.12

denim bleach. The filled load was 30 kg indigo dyed and stone washed garments.

In Table 4 relevant data collected during the batch electrolysis are summarised. Hypochlorite concentration was monitored every 10 min. Different NaCl concentrations of 0.24–0.94 M NaCl (14–55 g l^{-1}) were used in the experiments. The adjusted cell current was kept constant during each experiment. Within the first 40–54 min current efficiency ranged from 57 to 70%. In experiments 12–14 the duration of electrolysis was prolonged. Due the higher concentration of OCl$^-$ already present in the electrolyte current efficiency decreased to 45–52%. The increase in hypochlorite concentration almost ceased at a concentration of approximately 0.10–0.13 M active chlorine.

For comparison the total amount of active chlorine formed in the electrolyte can be calculated in terms of ml l^{-1} commercial 1.88 M hypochlorite solution (approx. 140 g l^{-1} NaOCl). In experiments 9–14 hypochlorite concentrations corresponding 27–35 ml l^{-1} commercial 1.88 M NaOCl were produced in the cell.

3.4. *Bleach process*

Following the formation of the bleach solution electrolysis was terminated and the filling of the electrolyser (145 l) was transferred into the drum washing machine which was filled with 30 kg of denim goods. Soft water was added to reach the required minimum level of 300 l and the bleach procedure was started. Typical conditions for the bleach step were 40 °C temperature and agitation for 20 min, followed by washing steps to eliminate residual oxidant from the bleached goods.

The addition of water lowered the concentration of hypochlorite in the washing machine to approximately 50% of the concentration determined at the end of electrolysis (Table 4). Thus reference bleach experiments were performed with oxidant concentrations 24–30 mM NaOCl (equivalent to 13–16 ml l^{-1} commercial 1.88 M NaOCl).

Analysis of the concentration of active chlorine in the bleach bath indicated an intensive reaction within the first 5 min. During this period more than 50% of the oxidant is consumed. Dependent on the presence of oxidable matter in the bath an additional 20–40% of oxidant have reacted within the following 15 min. In total 70–90% of the bleach chemicals are consumed within 20 min of the bleach.

For comparison with results obtained using commercial hypochlorite solution, standard bleach was performed at 24.4–28.2 mM NaOCl, corresponding to 13–15 ml l^{-1} of 1.88 M active chlorine. Details describing bleach effects and comparison of bleach results are given elsewhere [11, 20]. The comparison of the bleach effects indicated that, under similar process conditions e.g. concentration of oxidant, pH, temperature and duration a more intensive bleach effect is observed using electrochemically prepared bleach baths [11, 20]. This finding may be explained as being due to partial disproportionation of the commercial NaOCl solution to less bleaching $NaClO_3$ and NaCl during storage; however, detailed studies are in progress.

3.5. *Energy consumption*

A cell voltage of 4.5–6.8 V was required for a cell current of 1000 A. On the basis of an average current efficiency of 60%, production of 1 kg of chlorine requires a charge flow of 1260 Ah and consumes 5.67–8.57 kWh kg^{-1}. This corresponds to a volume of 7.9 l commercial NaOCl solution (1.88 g l^{-1} NaOCl).

Production of chlorine in chlorine-alkali electrolysis requires approximately 2.7 kWh per kg [21]. The higher energy consumption of the present cell can mainly be attributed both to lower current efficiency and non-optimised cell geometry. However, for the described technical application of in-site hypochlorite production energy costs are of minor relevance compared to the expected savings due to improved reproducibility of the bleach process and total chemical costs.

4. Conclusions

In-site formation of hypochlorite solution for denim bleach offers several advantages:

- defined conditions of the bleach leading to better reproducibility and process cost saving
- no losses of activity of hypochlorite during storage
- better defined bleach process conditions
- improved reproducibility of the bleach step
- possible regeneration of the bleach bath.

The current efficiency of the electrolysis depends on the concentration of oxidant present in the undivided cell.

Up to a concentration of c(Cl) = 0.1 mol l^{-1} current efficiency is between 60 to 80%. In laboratory experiments using anodic current densities from 60 to

500 A m^{-2} only small changes in current efficiencies were found.

For denim bleach processes active chlorine concentrations of $c(\mathrm{Cl}) = 0.12$ mol l^{-1} corresponding to approximately 30 ml l^{-1} commercial NaOCl solution are in use. The present undivided unipolar cell avoids mechanically sensitive components. Using a cell current of 1000–1200 A hypochlorite solutions in the required concentration level can be obtained. Anodic current density was adjusted to 400 A m^{-2}.

In technical scale tests NaCl solutions with a concentration of 0.236–0.944 M NaCl (13.8–55.2 g l^{-1}) were used as electrolyte and hypochlorite solutions of $c(\mathrm{Cl}) = 0.10$–0.12 M (active chlorine) were obtained with current efficiencies from 58 to 70%. The NaCl concentration was found to be of minor importance for the current efficiency thus further optimisation with regard to the lowered NaCl concentration is possible. The energy consumption per kg of active chlorine formed was determined at 5.7–8.6 kWh kg^{-1}.

By coupling the electrolyser to a commercial drum washing machine with a load of 30 kg of denim garments the electrochemically prepared oxidant solution was used for bleach processes. In comparison to commercial hypochlorite solution electrochemically prepared bleach baths showed more intensive bleach effects [11, 20].

The continuous regeneration of the bleach bath by circulation of the electrolyte through the drum washer is part of an ongoing study; however, for this process installation of exhaust fans is required to avoid accumulation of hydrogen in the drum washer.

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