Calcium-iron-D-gluconate complexes for the indirect cathodic reduction of indigo in denim dyeing: A greener alternative to non-regenerable chemicals

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ABSTRACT

With an annual production of approximately 7−10 billion m^2 the manufacturing of indigo dyed denim takes a substantial share in global textile production. At present the vast majority of dyeing processes with indigo still bases on the use sodium dithionite as reducing agent. For a successful replacement of the non-regenerable reducing agent by electrochemical processes, a combination of a regenerable redox system with an appropriate cell design is required. In the presented study, the use of embroidered electrodes in an 85 mA flow-through electrolyser for electrochemical indigo reduction has been investigated for the first time. Indirect cathodic reduction of indigo was achieved with use of a 0.1 M solution of a binuclear complex of calcium and iron with D-gluconate as a ligand. The electrochemically reduced indigo was then used in lab scale dyeing (1−3.5 g L^{-1} indigo), and the results were compared to reference dyeing experiments with sodium dithionite as reducing agent, by measuring the colour strength and CIElab colour coordinates. Comparison of the electrochemical technique for indigo reduction with the dithionite-based standard process indicates substantial potential for an improvement of the ecological profile of the dyeing process used at present. The electrical power demand for a full scale electrolyser is estimated to be in the range of 2.8−6.9 kW, leading to an energy consumption of 58−145 kWh d^{-1} as compared to a sodium dithionite consumption of 50−126 kg d^{-1}. Introduction of biobased and regenerable chemical systems instead of non regenerable chemicals in indigo dyeing offers significant potential for reduction of the chemical load released into wastewater. A reduction of the sulphate concentration in the wastewater from the current values of 640−1600 mg L^{-1} to values well below the legal limit of 200 mg L^{-1} sulphate will be possible. By reuse of the washing water and the reversible reducing agent, a reduction of both water consumption (by 80%) and chemical consumption (by 50%) are expected.

1. Introduction

Indigo (CI Vat Blue1) is one of the most widely used dyes in the textile industry. The annual production of indigo dyed fabric is estimated at 7 to 10 billion m^2 (Bechtold and Pham, 2019). The huge number is explained by the popularity of blue jeans. Indigo dyeing for denim production is completely different from other vat dyes processes (Paul, 2015; Bechtold and Pham, 2019). In the continuous dyeing process the yarns are immersed in a cold dyebath containing the reduced indigo (leuco form), squeezed, and then exposed in air to convert the leuco dye back to its original insoluble form. The affinity of the reduced indigo to the cellulose fibre is low, thus the immersion/oxidation cycle has to be repeated several times, to ensure the requested dyestuff fixation (Etters and Hou, 1991; BASF, 1995).

Dyeing with indigo requires the transfer of the insoluble, oxidised form of the dye into its soluble leuco form, which then exhibits affinity to cellulosic fibre (BASF, 1977; Blackburn et al., 2009). At the site of dyestuff production indigo reduction can be achieved by catalytic hydrogenation. With the introduction of reduced indigo solution as dyestuff product, the consumption of reducing agent in a dyehouse reduces by nearly 50% (Bechtold et al., 2004). However considerable amounts of reducing agent are required to maintain the indigo in its reduced form in the dyebath.

In most industrial processes, the reduction state in the dyebath is stabilised by continuous addition of sodium dithionite, as this chemical exhibits sufficient reduction potential < -700 mV at the required dyebath pH of 11.5−12.0. In this pH range the mono-anion form of indigo is the prevalent species, which exhibits highest affinity to the cellulose fibres. Thus besides conditions of stable redox potential, also the dyebath pH has to be maintained constant, to avoid long-term variation of dyestuff fixation on the goods, the so-called ending or topping (Etters, 1989a). However, the use of this reducing agent causes several problems, such as a limited stability in the dyebath and hazards during storage that necessitates careful handling (Etters, 1989b; Camacho et al., 1997). Another major concern results from the generation of sulphate, sulphite and thiosulphate ions in the wastewater released from the dyeing process.

A number of different approaches have been studied with the aim to replace dithionite in indigo dyeing. The use of organic-sugar-based reducing agents e.g. glucose, fructose, hydroxyacetone has been studied extensively (Blackburn and Harvey, 2004; Laksanawadee et al., 2018). A major drawback in the use of α-hydroxycarbonyls (Meksi et al., 2012) and glucose (Ben Ticha et al., 2013) arises from the rather low rate of reduction, which thus requires higher alkali concentrations e.g. pH 13 and elevated temperature e.g. 60 °C to achieve stable dyestuff reduction (Laksanawadee et al., 2018). Application of such conditions in indigo dyeing leads to higher dyestuff penetration and loss of the desired ring dyeing effect. Ring dyeing however, is a requirement to achieve high contrast and rapid wash down of indigo in the later garment wash. Also other non-regenerable reducing agents have been studied as ecological substitutes for dithionite such as sodium borohydride (Meksi et al., 2007, 2010) and iron(II)salts (Semet and Grüninger, 1995; Chavan and Chakraborty, 2001). These compounds can meet the technical requirements in terms of bath stability, efficiency and biodegradability, although at costs compared to use of sodium dithionite. In addition these reducing agents react to form non-regenerable follow-up products, which then are released in the effluent (Jermini, 1997).

Indirect electrochemical reduction of indigo by use of cathodically regenerable reducing agents constitutes a solution for this problem (Roessler and Jin, 2003; Bechtold and Turcanu, 2009). In these processes a regenerable redox system is used in the dyebath, which is then continuously regenerated by cathodic reduction (Bechtold et al., 1997a). The fundamentals of indirect electrochemical dyestuff reduction have been investigated in previous studies (Bechtold et al., 1992, 1996). For reduction of indigo in the dyebath a reversible redox system called mediator must be able to achieve a redox potential lower than −700 mV in the pH range between 11 and 12. The mediators investigated with analytical techniques include: substituted anthraquinones (Vuorema et al., 2006, 2008; Turcanu et al., 2011), iron chelates with various ligands such as: Fe(III)/Fe(II)−triethanolamine (Bechtold et al., 1996, 1997a; Xu et al., 2014) and Fe(III)/Fe(II)-D-gluconate (Bechtold and Turcanu, 2004). Also binuclear Ca-Fe-D-gluconate complexes or Ca-Fe-triethanolamine complexes have been investigated with analytical techniques (Xu et al., 2014; Yi et al., 2020).

Through cathodic reduction, the reversible redox system (Fe(III)-complex) is reduced continuously thus yielding the ferrous form. The reversible redox system takes the function of a redox mediator and acts as a regenerable reducing agent in the dyebath. The redox potential in the dyebath will depend on the type of complex and on the ratio between Fe(II)- and Fe(III)-form (Bechtold et al., 1997b). In technical scale dyeing the surplus of reducing agent in the dyebath has to be kept to a minimum, as after each immersion of the textile material into the dye bath the added leuco-indigo is oxidised into the blue pigment during an air exposure. During this oxidation step both reduced indigo and the surplus of reducing agent present on the material will be oxidised (Paul, 2015). Thus in each airing passage, the full Fe(II)-content of the dyebath will be oxidised and transferred into the corresponding Fe(III)-form. For a technically feasible iron complex system thus it is of outmost importance that the required negative redox potential in the dyebath can be established with the minimum concentration of Fe(II)-form (Bechtold et al., 1997b). Otherwise, the electrical power of the installation will rise to such a high level, that the electrochemical dyestuff reduction is not a cleaner alternative to the conventional process. A number of complexes proposed in the literature will be able to establish a sufficiently negative redox potential in the dyebath, however with unacceptably high ratio between Fe(II)- and Fe(III)-form (Bechtold et al., 1997b).

Cyclic voltammetry and batch electrolysis experiments have demonstrated the potential of binuclear complexes of Ca^{2+} and $Fe^{2+/3+}$ with D-gluconate for vat dye reduction, however the potential of these biobased and regenerable reducing systems for indigo dyeing has not been explored up to now (Bechtold et al., 2002).

For an introduction of the indirect cathodic dyestuff reduction in technical indigo dyeing three relevant research questions have to be answered:

- Are there any changes in the dyeing behaviour of the indigo with regard to colour uptake and shade, compared to reference dyeings?
- What dimensions will be required of an electrolyser to compensate for the oxidative load from the air-oxidation step, and to achieve stable reduction of the indigo in the dyebath?
- Will the technology lead to improvements in the ecological profile of the dyeing process?

In this paper, we investigate the use of a mixed complex of calcium, iron and D-gluconate as an electrochemically reversible redox system for indigo reduction and dyeing. A new designed flow through electrolyser with embroidered stainless steel through electrodes was used for batch electrolysis experiments. The influence of the Ca^{2+} concentration was studied on the development of the reduction potential as function of iron(II/III) concentration in the complexes was studied, to determine the minimum concentration of iron(II) required to achieve the necessary reduction potential for indigo reduction. The cathodically reduced indigo dyebaths then were used for dyeing experiments and results were compared to reference dyeings with use of dithionite. For the first time, we present a set of experiments, that directly permits an estimation of the cell dimensions for a full scale operation in continuous indigo dyeing. From the results of the batch experiments an estimation of the overall power and resources consumption of a technical scale installation for electrochemical indigo dyeing is presented. Results are compared with the dithionite based standard process, to present an assessment of the environmental benefits of the new technology.

2. Experimental

2.1. Chemicals and materials

The chemicals used were analytical of grade quality: sodium hydroxide (NaOH, ≥99 %wt p.a., VWR pro labo, Germany), iron(III) chloride hexahydrate (FeCl$_3$ × 6H$_2$O, ≥98%wt, Roth, Germany), calcium chloride dihydrate (CaCl$_2$ × 2H$_2$O, ≥97% p.a., Merck, Germany), sodium D-gluconate (NaDGL, 100% pure, Merck, Germany), ammonium acetate (NH$_4$CH$_3$CO$_2$, ≥97% p.a., Roth, Germany), acetic acid (CH$_3$COOH, 100 %wt pure, Roth, Germany), 1,10-phenanthrolinium chloride monohydrate (99.5 wt% p.a, Merck, Germany), hydroxylamine hydrochloride (NH$_3$OHCl, ≥99.5% p.a., Roth, Germany) and sulphuric acid (H$_2$SO$_4$ with 96 wt% content in water, 1.84 g mL^{-1}, Merck, Germany).

The indigo dye (C.I. Vat Blue 1, C$_{16}$H$_{10}$N$_2$O$_2$ granulate) and solution of hydrogenated indigo solution (20 %wt) were obtained from DyStar Textilfarben (Germany). The wetting agent (Primasol NF®, alkylphosphate) and the dispersing agent (Setamol WS®, lignosulphonate) were technical grade products (BASF, Ludwigshafen, Germany). Technical grade sodium dithionite (Na$_2$S$_2$O$_4$) was used as reducing agent.

For dyeing experiments a scoured and bleached 100% cotton fabric with the following specifications was used for dyeing: mass per area 171.3 g m^{-2}, warp count of 25 yarns cm^{-1}, weft count 23 yarns cm^{-1}.

2.2. Electrochemical setup

A flow cell equipped with embroidered electrodes as anode and as cathode was used as electrolysers. A stainless steel yarn was used as the conductive element on a polypropylene (PP) non-woven support. A micrograph of the embroidered electrode is provided in the supplementary material (Fig. S1). The cathodic and the anodic compartments were separated by a Nafion type cation exchange membrane (De Nora Rodenbach, Germany). The characteristics of the flow cell are presented in Table 1.

An alkaline solution with different composition of the binuclear Ca^{2+}-Fe^{3+}-D-gluconate complex was used as catholyte. Five different catholytes were compared. The respective compositions are given in Table 2. A 0.5 M or 1 M NaOH solution served as anolyte. The redox potential and pH of the catholyte was measured outside of the cell with a Pt electrode and a potentiometer (Schott Glaswerke, Mainz, Germany). Redox potential values are related to a (Ag/AgCl, 3M KCl) reference electrode. The experiments were carried out at room temperature. The electrical energy was supplied by an adjustable power supply. In the electrolyte reservoir the indigo containing catholyte was stirred slightly, to avoid any

Table 2
Composition of catholytes studied in the batch electrolysis experiments, initial pH, catholyte pH and ratio of Fe(II)/Fe(total) at −700 mV catholyte potential.

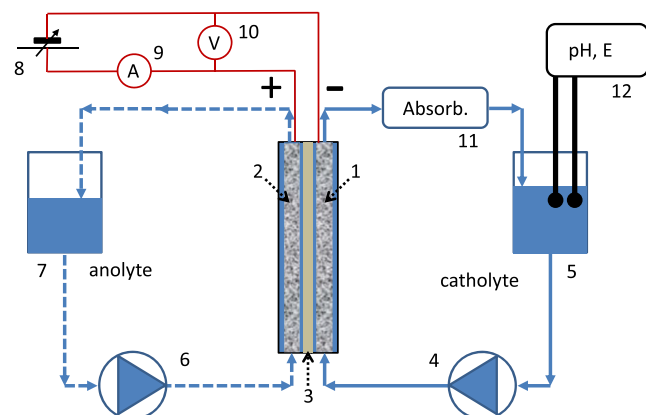| Catholyte | Concentration | | | | Catholyte potential | |
| | Ca^{2+} | Fe^{3+} | D-gluc. | Start | −700 mV | |
	M	M	M	pH	pH	Fe(II)/Fe(total) %
1a	0.1	0.1	0.11	11.6	12.6	10
1b	0.1	0.1	0.11	10.6	11.6	15.5
2a	0.08	0.1	0.11	12.0	12.9	19
2b	0.08	0.1	0.11	10.5	12.5	20.5
3	0.1	0.1	0.2	11.6	12.2	10

Fig. 1. Scheme of the experimental setup used for indirect cathodic indigo reduction: 1 cathode, 2 anode, 3 cation exchange membrane, 4 catholyte circulation, 5 catholyte reservoir, 6 anolyte circulation, 7 anolyte reservoir, 8 power supply, 9 amperemeter, 10 voltmeter, 11 photometer, 12 potentiometer for measurement of pH and redoxpotential.

settling of the oxidised dye during the electrolysis experiment. Fig. 1 shows a schematic drawing of the electrolyser and the circulations of catholyte and anolyte. At the end of the electrolysis the catholyte was collected and used for indigo dyeing experiments.

2.3. Electrolysis experiment

Preparation of a catholyte with the composition 0.1 M FeCl$_3$, 0.11 M D-gluconate (DGL) and 0.1 M CaCl$_2$ is described as a representative example. A volume of 100 mL of 1 M FeCl$_3$ solution and 110 mL of 1 M sodium D-gluconate solution were mixed in a beaker with 500 mL of deionised water to form the Fe-D-gluconate complex. Then 40 mL of 8.75 M NaOH (350 g L^{-1}) were added, followed

Table 1
The characteristics of the flow through electrolyser.

Cell component	Characteristics
Cathode	Embroidery with a geometric area 15 cm × 18 cm (270 cm^2)
	Coverage by embroidered stainless steel thread 45% (122 cm^2) polypropylene support
Catholyte	Alkaline complex solution
Catholyte circulation	12 mL min^{-1}
Anode	Embroidery with a geometric area 15 cm × 18 cm (270 cm^2)
	Coverage by embroidered stainless steel thread 45% (122 cm^2) polypropylene support
Anolyte	0.5 M or 1 M NaOH solution (Bechtold and Turcanu, 2009)
Anolyte circulation	8 mL min^{-1}
Membrane	Nafion type cation exchange membrane
Electrical power	0.15 W
Cell current	85 mA
Current density	0.31 mA cm^{-2}
Cell voltage	1.85 V

by the addition of 100 mL of 1 M $CaCl_2$ solution. Finally 15 mL of 9.75 M NaOH were added to the solution, in order to reach an initial pH of 11. After complete dissolution of the initially precipitated Ca-Fe-D-gluconate complex, the solution was made up to a volume of 1 L.

A 0.5 M or 1 M solution of NaOH in water was used as anolyte (Bechtold and Turcanu, 2009). A catholyte volume of 250 mL was used for the electrolysis experiments, but for dyeing experiments, the catholyte volume was increased to 550−590 mL. The anolyte volume was set at 250−500 mL. The higher volume of anolyte was used in the case of the lower NaOH concentration in the anolyte.

After filling the catholyte and the anolyte compartments, the cell current was switched on and the redox potential lowered continuously. Once the redox potential in the catholyte had reached the threshold value of −720 mV (vs. Ag/AgCl, 3M KCl reference electrode), indigo dye was added to the solution either as oxidised powder or leuco-indigo solution. Following the addition of indigo powder, the electrolysis was continued to achieve complete reduction of the dye. The reduction and dissolution of indigo was monitored as function of the electrolysis time by measurement of the absorbance of the reduced indigo in the catholyte at 405 nm (0.1 mm flow cuvette, single beam filter photometer, Merck SQ 300, Merck, Darmstadt, Germany) (Laksanawadee et al., 2018). In experiments with addition of pre-reduced indigo solution, the dyebath first was brought to −730 to −740 mV, before the required volume of reduced indigo solution was added. Then the catholyte was circulated to achieve homogeneous dyestuff concentrations and used for dyeing experiments (Bechtold et al., 2008).

2.4. Determination of Fe(II)-concentration

The determination of cathodically formed Fe(II)-complex in the catholyte (Ca-Fe-D-gluconate) was performed by photometry of the Fe(II)-1,10-phenanthroline complex at a wavelength of 520 nm. The phenanthroline method permits the determination of both the concentration of Fe(II)-complex formed and the total iron concentration. To analyse the iron concentrations in the catholyte a volume of 2 mL electrolyte was neutralised with addition of 5 mL sulphuric acid (20 %wt) and made up with deionised water to a volume of 100 mL. To form Fe(II)-phenanthroline complex, 3 mL of the neutralised catholyte were mixed with 5 mL of buffer solution (50 g NH_4OAc, 50 mL acetic acid in 250 mL solution, pH 4.97), and 2 mL of 1,10 phenanthroline solution (0.5 g phenanthrolinium chloride in 100 mL of deionised water) and made up to 100 mL. For determination of the total iron concentration, 2 mL of hydroxyl-amine solution (5 g of NH_3OHCl in 50 mL of deionised water) was added as reducing agent to the assay before the solution was made up to 100 mL (DIN, 1983).

Photometric measurements were performed at 520 nm using a double beam spectrophotometer (HITACHI U-2000, Japan). The turnover of Fe(III)-complex into Fe(II)-complex in the solution was calculated according to equation (1) (DIN, 1983; Bechtold et al., 2002):

$$Turnover\ (\%) = 100 \times absorbance\ Fe(II)/absorbance\ total\ Fe(II/III) \quad (1)$$

2.5. Preparation of dyebath for reference dyeing experiments

In order to compare samples dyed with cathodically reduced indigo to the conventional process, a dyebath with use of sodium dithionite as a reducing agent was prepared according to the technical instructions of the indigo producer (BASF, 1977). A volume of 100 mL indigo stock vat was prepared by adding 0.4 g of dispersing agent (lignosulphonate, Setamol WS®, BASF), 0.1 g of wetting agent (alkylphosphate, Primasol NF®, BASF), 8 g of indigo powder, 7.5 mL of NaOH (50 %wt) solution and 6 g of $Na_2S_2O_4$ to the required volume of 50 °C hot water followed by a vatting time of 30 min. The dye liquor was prepared by adding the calculated amount of the stock vat dye (12.5 mL of stock vat correspond to 1 g L^{-1} indigo) to a solution containing 1 g L^{-1} of dispersing agent, 1 g L^{-1} of wetting agent, 3 mL of 50%wt NaOH solution and 1.5 g L^{-1} of $Na_2S_2O_4$.

To determine the concentration of reduced indigo in the electrolyte during electrolysis, a calibration curve was set up using indigo concentrations in the range of 1 g L^{-1} to 4 g L^{-1}. These solutions were prepared from the stock vat solution using sodium dithionite as a reducing agent. A volume of 100 mL solution was prepared by adding an amount of the stock vat (1.25 mL−5 mL) to a solution containing 0.1 g of dispersing agent, 0.1 g of wetting agent, 0.3 mL of 50%wt NaOH solution and 0.15 g (1.5 g L^{-1}) of $Na_2S_2O_4$. For on-line measurement of reduced indigo concentration, a flow through cuvette with path length of 0.1 mm was used to measure the absorbance of reduced indigo at 405 nm in the electrolyte without dilution (filter photometer Merck SQ 300, Merck, Darmstadt, Germany).

2.6. Dyeing procedure

Dyeing experiments were performed on a laboratory pad dyeing machine with a speed of 0.1 m min^{-1} and a pressure of 2 bar. After dipping the fabric in the dye bath and squeezing out of excess dyebath to a pick-up (*PU*) of 80 L per 100 kg goods, the samples were oxidised by air for approximately 2 min. For dyeings with 2 or 3 dips, fresh dyebath solution was used for every dip, to avoid unwanted oxidation of the dyebath during the time of aeration between two consecutive dips. The dyed samples then were washed thoroughly in cold tap water and dried at room temperature.

2.7. Colour measurement

The results of the dyeing experiments were evaluated by measuring the colour strength in terms of the Kubleka-Munk value (K/S) at 660 nm (equation (2)) and calculation of the CIELab colour coordinates from the reflectance curves of the dyed samples (Konica Minolta CM-36110d Chroma-Meter, geometry = d/8°; illuminant: D65) (Kubelka and Munk, 1931). In the CIELab colour coordinate system the L* value is a measure for the lightness (black L* = 0, white L* = 100), the a* value describes the position on the red-green axis (positive a* = red, negative a* = green) and the b* value describes the position on the yellow-blue axis (positive b* = yellow, negative b* = blue). Values given are calculated as mean of four measurements.

$$\frac{K}{S} = \frac{(1-R)^2}{2R} - \frac{(1-R_0)}{2R_0} \quad (2)$$

where R is the decimal fraction of the reflectance of dyed fabric compared to the standard white (100% reflectance, R = 1), R_0 is the decimal fraction of the reflectance of undyed fabric, K is the absorption coefficient and S is the scattering coefficient according Kubelka-Munk.

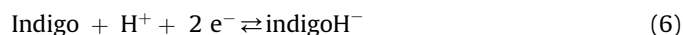## 3. Results and discussion

3.1. Selection of the mediator composition

The redox potential in solution, that can be achieved with a

certain iron complex depends on the type of complex present and on the ratio between Fe(II)-form and Fe(III)-form of the respective complex. Experiments with Fe(II/III)-D-gluconate and Fe(II/III)-hepta-D-gluconate complexes in presence of Ca^{2+} ions indicated, that a more negative redox potential could be achieved for a given ratio Fe(II)/Fe(III). This observed change in redox potential is explained with formation of binuclear Ca-Fe-D-gluconate complexes (Bechtold et al., 2002; Bechtold and Turcanu, 2004).

The influence of the calcium concentration on the build-up of the required redox potential of the Fe(II/III)-complexes was studied in cathodic reduction experiments in absence of indigo. For purposes of technical indigo dyeing an iron complex is required, which permits the pre-establishment of a negative redox potential in the dyebath at minimum Fe(II)-concentration, as the Fe(II)-form will be oxidised completely during each step of airing after immersion into the dyebath. The power consumption for regeneration of the Fe(II)-concentration in the dyebath thus will be dependent on the Fe(II)-concentration required to maintain stable reduction conditions in the indigo dyebath.

When the concentration of Fe(II/III)-ions in the electrolyte is higher than the concentration of Ca^{2+} ions, two types of complexes are present in the electrolyte, the Ca-Fe-D-gluconate complexes and the Fe-D-gluconate complexes (Bechtold et al., 2002; Bechtold and Turcanu, 2004). The redox reactions for Fe(II)-complex formation and indigo reduction in the catholyte can be formulated as shown in equations (3)–(6).

$$Fe(III) - DGL + e^- \rightleftharpoons Fe(II) - DGL \tag{3}$$

$$Ca - Fe(III) - DGL + e^- \rightleftharpoons Ca - Fe(II) - DGL \tag{4}$$

$$Indigo + 2e^- \rightleftharpoons indigo2^- \tag{5}$$

$$Indigo + H^+ + 2e^- \rightleftharpoons indigoH^- \tag{6}$$

A scheme of the electrochemical processes in the cell in presence of indigo is given in Fig. 2. The redox potential in solution thus is dependent on the relative concentrations of at least four iron complexes.

To achieve maximum affinity of the reduced indigo, the dyebath pH usually is maintained in the pH range between 11.5 and 12.5. Thus in this study, two electrolytes (composition 1 and composition 2, Table 2) were compared in this pH range with regard to their electrochemical behaviour and the dyeing behaviour of indigo.

Starting from the oxidised Fe(III)-form of the Ca-Fe-D-gluconate complex, the build-up of reduction potential was monitored in batch electrolysis experiments. The experiments were performed under galvanostatic conditions (current 85 mA). The build-up of reduction potential and pH as function of time are given in Fig. 3a and b for the recipes type 1 and type 2 (Table 2).

Besides measurement of redox potential and pH in the catholyte, the concentration of Fe(II)-complex present in the electrolyte at certain redox potential was determined. In the experiments, aqueous NaOH was used as anolyte, thus an increase in pH in the catholyte is observed as function of charge transport through the membrane. This increase in pH also contributes to the observed reduction potential in the catholyte. In Fig. 3a and b, the build-up of the redox potential and the increase in pH in the catholyte solution are shown as a function of electrolysis time. For electrolytes 1a and 1b a rapid build-up of reduction potential is observed within the first 20−25 min of electrolysis. Below −550 mV, the change in reduction potential slows down, which is due to the build-up of significant concentrations of the Ca-Fe(II)-D-gluconate complex. The change in redox potential as function of electrolysis time is a consequence of the galvanostatic experiment. Due to application of a constant current, a proportional change in concentration of Fe(II)-complex is achieved in the catholyte. The measured redox potential however follows the Nernst equation, thus in a simplified approach a logarithmic dependency on the concentrations of Fe(II)-complex and Fe(III)-complex will be observed (Bechtold and Turcanu, 2002). In catholytes 2a and 2b, only 80% of the stoichiometric amount of Ca^{2+}-ions required to form the Ca-Fe-D-gluconate complex, is present in the solution. Thus approximately 20% of the Fe-ions are bound as Fe-D-gluconate complex. This complex exhibits a lower reduction potential, thus formation of Fe(II)-D-gluconate precedes the formation of the Ca-Fe(II)-D-gluconate complex. As a result, a retarded build-up of the negative reduction potential is observed in catholytes of composition 2a and 2b.

For the alkaline Fe(II/III)-triethanolamine complex, model calculations have been published in the literature, that describe the
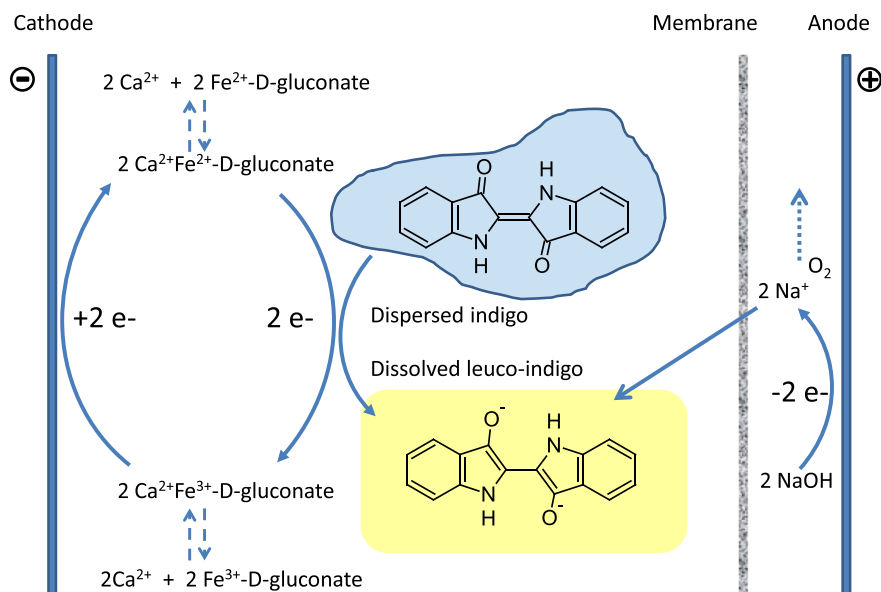

Fig. 2. Scheme of reactions occurring in the electrochemical cell during reduction of dispersed indigo by Ca-Fe-D-gluconate complex.
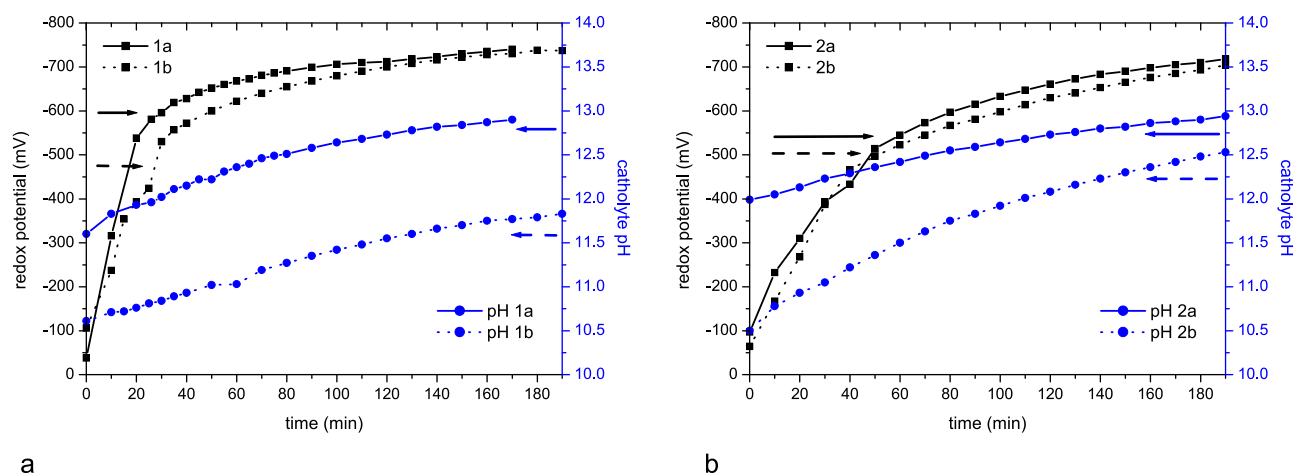
Fig. 3. Batch electrolysis experiments at galvanostatic conditions. Build-up of reduction potential and change in pH in catholyte during electrolysis. Fig. 3a (fx2) catholyte 1a, initial pH 11.6 and (fx3) catholyte 1b, initial pH 10.6; Fig. 3b (fx4) catholyte 2a, initial pH 12.0 and (fx5) catholyte 2b, initial pH 10.5.

build up of reducing conditions as function of the experimental parameters (Bechtold and Turcanu, 2002). The formation of a certain redox potential as function of time depends not only on the reduction state of the Fe(II/III)-complex. Other determining factors to be considered are for example the applied cell current, the electrochemical efficiency of the electrolyser, the volume of electrolyte in the cell, as well as by the total concentration of iron complex used in the electrolyte.

For an assessment of the suitability of a complex system to permit efficient use in technical scale indigo dyeing, the ratio of Fe(II)-complex compared to the total iron concentration represents the more robust measure. A detailed analysis of the reduction state in the catholyte, as a function of the conversion of Fe(III) into Fe(II) is given in Fig. 4a–d.

The formation of different complex species and the redox behaviour of Fe(III)-complexes with D-gluconate have been studied in the literature (Bechtold et al., 2002). The redox potential of the Fe(II/III)-D-gluconate complex depends on the solution pH, as release or uptake of protons are involved in the redox reaction. In presence of Ca^{2+} ions, binuclear complexes are formed in a stoichiometric reaction. In case of under-stoichiometric amounts of

Ca^{2+} ions, the Ca-Fe(III)-D-gluconate complex forms and the surplus of Fe(III)-D-gluconate complex remains. The redox potential of the Fe(III)-D-gluconate complex is less negative, thus during electrochemical reduction the Fe(III)-D-gluconate complex has to be reduced, before the Ca-Fe(III)-D-gluconate complex is reduced. As a consequence, the formation of a redox potential below −700 mV is retarded in electrolytes, where the concentration of Ca^{2+} ions is not equivalent to the concentration of Fe(III)-D-gluconate. Because of the Nernst equation, the value of −700 mV is reached at different Fe(II)-concentration, depending on the composition of the complex and NaOH concentration. Therefore, these investigations were performed to determine the optimum recipe, which requires the minimum Fe(II)-concentration at pH 11.5–12.0 for the indirect reduction of indigo at −700 mV.

The different curves for the build-up of the reduction potential as function of Fe(II)-concentration clearly demonstrate dependence of the reduction potential on both the concentration of Ca^{2+} ions and the pH of electrolyte.

For successful reduction of indigo dye, a reduction potential of lower than −700 mV has to be achieved in solution. The ratio of Fe(II)/Fe(II/III) to achieve a reduction potential of −700 mV and the
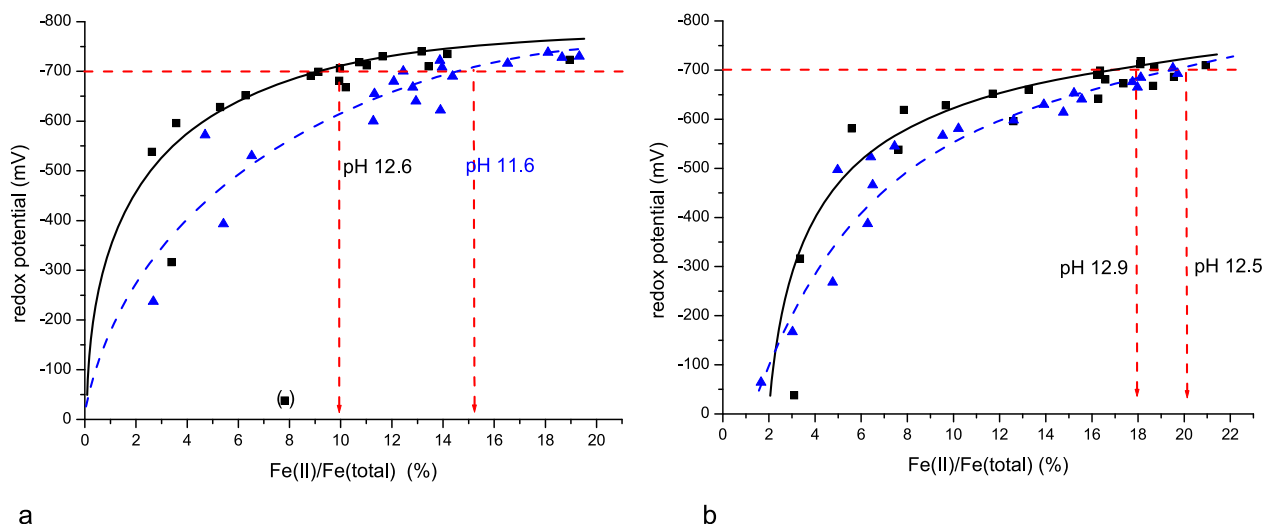

Fig. 4. Batch electrolysis experiments at galvanostatic conditions. Reduction potential in the catholyte as function of ratio Fe(II)/Fe(total). Fig. 4a (fx6) catholyte 1a, initial pH 11.6 and (fx7), catholyte 1b initial pH 10.6; Fig. 4b (fx8) catholyte 2a, initial pH 12.0 and (fx9) catholyte 2b, initial pH 10.5.

respective pH value at this point are also marked in Fig. 4a and b. In case of recipe 1a at pH 12.6, a share of 10% of the total iron present as Ca-Fe(II)-D-gluconate complex already is sufficient to achieve a potential of -700 mV. At pH 11.6 (recipe 1b), the amount of Fe(II)-complex required to reach -700 mV increases to 15.5%. In recipes 2a and 2b (Fig. 4b) the concentration of Ca^{2+} ions was reduced to 0.080 M, while the concentration of Fe-ions was maintained at 0.1 M. Thus 20% of the iron complexes initially present in the catholyte, are Fe(III)-D-gluconate complexes and 80% are present as Ca-Fe(III)-D-gluconate complex. The reduction potential of the Fe(III)-D-gluconate complex is less negative compared to the Ca-Fe-D-gluconate complex. Thus at the beginning of the reduction, substantial concentrations of Fe(II)-D-gluconate have to be formed first, before the potential can reach the target value of -700 mV. At pH 12.9, a share of 19% of the total iron has to be transferred into the Fe(II)-form to reach a redox potential of -700 mV. This value increases to 20.5% Fe(II)/Fe(II/III) at pH 12.5.

For an efficient use of reducing agent in technical indigo dyeing, the surplus of reducing agent to achieve a reduction potential of -700 mV should be as low as possible, as this amount will be oxidised completely during the air passage following each immersion of the yarn into the dyebath. As a consequence, the recipe 1 with the complex (Ca-Fe-D-gluconate) in 1:1:1.1 stoichiometry was chosen as a mediator solution for reduction of dispersed indigo and dyeing experiments.

3.2. Reduction of dispersed indigo by indirect electrolysis

Based on the results of the batch electrolysis experiments with different Ca-Fe-D-gluconate solutions, the composition of the electrolyte for batch reduction of indigo was defined with 0.1 M $FeCl_3$, 0.1 M $CaCl_2$, 0.11 M D-gluconate. The experimental procedure follows an approach, which has been reported for vat dyes using the Fe(III)-triethanolamine complex (Bechtold and Turcanu, 2009). To demonstrate the successful reduction of oxidised indigo, the complex was prepared in Fe(III)-form and then reduced to a solution potential of -720 mV. The solution potential of -720 mV was chosen to achieve stable reducing conditions for reduced indigo. Then indigo powder was added, and reduction into leuco-indigo was monitored by on-line photometry and redox potential measurement. As a result of the addition of oxidised indigo the redox potential increases to more positive values.

The electrochemical reduction was continued until the redox potential had reached -720 mV again. At a solution potential below -720 mV, the concentration of Ca-Fe(II)-D-gluconate complex increases further and the concentration of the corresponding Ca-Fe(III)-form decreases accordingly. This reduces the concentration of the electroactive Fe(III)-complex and thus would lead to a lower current efficiency of the mediator system. The reduction of the dispersed blue indigo powder into the yellow leuco-form was monitored by on-line measurement of the absorbance at 405 nm. By determination of the dissolved indigo in solution, the actual concentration of reduced indigo available for the dyeing process was determined. Representative examples of the reduction experiments are given in Fig. 5a and b.

The increase in absorbance at 405 nm demonstrates the successful reduction of oxidised indigo by the Ca-Fe(II)-D-gluconate complex. The absorbance of reduced indigo at 405 nm was used to establish a calibration curve, to determine the actual concentration of reduced indigo in the solution. The calibration curve is given in the supplementary information (Fig. S3). Thus results of dyeing experiments can be related to the actual concentration of indigo present in the dyebath, and become independent on any losses of indigo in the electrolyser e.g. through deposition of oxidised indigo e.g. on the cation exchange membrane or inside the silicone tubes used. The concentration of reduced indigo in the dyebath is important, to relate the colour depth of test dyeings with cathodic dyestuff reduction, to results of standard dyeings. These were obtained use of a stock vat or with use of pre-reduced (hydrogenated) indigo.

3.3. Results of dyeing experiments

The dyeing behaviour of electrochemically reduced indigo powder and of pre-reduced indigo solution (indigo solution BASF 20%) was investigated in dyeing experiments with different dye concentration. The dyeing results were evaluated by determination of the K/S value as measure for the colour strength (wavelength 660 nm) and the CIELab coordinates of the dyed samples. Reference dyeings with use of sodium dithionite as a reducing agent were performed in order to allow a comparison between the electrochemical process and the conventional dyeing process.

According to indigo concentrations used in technical dyeing processes, concentrations in the range of $1-3$ g L^{-1} indigo were used in the dyeing experiments. The reduced form of indigo exhibits low affinity to the cotton yarn, thus in technical dyeing the desired colour depth is built up through repetitive immersion of the material into the dyebath each step followed by air oxidation (Paul, 2015).

Dyeings with one dip and three dips, were performed to study the build-up of colour depth. The results of a single dip dyeing characterises the affinity of the dyestuff to the cotton material, while the build-up of colour depth during repetitive dyeing is characterised by experiments with use of three dips.

Fig. 6a and b the colour strength of the dyed samples performed with 1 dip and 3 dips as a function of the dyestuff concentration in the dyebath are shown.

For both dyeings with use of 1 dip and with 3 dips a direct relation is observed between concentration of reduced indigo in the dyebath and colour depth in terms of K/S value measured at 660 nm. The results are independent of the reduction process applied, which demonstrates that the dyeing behaviour of the reduced indigo is not dependent on the reduction process used. No significant difference in colour depth was observed between dyeings with use of indigo powder, or hydrogenated indigo in form of a leuco-indigo solution.

The build-up in colour depth with increasing number of dips also can be recognised by comparison of K/S values for a given indigo concentration, e.g. at an indigo concentration of 3.5 g L^{-1} a K/S value of 4 is obtained with 1 dip (Fig. 6a), which increases to a K/S value of 10 after 3 dip dyeing.

The CIELab coordinates of the dyed samples were measured, to assess possible differences in shade of the dyeings. Fig. 7 shows the L* coordinate and the b* coordinate for dyeings with dithionite reduction and electrochemical dyebath reduction. The L* was chosen to characterised the lightness of the dyeing and the b* coordinate is a measure for the intensity of the blue shade. The complete figures of the respective CIELab coordinates are given in the supplementary information (Table S1).

The results given in Fig. 7a demonstrate, that a change in the reduction technique used does not lead to substantial differences in colour in 1 dip dyeing. In Fig. 7b the development of the L* value of the different dyeings is similar, while differences in the b* values appear between the two reduction techniques. In these experiments dithionite dyeing exhibits the more negative b* coordinates, which indicates a more brilliant shade. For a detailed analysis, further extension of the experimental conditions has to be undertaken to evaluate the influence of all possible factors in detail. Representative parameters to be investigated in a more technical approach should consider dyebath pH, total concentration of salt in
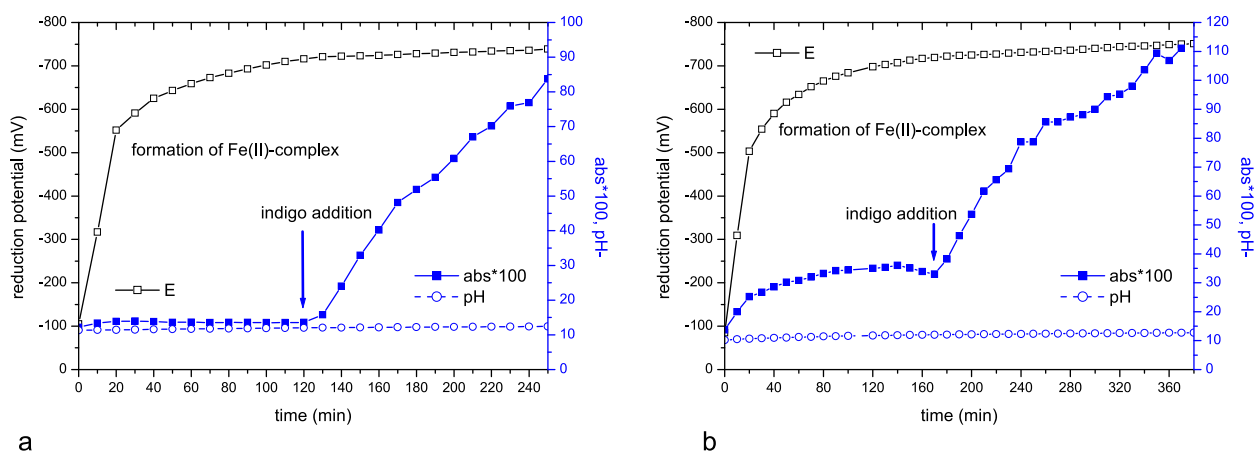
Fig. 5. Indirect cathodic reduction of indigo powder. Redox potential and pH in the catholyte (composition 1; 0.1 M FeCl$_3$, 0.1 M CaCl$_2$, 0.11 M D-gluconate) and absorbance at 405 nm as function of time (cell current 85 mA): a) 1.23 g L^{-1} indigo reduced (2 g L^{-1} indigo added), initial pH 11.3, end pH 12.4; b) 1.81 g L^{-1} indigo reduced (3 g L^{-1} indigo added), initial pH 10.2, end pH 12.7.
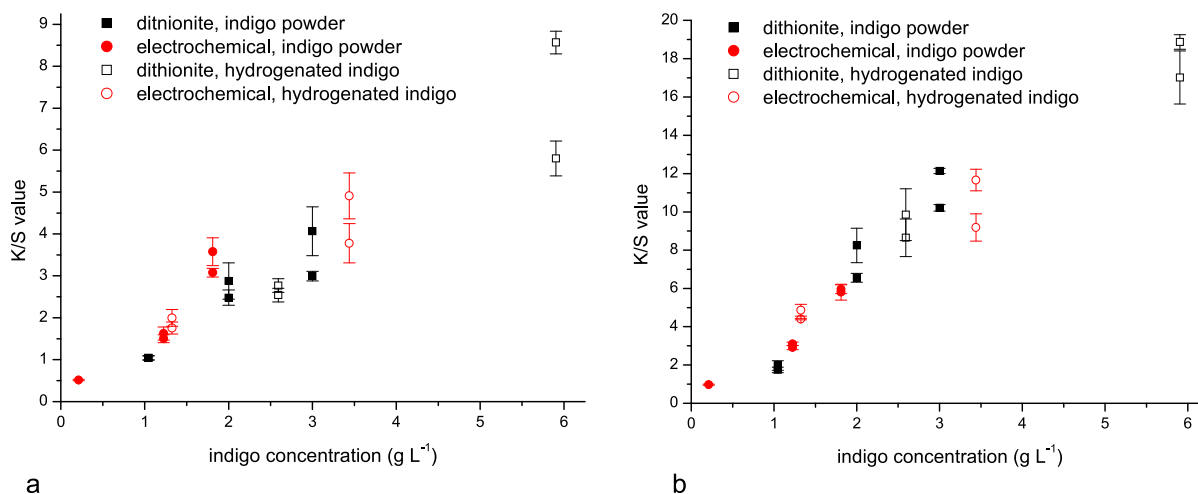

Fig. 6. Colour depth of dyeings as function of reduced indigo concentration for 1 dip and 3 dip dyeing (dip = immersion in dyebath followed by air oxidation) a) 1 dip dyeing; b) 3 dip dyeing. ■ dithionite reduction powder indigo; □ dithionite reduction, leuco-indigo solution; ● electrochemical reduction; ○ electrochemical reduction, leuco-solution (K/S values given as mean and standard deviation of four measurements). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)
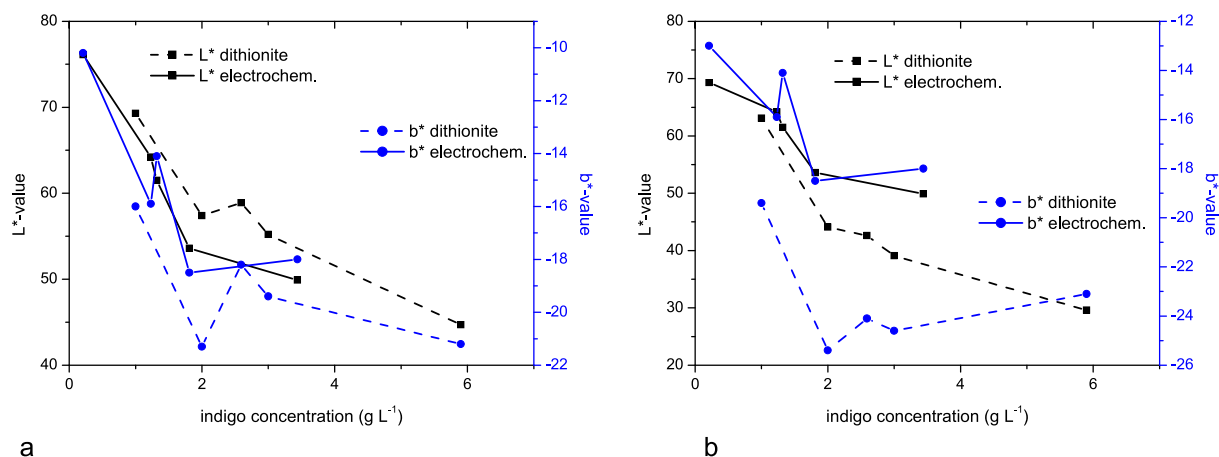

Fig. 7. CIELab coordinates L* and b* of dyeings with a) 1 dip and b) with 3 dips as function of dyestuff concentration in the bath (dashed lines L* and b* dithionite reduction, solid lines L* and b* electrochemical reduction).

the dyebath, concentration of reducing agent in the dyebath.

3.4. Technical layout for electrochemical indigo dyeing

Based on the data elaborated in this study, an assessment of the ecological profile of a full scale installation is possible. A flow scheme for a plant installation in technical scale is given in Fig. 8. The dyebath is circulated through the electrochemical cell, where the concentration of Fe(II)-complex is regenerated to maintain stable indigo dyestuff reduction in the dyebath. From the experimental results given in this work, a first comparison between the existing dithionite based technology and the electrochemical dyestuff reduction using the Ca-Fe-D-gluconate complex can be undertaken. Direct recycling of mediator complex and water is possible through collection of a concentrated waste stream from the washing step and use in the prewetting operation. Integration of Ultra- and Nanofiltration will permit a more complete recovery of indigo, chemicals and water.

3.5. Current efficiency and size of electrolyser

From the charge flow required for reduction of a certain amount of indigo, the current efficiency of the electrochemical system can be calculated according Faraday's law (equations (7)–(9)).

$$C_{red.indigo} = I*t = n_{red.indigo}*z*F = c_{red.indigo}*V_{catholyte}*z*F \qquad (7)$$

$$C_{electrochem.} = I_{exp.} * t_{exp.} \qquad (8)$$

$$\eta_{curr.} = \frac{C_{red.\ indigo}}{C_{electrochem.}} \qquad (9)$$

The current efficiency $\eta_{curr.}$ for indigo reduction achieved in the electrochemical experiments can be calculated by comparison of the analytically determined charge flow ($C_{red.indigo}$, in As) calculated from the concentration of reduced indigo $c_{red.indigo}$ (M) and the volume of catholyte $V_{catholyte}$ (L), with the total charge flow ($C_{electrochem.}$ in As). F represents the Faraday constant (96485 As mol^{-1}) and z represents the number of electrons transferred. The electrochemically required charge flow $C_{electrochem.}$ (As) can be calculated from the cell current $I_{exp.}$ (A) and the time $t_{exp.}$ (s) actually used for dyestuff reduction.

For the experiment given in Fig. 5a, a current of 85 mA had been applied for 130 min, to achieve a concentration of 1.23 g L^{-1} reduced indigo in a volume of 580 mL of catholyte. The reduction of 2.7 mmol indigo requires a charge flow $C_{red.indigo}$ of 523 As, while a real charge flow $C_{electrochem.}$ of 663 As had been applied. Thus a current efficiency $\eta_{curr.}$ of 79% had been achieved in this experiment.

In the experiment given in Fig. 5b, a current of 85 mA had been applied for 200 min, to achieve a concentration of 1.81 g L^{-1} reduced indigo in a volume of 545 mL of catholyte. The reduction of 3.8 mmol indigo requires a charge flow $C_{red.indigo}$ of 726 As. A real charge flow $C_{electrochem.}$ of 1020 As had been applied, thus a current efficiency $\eta_{curr.}$ of 71% had been achieved in this experiment.

The experimental results demonstrate, that a current efficiency of 70−80% can be achieved without optimisation of the installation. Thus a current efficiency of 80% can be taken as a realistic value for further estimation of plant dimensions.

In state-of-the-art technology, continuous addition of dithionite into the dyebath is required to compensate for intake of oxygen and to maintain the indigo in its reduced state. The dimension of an electrolyser to substitute conventional dithionite addition can be estimated from the dithionite consumption of a conventional plant. Representative conditions of operation of a full scale indigo dyeing unit for denim production are summarised in Table 3.

The concentration of dithionite in the dyebath is maintained at a level of 1 g L^{-1}, which corresponds to a concentration of 0.011 M reducing equivalents to maintain indigo in the reduced state. With use of 0.1 M Ca-Fe-D-gluconate complex, the share of complex to achieve −700 mV is dependent on the dyebath pH, and ranges between 10% and 15% of the total complex concentration. Thus under the conditions studied in this work the concentration of the reducing Fe(II)-form is between 0.01 M and 0.015 M, which is comparable to the reducing equivalents with use of 1 g L^{-1} dithionite in the dyebath.

Using Faraday's law (equation (6)), the reducing equivalents

Table 3
Representative conditions of operation of a full scale indigo dyeing unit and estimated data for a substitution with an electrochemical reduction unit (Bechtold and Pham, 2019).

| Parameter	Value	Unit
Colour depth, indigo	1	%wt
Production speed	35	m min^{-1}
Hours per day	21	h d^{-1}
Mass per length	340	g m^{-1}
Total production	15,000	kg d^{-1}
Water consumption	5	L kg^{-1} goods m^3 d^{-1}
	75	
Chemical reduction		
Dithionite concentration	1	g L^{-1}
Dithionite consumption	40−100	g min^{-1}
	50−126	kg d^{-1}
Electrochemical reduction		
Cell current	924−2309	A
Electrical power	2.8−6.9	kW
Energy consumption	58−145	kWh d^{-1}
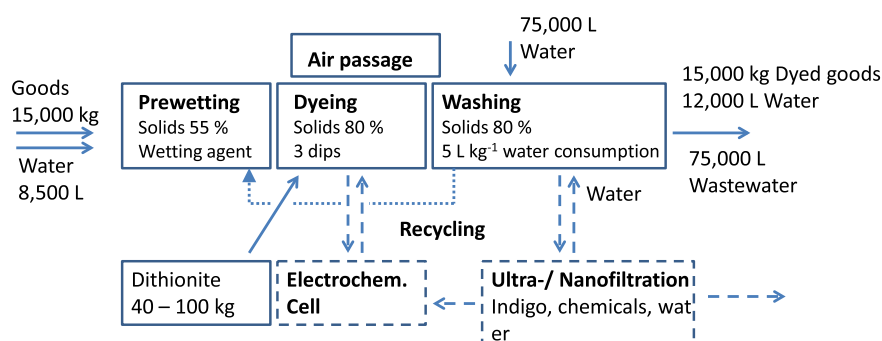
Fig. 8. Scheme of indigo dyeing with representative figures of production, chemical and water consumption per day. The installation for indirect electrochemical dyebath reduction and recycling of waste water is given in dashed squares. Option of direct mediator and water recycling is indicated with dotted line.
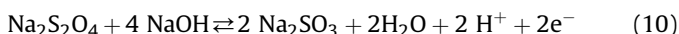
added to the dyebath in form of dithionite can be transferred into a theoretical cell current required. A consumption of $40-100$ g min^{-1} sodium dithionite is equivalent to a theoretical cell current of $739-1847$ A. Taking into consideration a realistic current efficiency of 80%, the required cell current will be in the dimension of $924-2309$ A.

3.6. Energy consumption

The power of an electrolyser can be estimated on the basis of the experimental cell voltage. A cell voltage of 1.85 V was required, to achieve the comparable low cell current of 85 mA (current density 0.31 mA cm^{-2}). A cell voltage of 1.9 V was sufficient to achieve a cell current of 200 mA. Taking into consideration that a commercial cell will have to operate at higher current density, a cell voltage of 3 V was considered to estimate the power consumption of the electrolyser. Dependent on the cell current of $924-2309$ A, the electrical power of the installation will range from 2.8 to 6.9 kW. For a 21 h time of production per day, the overall energy consumption of the electrolyser thus will be $58-145$ kWh instead of a dithionite consumption of $50-126$ kg. Based on average costs of 1 € per kg sodium dithionite of 0.1 € for 1 kWh, the energy costs of the electrochemical dyestuff reduction will be approximately 12% of the costs for use of chemical reduction.

3.7. Chemical consumption and wastewater load

The chemical consumption of both processes also can be compared with regard to the chemicals released from the dyeing step into the wastewater. In an ideal case for sodium dithionite, the total amount of dithionite is transferred first into sodium sulphite, which then oxidises with air oxygen into sodium sulphate (equations (10) and (11)) (Bechtold and Pham, 2019).

$$Na_2S_2O_4 + 4\ NaOH \rightleftarrows 2\ Na_2SO_3 + 2H_2O + 2\ H^+ + 2e^- \qquad (10)$$

$$Na_2SO_3 + \tfrac{1}{2}\ O_2 \rightleftarrows Na_2SO_4 \qquad (11)$$

Taking into account the dithionite and water consumption of a technical installation (Table 3), the concentration of Na_2SO_4 in the waste water will range between 0.95 g L^{-1} and 2.36 g L^{-1}. Such concentrations then lead to a sulphate concentration in the waste water of $640-1600$ mg L^{-1}, which is far beyond the legal limit of 200 mg L^{-1} sulphate for waste water released from a textile dyehouse.

In absence of any recycling, the Ca-Fe-D-gluconate complex is released completely into the wastewater. While no waste water limits for Ca^{2+} or Fe^{3+} have been defined, the chemical oxygen demand (COD) value for the oxidation of the sodium gluconate has to be taken into account. As oxidation of 1 g Na-D-gluconate will require 0.99 g O_2 as COD, the released amount of Na-D-gluconate permits direct estimation of the contribution to the COD load in the waste water. In the dyeing experiments, the Na-D-gluconate concentration was set with $c_{gluc.}$ 0.11 M, which then results in a COD load of 481 mg O_2 per L of wastewater (equation (12)). Further reduction of the COD value can be achieved by simple regeneration operations e.g. through collection of concentrated waste water streams and reintroduction into the dyeing process.

$$COD = c_{gluc.} * f * M_{O2} * \frac{PU}{100} * \frac{1}{\left(W + \frac{PU}{100}\right)} \qquad (12)$$

$c_{gluc.}$ D-gluconate concentration (M), f stoichiometric factor to transfer mass of D-gluconate into COD (f = 990 mg g^{-1}), M_{O2}

molecular mass of oxygen (g mol^{-1}), PU pick-up of goods at the entry into the washing unit (L per 100 kg goods), W consumption of water in the washer (L kg^{-1}).

The COD value of the released waste water is due to the biodegradable D-gluconate, thus biodegradation of the wastewater in a waste water treatment plant will be possible without complications.

The release of D-gluconate into the waste water still leads to a considerable consumption in D-gluconate. Based on the present study, the total loss in D-gluconate would reach a value of 288 kg per day. In addition, substantial amounts of $FeCl_3$ (195 kg) and $CaCl_2$ (133 kg) would be consumed without implementation of recycling techniques. As the reduction power of the complex can be regenerated, introduction of recycling techniques to recover the major part of valuable Ca-Fe-D-gluconate from the waste water will be the decisive next step to close the loop of chemicals and water as indicated in Fig. 8. By reuse of the washing water and the reversible reducing agent, both a reduction in water consumption for indigo dyeing by 80% and in chemical consumption by 50% are expected.

4. Conclusions and further perspectives

Indirect electrochemical reduction using reversible redox couples offers new aspects for a greener indigo dyeing method. The use of embroidered electrodes in a flow through electrolyser permits straightforward design, manufacturing, and assembly of electrolysers with high internal surface. For an efficient use of the Ca^{2+}, Fe^{3+} and D-gluconate complexes, the binuclear complexes of with a 1:1:1.1 stoichiometry were found best suited as mediators for indirect cathodic reduction of indigo. These complexes require a low concentration of Fe(II)-complex to achieve a reduction potential of -700 mV in the pH range of $11.5-12.5$. Reduction of the ratio of Ca^{2+} to Fe^{3+} in solution e.g. to 0.8:1 leads to an increase in Fe^{2+} concentration required to achieve a redox potential of -700 mV, which then directly increases loss of reduced species in the air oxidation step. This would increase the required size of an electrolyser substantially.

The comparison of test dyeings with electrochemically reduced indigo demonstrated the suitability of the technology for indigo dyeing, as only minor differences in colour depth and shade were observed in comparison to reference dyeings with dithionite as reducing agent.

Model calculations based on the experimental results demonstrate the potential of the technology to substitute the use of non-regenerable chemicals by regenerable redox systems. The estimated costs for electrical power range in the level of $10-15$% of the dithionite costs.

To achieve an improvement in the ecological profile of the indigo dyeing process, a recovery and regeneration of the reversible redox system is essential. The reuse of the chemicals will lead to a substantial reduction in chemical consumption and in parallel, to a reduction in fresh water consumption. The calculations of the chemical consumption of the process indicate the need for recovery of the Ca-Fe-D-gluconate from the waste water stream, which will lower both the costs for the chemicals and permit savings in water consumption. Further reduction in chemical consumption also will be possible through further reduction of the concentration of the Ca-Fe-D-gluconate complex and by use of efficient electrolysers with high cathode surface.

The development of an efficient electrochemical cell and scale up of the process are part of an ongoing research programme to integrate the technology in full scale operation. Besides design of robust electrochemical equipment, optimisation of the electrode design to operate at lowest concentrations of mediator complex will be required.

Future investigations will have to include appropriate strategies to recover and regenerate the mediator complex from the waste water. Research will be required, to investigate influence of soluble substances released from the processed cotton into the dyebath, which could reduce the performance of the electrochemical system.

An important aspect to be considered during scale up of the technology will address the influence of sulphur dyes used for dyeing of many indigo shades in form of bottoming or topping operations. Studies to investigate the compatibility of the electro-chemical indigo reduction with sulphur black thus will be part of future research efforts.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

Maha Abdelileh: Investigation. **Avinash P. Manian:** Investigation. **Dorian Rhomberg:** Resources. **Manel Ben Ticha:** Supervision, Investigation. **Nizar Meksi:** Supervision, Funding acquisition, Investigation. **Noemí Aguiló-Aguayo:** Project administration. **Thomas Bechtold:** Project administration.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jclepro.2020.121753.

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