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Direct electrochemical reduction of indigo: process optimization and scale-up in a flow cell

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Abstract

Reducing agents required in the dyeing process for vat and sulfur dyes cannot be recycled, and lead to problematic waste products. Therefore, modern economical and ecological requirements are not fulfilled. The industrial feasibility of the direct electrochemical reduction of indigo as a novel method has been determined and a preliminary optimization of electrolytic conditions was performed using a laboratory-scale flow-cell system. The role of current density, pH, temperature and the rate of mass transport are discussed. The influence of particle size reduction by the application of ultrasound is critically considered.

1. Introduction

Vat dyes, such as indigo, are traditionally used to dye cellulosic fibres as they show excellent colour fastness. Until now in most industrial processes vat dyes are chemically reduced by sodium dithionite. This procedure is necessary to attain a water soluble form of the dyestuff, the so called leuco dye with an affinity to the cellulosic fibre. After diffusion into the fibre it will remain fixed there after having been oxidized back to the water-insoluble form. This process produces large amounts of sodium sulphate and sulphite as byproducts which increase the costs for waste water treatment in the corresponding textile plants. Hence, the need to develop and use ecofriendly alternatives is becoming very important. Investigations were focused on the replacement of sodium dithionite by an organic reducing agent (i.e., α-hydroxyketones [1, 2]) of which the oxidation products are biodegradable [3], or the use of ultrasound to accelerate the vatting procedure and increase the conversion [4, 5].

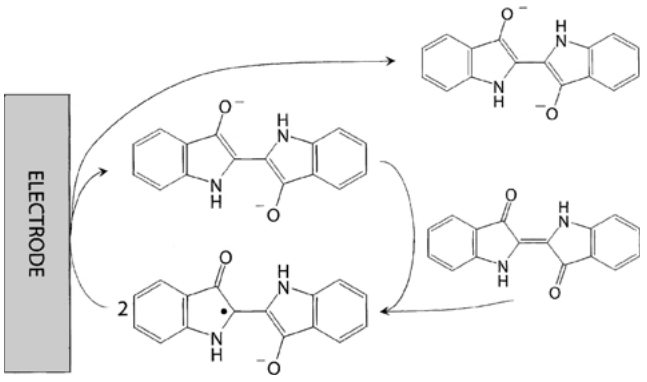
Electrochemistry would be an elegant way to reduce dye molecules, because it minimizes the consumption of chemicals, but indigo present in an aqueous suspension cannot be reduced electrochemically under these conditions. Therefore, an electrochemical reduction process employing a redox mediator (complexes of iron with triethanolamine or gluconic acid) has been developed [6–9]. However, the mediator is expensive, in case of triethanolamine as complexing agent toxicologically not completely harmless, and the specific reactor performance is low. A novel route for the environmentally friendly production of water soluble indigo which is also based on electrochemical reduction has been described recently [10–12]. The invention relates to a method for the direct electrochemical reduction of vat and sulfur dyes in aqueous solutions which does not require a soluble reducing agent, nor the permanent presence of a redox mediator. The process is based on a reaction mechanism in which a radical anion is formed in a comproportionation reaction between the dye and the leuco dye and a subsequent electrochemical reduction of this radical. To start the process an initial amount of the leuco dye has to be generated by a conventional reaction, that is, by adding a small amount of a soluble reducing agent. However, once the reactions have set in, it is not needed anymore and the further process is self-sustaining. Scheme 1 illustrates schematically the mechanism of the direct reduction.

Conventional H-cells were used in preliminary experiments. The results were then used as a guide in designing and operating the continuous flow cells. In the present work, direct electrochemical reduction has been studied in a divided flow cell to determine the industrial feasibility of the method and to optimize electrolytic conditions.

2. Experimental details

2.1. *Chemicals*

All aqueous solutions were prepared with deionized water. Indigo was supplied from BASF, Ludwigshafen,



Scheme 1. Mechanism of the direct electrochemical reduction of indigo.

Germany. Sodium hydroxide (Fluka, 71695, p.a.), sodium dithionite (Fluka, 71700, pract. 85%), and Nitrogen 4.5 were used as-received for experiments.

2.2. *Apparatus*

A small multipurpose plate and frame cell (EC Electro MP-Cell from ElectroCell AB, Sweden) was chosen for the scale-up procedure. The cell permits the use of a combination of spacers and gaskets compressed (by a torque wrench to a value of 25 Nm) between two end plates. As working electrode configuration a flat nickel plate electrode plus a nickel expanded mesh three-dimensional electrode (100 mesh, G. Bopp + Co. AG) was used. The metal meshes were spot-welded to the plate to ensure good electrical conductivity and stack with thin (~0.2 mm) nickel strips at the edges and at the middle between the meshes in a vertical way. This provided equal access for the electrolyte to all the surface of the meshes. The mesh was attached to both sides of a Ni-backplate so that the electrode is used double sided (anode – membrane – mesh/Ni-backplate/mesh – membrane – anode). Nickel was also used as anode material and the cell was divided into two compartments by a Nafion-324 membrane (DuPont). The schematic construction of the pilot plant used in the experiments is given in Figure 1. Both electrolytes were pumped from a reservoir through the cell in a flow-through pattern. In case of the catholyte, an additional circuit (bypass) was installed to circulate the suspension always independent from the flow rate through the cell to avoid sedimentation of the dispersed dyestuff. In this bypass a connection for the online spectrophotometric measurement was implemented. Cells are connected to a thermostat (Colora Messtechnik GmbH). A potentiostat (Soerensen, DCR 10-40B) was used both for galvanostatic and potentiostatic electrolysis experiments. Cell potential, cathode potential and current were measured with multimeters (Metex M 3610).

To analyse the effect of ultrasound on the properties of the dye dispersion a spiral shaped part of the catholyte-circuit tube was mounted in an ultrasonic bath.

A sieve-machine (AS 200, Fa. Retsch) with several sieves was used to obtain well defined fractions of indigo particles. Particle size analysis was measured by laser diffraction (Sympatec Helos system H0702). The effect of ultrasound on the particle size distribution was investigated by the application of ultrasound on the sample reservoir of the particle size analyser.

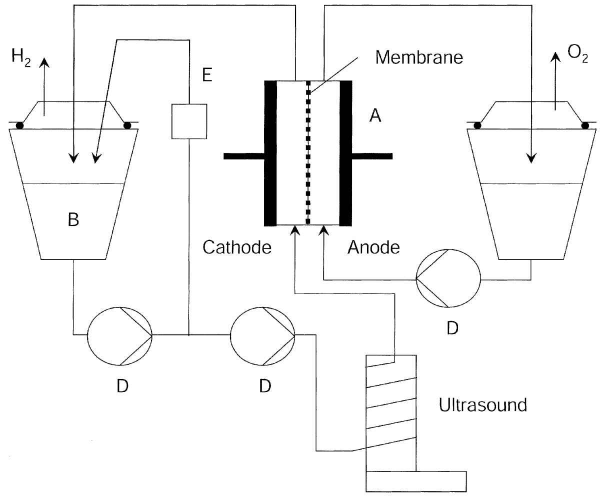


Fig. 1. Laboratory flow-cell system. (A) flow-cell (ElectroCell AB); (B) catholyte tank; (C) anolyte tank; (D) pump; (E) online spectrophotometer.

2.3. *Procedure*

Cathodic solutions of indigo were composed of sodium hydroxide 1 M and 1 g l^{-1} of indigo (sieve fraction between 0.06–0.08 mm). They were deoxygenated during at least two hours before the experiment and maintained under an nitrogen atmosphere during measurements. Various understoichiometric amounts of dithionite in aqueous solution (prepared after degassing the water for 2 h) were added by an injection needle through a septum to reduce indigo. In all experiments the ratio of dithionite to indigo was smaller than the stoichiometric one to generate the red coloured radical species. Anodic solutions consisted of NaOH 1 M. All reduction experiments were performed at 50 °C. In the case of different pH-values, the difference in ionic strength in comparison with a 1 M NaOH (pH 14) was adjusted with NaCl.

3. Results and discussion

A series of galvanostatic runs was carried out to assess the effect of operating parameters such as current density, pH, temperature and flow rate of the catholyte on the electrochemical kinetics.

3.1. *Influence of cathodic current density*

Figure 2 shows clearly the typical behaviour of an electrochemical batch reactor. The concentration decay is linear up to a current density of 0.3 mA dm^{-2} and approximately 200 min reaction time and the reaction can be described by a zero order kinetic law. Further

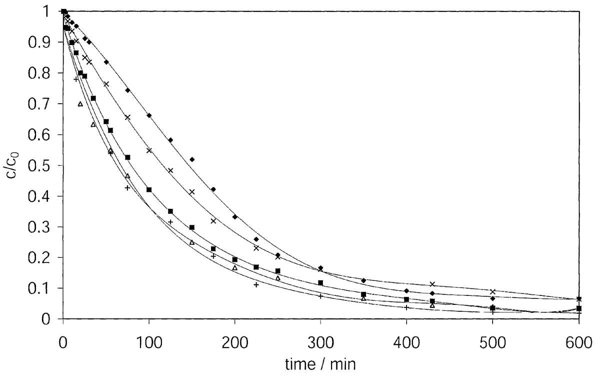


Fig. 2. Influence of current density for the galvanostatic reduction of indigo radical. System parameters: 1 M NaOH, 50 °C, Ni-electrode: 600 cm^2, total indigo concentration: 1 g l^{-1}, 10% of indigo was reduced with dithionite at the beginning. Catholyte flow rate: 20 cm^3 s^{-1}. Current density: (+) 0.1, (△) 0.01, (■) 0.005, (×) 0.0025 and (◆) 0.001 mA cm^{-2}.

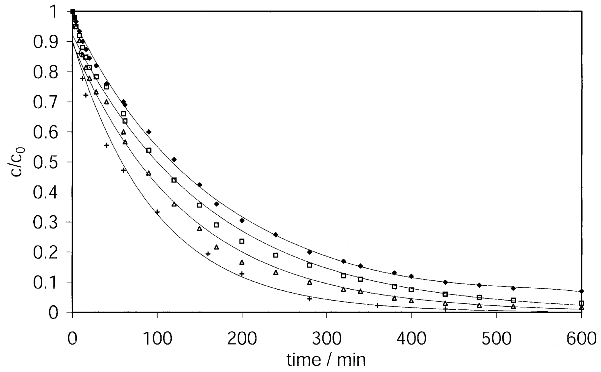


Fig. 4. Influence of temperature on the galvanostatic reduction of indigo radical. System parameters: 1 M NaOH, Current density: 0.0025 mA cm^{-2}, Ni-electrode: 600 cm^2, total indigo concentration: 1 g l^{-1}, 10% of indigo was reduced with dithionite at the beginning. Catholyte flow rate: 20 cm^3 s^{-1}. Temperature: (+) 80, (△) 70, (□) 60 and (◆) 50 °C.

electrolysis and reduction at a higher current density result in an exponential decay. Time dependence of current efficiency is shown in Figure 3. A region with a constant efficiency of approximately 90% can be reached in case of low current densities up to 0.25 mA dm^{-2}. In all other cases the efficiency is much lower and shows an exponential decrease with time. This is also the case at a current density of 0.1 mA dm^{-2} after 250 min reaction time. The results compare well with previous work, indicating that the reduction of radical species is mass transfer controlled [12]. Without adding further indigo pigment, after some time the concentration of the radical has become so small that the galvanostatic current density exceeds the limiting current density and mass transport control dominates. The electrode potential becomes more negative, and a side reaction takes place at the cathode in the form of hydrogen liberation.

3.2. *Influence of temperature*

In Figure 4 the temperature dependence of the electrochemical reduction reaction rate is shown. The reaction is much faster at a higher temperature and this compares well with previous presented results [11, 12]. However, the curves shown in Figure 4 were not measured at the same radical concentration, because the equilibrium concentration of the radical is increasing with temperature. Therefore, the higher reduction rate is based on both, enhanced electrode kinetics and increasing radical concentration.

3.3. *Influence of pH*

The influence of catholyte-pH is shown in Figure 5. It is obvious that reaction rate is clearly enhanced with increasing pH. Only a slight increase in electrode kinetics has been observed in previous studies [12]. Therefore, this effect is mainly based on the higher radical concentration, because it has been observed that the equilibrium between radical, indigo and leuco indigo is shifted to the radical side with higher pH. This stabilizing effect might be caused by the presence of the more soluble ionic forms of the indigo species, because nonionic or 'acid' forms of reduced indigo are poorly water-soluble substances.

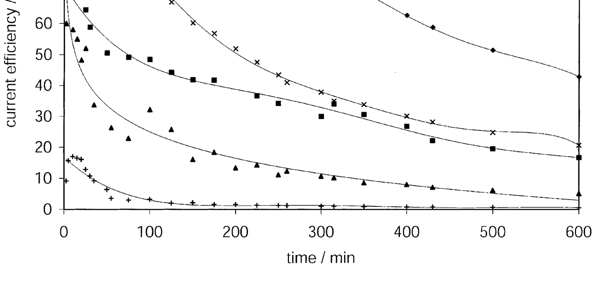


Fig. 3. Time dependence of the current efficiency for the galvanostatic reduction of indigo radical. System parameters as in Figure 6.

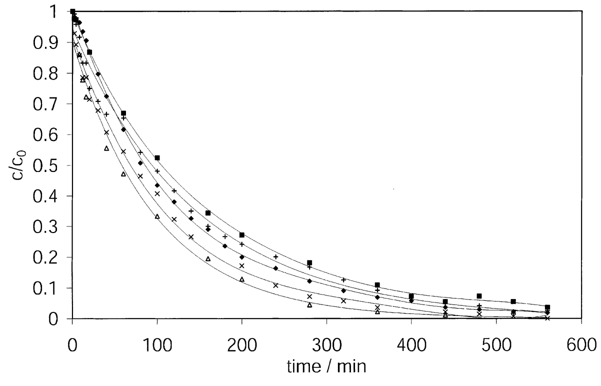


Fig. 5. Influence of pH on the galvanostatic reduction of indigo radical. System parameters: 50 °C, Current density: 0.0025 mA cm^{-2}, Ni-electrode: 600 cm^2, total indigo concentration: 1 g l^{-1}, 10% of indigo was reduced with dithionite at the beginning. Catholyte flow rate: 20 cm^3 s^{-1}. pH: (■) 10, (+) 11, (◆) 12, (×) 13, (△) 14.

3.4. *Influence of catholyte flow rate*

Figure 6 shows the influence of catholyte flow rate on the limiting current. At higher velocities, mass transport of the radical species to the cathode is enhanced. The result is a higher limiting current and, therefore, a higher rate of concentration decay in the mass transfer controlled region.

3.5. *Influence of particle size and the use of ultrasound*

Ultrasound was applied to the electrolyte before entering the reactor in order to influence the properties of the dye dispersion. It is obvious from Figure 7 that in the presence of ultrasound the reaction rate of radical reduction is enhanced slightly.

Figure 8 shows the particle size distribution of a commercial available indigo (BASF AG, Ludwigshafen, Germany) and the effect of ultrasound on the particle size distribution can be seen in Figure 9. It is obvious that larger particles or agglomerates of solid particles (>100 μm) are effectively broken down and smaller particles with a size between 1 and 10 μm are created. This is in agreement with results obtained by Lindley [15], that ultrasound can reduce the particle size of nonmetallic particles down to usually 1–10 μm. A longer application of ultrasound leads only to a change in the surface of the particles, but no more smaller particles are produced [13, 14]. Therefore, the positive effect is based mostly on the increase of the active reaction surface due to reduction of the particle diameter. This can increase the production rate of radical species, but on the other hand it is also possible, that on the larger organic/water-interface more radical will adsorb and, therefore, the free bulk concentration will be lower. However, it has never been observed in the u.v.–vis. spectra, that the radical concentration is decreasing after the application of ultrasound. Rather a slight increase was obtained, probably indicating that radical can be generated also by ultrasound.

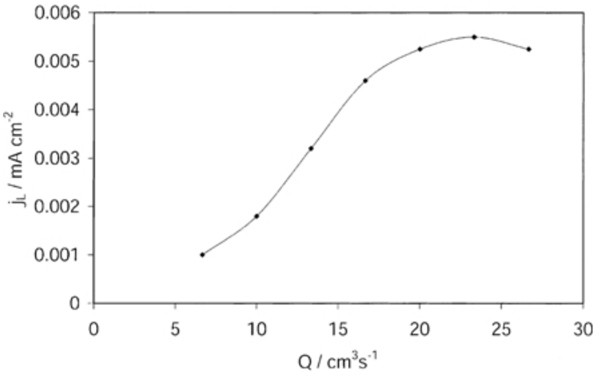


Fig. 6. Influence of catholyte flow rate on the limiting currents of the electrochemical reduction of indigo radical. System parameters: 1 M NaOH, 50 °C, Ni-electrode: 600 cm^2, total indigo concentration: 1 g l^{-1}, 10% of indigo was reduced with dithionite at the beginning.

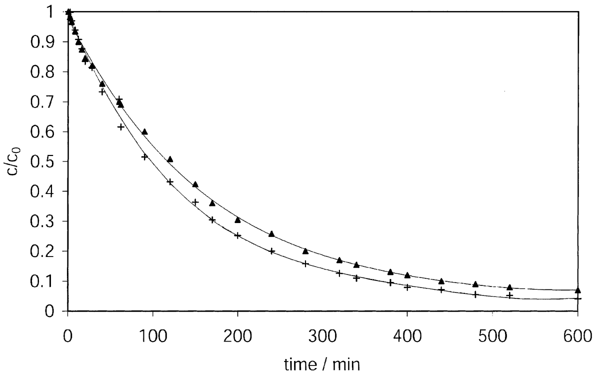


Fig. 7. Influence of ultrasound on kinetics of the galvanostatic reduction of indigo radical. System parameters: 1 M NaOH, 50 °C, Current density: 0.0025 mA cm^{-2}, Ni-electrode: 600 cm^2, total indigo concentration: 1 g l^{-1}, 10% of indigo was reduced with dithionite at the beginning. Catholyte flow rate: 20 cm^3 s^{-1}. Key: (▲) without ultrasound; (+) with ultrasound.

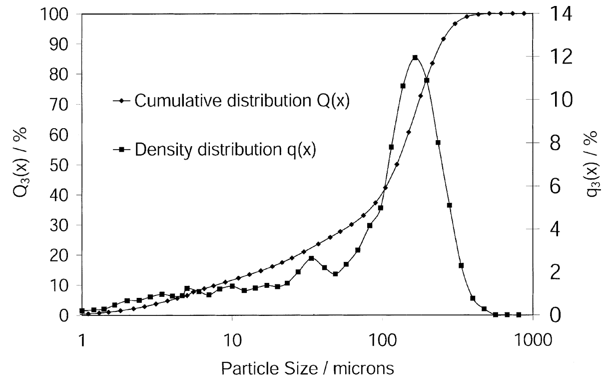


Fig. 8. Particle size distribution of BASF indigo.

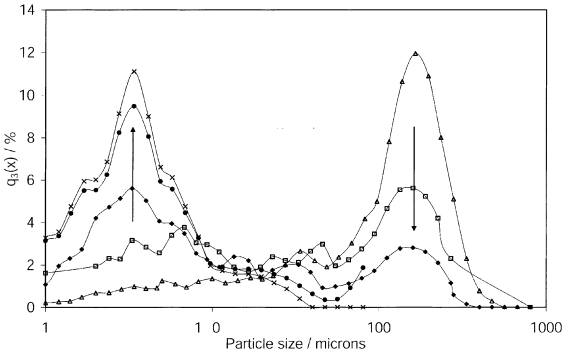


Fig. 9. Influence of ultrasound on the particle size distribution. Ultrasound applied: (△) none, (■) 1 s, (◆) 2 s, (●) 5 s and (×) 10 s.

3.6. *Influence of organic solvents*

The acceleration of the vatting procedure by methanol is a well known phenomenon. For example, a content of 20 ml l^{-1} MeOH is used as a catalyst in the vatting of indigo with ultrasonic generators [4]. This effect maybe based on the fact, that methanol can dissolve indigo and its correlated species, the radical and the leuco dye, much better than water. Organic species adsorbed on the indigo particles will be washed out into the bulk. However, a lasting stabilization effect of the radical species was only observed at concentrations higher than 20 vol % of the organic solvents (i.e., methanol, isopropanol, ethanol, DMF), but it is impossible to use such high amounts of organic solvent in the dyebath.

4. Conclusions

The industrial feasibility of the novel route for the environmentally friendly production of water soluble leuco indigo by direct electrochemical reduction of indigo in aqueous solutions has been studied in a divided flow cell. Optimized conditions in the system were sought and a scale-up in indigo concentration to 1 g l^{-1} was achieved. Increasing pH and temperature can enhance the reduction rate and a better mass transfer was achieved by higher flow velocities in the reactor. In the presence of ultrasound reaction rate is enhanced slightly, based on increased active reaction surface due to reduction in particle diameter. However, the radical concentration still is low and, consequently, so is the specific reactor performance. Current efficiency is also limited to a maximum of 90% at very low current densities.

Organic solvents can increase the radical concentration and, consequently, the reaction rates, but lasting effects were only observed at non-viable concentrations of higher than 20 vol %. Therefore, future work will include a study of the influence of important parameters on the concentration of the radical species like surfactants and an optimization of this new electrochemical process.

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