

Direct Electrochemical Reduction of Indigo

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Abstract: Increasing ecoefficiency of textile wet processes has become an important topic in our research group. Reducing agents required for the application of vat and sulfur dyes cannot be recycled, and they lead to problematic waste products. Therefore, modern aspects of economical and ecological requirements are not fulfilled. The application of direct electrochemical reduction of indigo as a novel route has been investigated by spectrophotometric and voltammetric experiments in laboratory cells. Experiments yield information about the reaction mechanism and the kinetics, and they show the possibility of this new route for production of water-soluble indigo, which offers tremendous environmental benefits.

Keywords: Electrochemical reduction · Indigo · Indigo radical · Leuco indigo · Vat dyes

1. Introduction

Research activities in the field of industrial chemistry are characterized by a highly transdisciplinary cooperation between specialists of various scientific orientations and strengthen the links between academic and industrial research efforts. The objective of these activities is to reach a deeper understanding of the basic principles governing the dynamic behavior and the selectivity of chemical processes of industrial importance. Research techniques are drawn from synthetic chemistry, from chemical engineering (*e.g.* laminar and turbulent reactive flow) as well as from physical (*e.g.* electrochemistry) and biological chemistry (*e.g.* aerobic and anaerobic degradation of organic wastes).

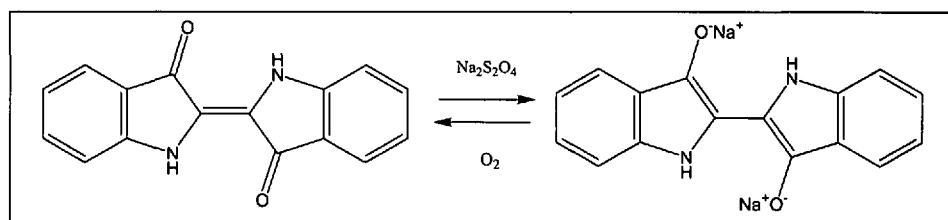
Recently, process optimization and waste management have become major topics for research groups involved in industrial chemistry. Thus, a significant part of our efforts is focused on environ-

mental problems, particularly those originating from the textile industry. Wet processing in dyeing and finishing can lead to effluents which have been subject to criticism for many decades. Forty years ago the dominant problems were large amounts of foam in river beds and effluent hazards sometimes leading to the extinction of fish populations and other aquatic organisms. Due to the enforcement of environmental regulations this has changed considerably.

Nevertheless, there is a continuing need for improving the ecoefficiency of critical textile wet processes in dyeing and finishing. For example dyestuffs such as sulfur and vat dyes, especially indigo, play an important role in today's dyeing industry (market about 120000 t/a). The present use of this dye category is based on the application of sodium dithionite to attain a water-soluble form of the dye by reduction (= leuco dye). The reduced dyestuff has a high affinity to cellulosic fibers, will penetrate the fiber and will remain fixed inside after having been reoxidized back to the water-insoluble form (Scheme 1).

The disposal of dyeing baths and rinsing water causes various problems, because the necessary reducing agents will be ultimately oxidized into species that can hardly be regenerated. Thus, sulphite, sulphate, thiosulphate and toxic sulphide heavily contaminate waste water from dyeing plants (worldwide approximately 180000 t/a). In addition, as a result of the considerable excess of reducing agent required to stabilize the oxidation-sensitive dyeing baths, the waste water may contain excess dithionite which affects aerobic processes in wastewater treatment. Therefore, many attempts are being made to replace the environmentally unfavorable sodium dithionite by ecologically more attractive alternatives. Previous investigations were focused on:

- the replacement of sodium dithionite by an organic reducing agent (*e.g.* glucose, α -hydroxyketones [1]) of which the oxidation products are biodegradable;
- the use of ultrasound to accelerate the vating procedure and to increase the conversion [2][3];



Scheme 1. The principle of dyeing with indigo (Vatting)

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- the electrochemical reduction employing a redox mediator (*e.g.* Fe(II)-triethanolamine [4–7]) which is expensive and toxicologically not completely harmless.

The above-mentioned alternatives can increase the biocompatibility of the vatting process, but there is still potential for improvement. Electrochemistry would be an elegant way to reduce the dye because it minimizes the consumption of chemicals and the effluent load. In the following it is shown how a new alternative for the reduction of indigo was developed just on the basis of observations, and some preliminary results are discussed.

2. Development of a Novel Route to an Environmentally Friendly Reduction of Indigo

2.1. Preliminary Observations

VIS-spectra of indigo dispersions in aqueous solutions show a small absorption at about 700 nm corresponding to indigo particles in the system. After adding a reducing agent (*e.g.* dithionite) a peak is observed at 410 nm, which can be correlated to leuco indigo, the reduced form of the indigo pigment. If the molar ratio of dithionite to indigo is smaller than stoichiometric, additional peaks can be found at 540 and 495 nm. It is assumed that these peaks are due to the well-known cherry-red colored indigo radical [8][9], and that this species is formed in a comproportionation reaction between leuco indigo and indigo. An EPR-spectrum, together with simulation, clearly showed that the structure of the radical species is in fact identical to the one assumed (Table 1 and Fig. 1).

Table 1. Coupling constants measured by EPR spectroscopy

Related atoms	Coupling [G]
5,5' ¹ H	0.66
7,7' ¹ H	0.66
6,6' ¹ H	1.98
4,4' ¹ H	1.67
1,1' ¹⁴ N	0.66

2.2. Electrochemical Reduction of Indigo

It is possible to reduce solid indigo microcrystals immobilized on the surface of several electrode materials in buffered

aqueous solution [10][11], and the results are closely related to those obtained for indigo dissolved in solvents. However, if indigo is not immobilized but present in an aqueous suspension it shows a distinctly different behavior, and it cannot be reduced electrochemically under these conditions. On the other hand radicals are usually electrochemically active species and previous studies on the electrochemistry of indigo dissolved in DMSO, DMF or in pyridine have reported that indigo can be reversibly reduced to its leucoform in two one-electron processes with the radical as an intermediate species

[10]. In addition, the investigation of redox reactions of its soluble derivate indigo-carmin in aqueous solution led to comparable results [12][13].

The electrochemical activity of the soluble species in this system was investigated by reducing indigo in a 1 M aqueous sodium hydroxide solution with sodium dithionite, inducing the formation of the radical by adding an excess amount of indigo, and then taking current-voltage curves at nickel electrodes (Fig. 2). The voltammograms show that the radical can be easily reduced, and that the reduction product – leuco indigo – is stable under

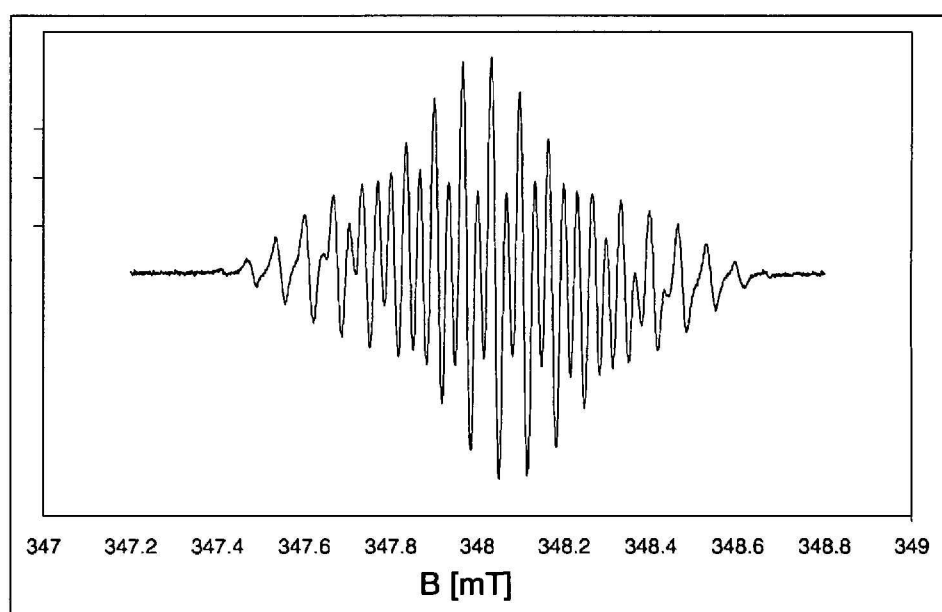


Fig. 1. X-band CW-EPR spectrum of the red colored indigo radical at room temperature in 1 M NaOH, generated by sodium dithionite. The spectrum was recorded at room temperature on a Bruker ESP 300 spectrometer (microwave frequency 9.76 GHz) with the use of a flat cell. A microwave power of 2 mW, a modulation amplitude of 0.01 mT and a modulation frequency of 100 kHz was used.

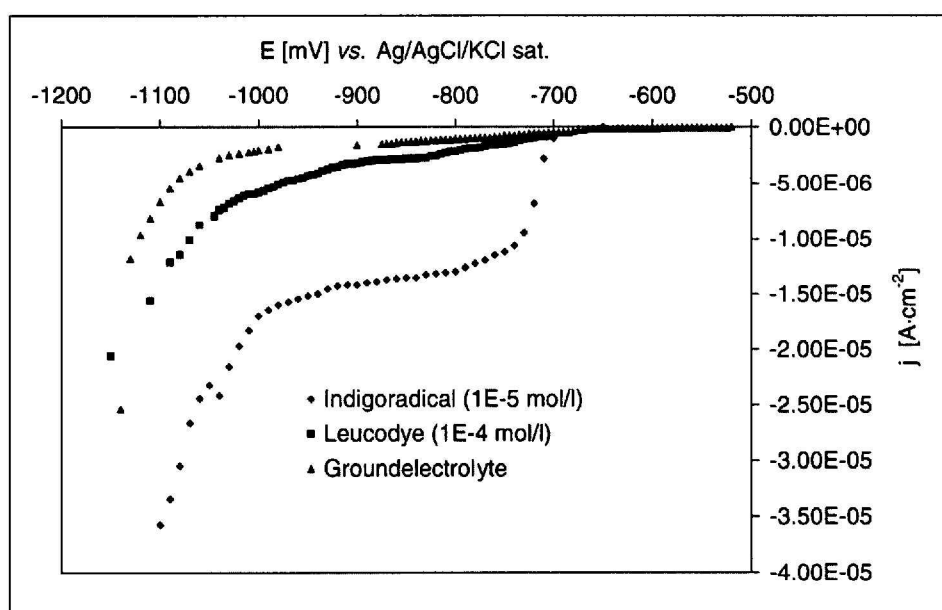


Fig. 2. Voltammograms of different indigo derivatives in 1 M NaOH, 1g/l Setamol, Ni-electrode, 50 °C (reference electrode Ag/AgCl 3 M).

these conditions. The curve exhibits a plateau, thus confirming the assumption of a diffusion-controlled electrode reaction. At potentials more negative than -900 mV (vs. Ag/AgCl 3 M) it appears that leuco indigo is also reduced to another substance, but this increase in current could be correlated to the reduction of sodium dithionite in the system, because this molecule shows a cathodic wave $E_{1/2}$ at -1030 mV [14][15]. Beyond -1100 mV the current density increases in all three cases due to side reactions, e.g. the cathodic evolution of hydrogen from the reduction of water.

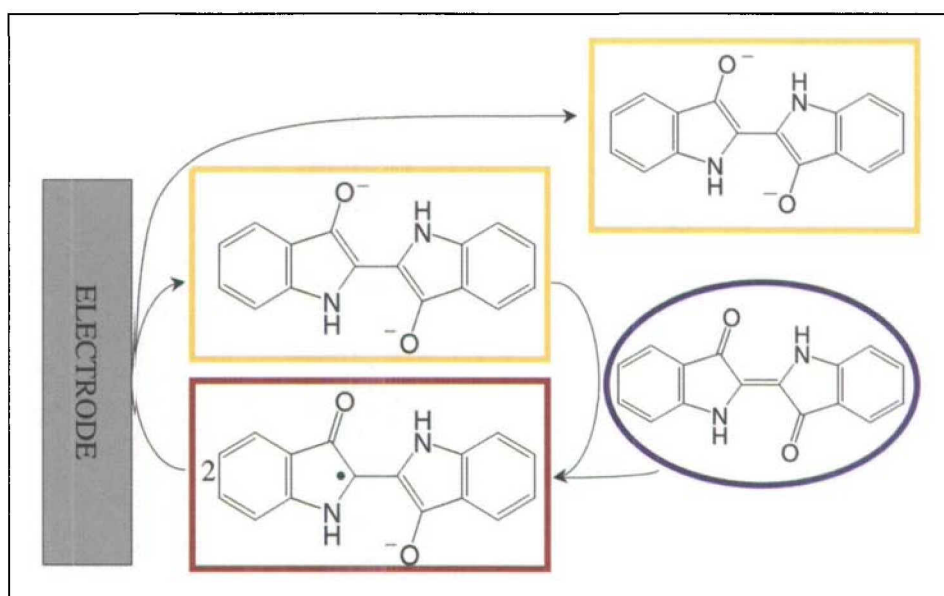
2.3. Principle of the Process

The above-mentioned observations and results were the origin of a novel route for the reduction of indigo. 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 [16]. 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. In order to start the process, an initial amount of the leuco dye has to be generated by a conventional reaction, e.g. 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 2 illustrates the mechanism of the direct reduction under steady conditions.

Online spectrophotometric inspection of the reduction process provided more detailed information of reduction products and reaction kinetics. Fig. 3 shows typical experimental concentration profiles as obtained for a batch reduction reaction using a diode array spectrophotometer. The result is in perfect correlation with the suggested consecutive mechanism. The radical anion as a product of the comproportionation reaction between indigo and the leuco dye continuously undergoes the secondary electrochemical reduction and acts as an intermediate species only.

3. Electrolysis Experiments

In order to optimize the process for industrial conditions, the choice of the electrode material plays an important role. Copper turned out to be the most suitable of the materials tested so far in



Scheme 2. Mechanism of the direct electrochemical reduction of indigo

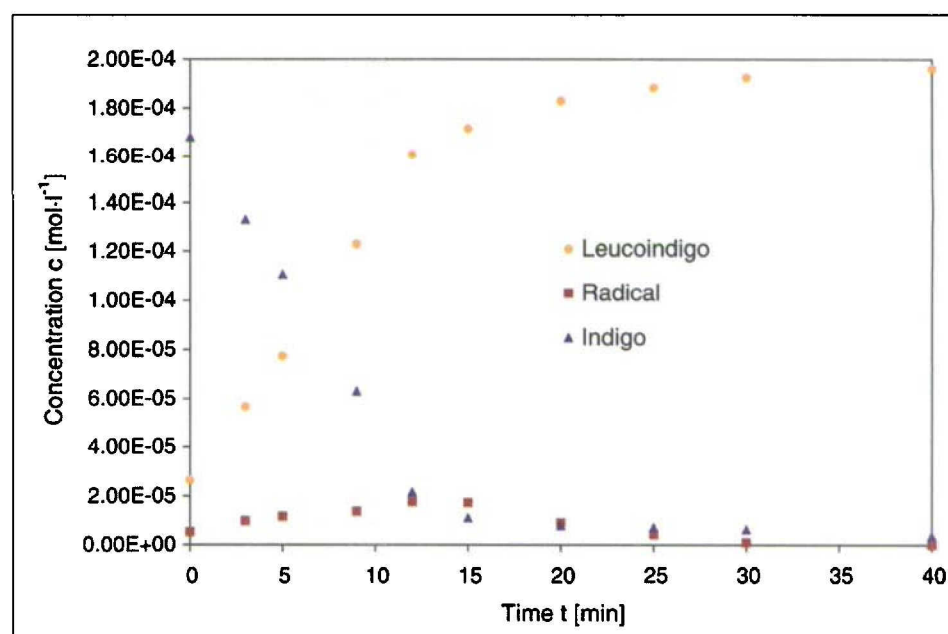


Fig. 3. Concentration profile for the three indigo species during direct electrochemical reduction at 50 °C, 1 M NaOH, 1 g/l Setamol, 0.005 mA/cm², 400 cm² Ni-electrode, total indigo concentration $1E-4$ M, molar ratio indigo/moles dithionite at $t=0$: 7/1.

terms of reaction rate. Titanium gives only very low current densities and, therefore, is not a useful material for this process. Lead shows good catalytic properties for the radical reduction, but it is dissolved during electrolysis, thus producing high background currents in comparison to the other materials.

A series of galvanostatic reduction runs was carried out in order to assess the effect of other operating parameters such

as current density and temperature on the reduction kinetics. Table 2 indicates an increase in reaction rate when the current density is raised, but the experimental current efficiency decreased very fast. Current efficiency Φ is an important parameter in electrochemical engineering and represents the fraction of electrical charge used for the desired reaction. Only in the case of the low current density of 0.001 mA/cm² can a region with a con-

Table 2. Results of the galvanostatic electrolysis experiments at different current densities (50 °C, Ni-net-electrode (200 cm²), concentration of the radical at t = 0: 2·10⁻⁵ M)

Current density j [mA·cm ⁻²]	Conversion X [%] after 40 min	Current efficiency Φ [%]
0.001	65	80
0.0025	70	55
0.005	79	40
0.01	85	20
0.1	90	5

stant efficiency of approximately 80% be reached. In all other cases the efficiency is much lower and shows an exponential decrease with time due to the side reaction of hydrogen evolution. This behavior is explained by the fact that – without adding further indigo pigment – after some time the concentration of the radical is so small that the galvanostatic current density exceeds the limiting current density. The electrode potential becomes more negative, and a side reaction such as hydrogen liberation takes place. This is also evident from the sudden change in cell voltage.

From an analysis of the temperature dependence of the electrochemical reduction reaction it can be observed that at a higher temperature the reaction is much faster. The apparent activation energy of this electrode process was calculated from the relationship between $\log j$ vs. $1/T$ at a constant cathodic potential (Fig. 4) and the value is $E_A = 22.58 \pm 1.18$ kJ/mol (-0.9 V vs. Ag/AgCl 3 M).

4. Conclusions

The radical anion can be easily reduced and the reaction product is stable under these conditions. The electrochemical reaction rate is limited by diffusional transport, and at potentials more negative than -1.1 V (vs. Ag/AgCl 3 M) the current density increases due to the cathodic liberation of hydrogen. However, the radical concentration is very low, and, as a consequence so are the limiting currents and the reaction rates. In addition, current efficiency is limited to a maximum of 80% because of the side reaction of hydrogen production. Therefore, these results are just the basis for further work on the scale-up and the optimization of an ecologically and economical electrochemical process used in textile dyeing processes.

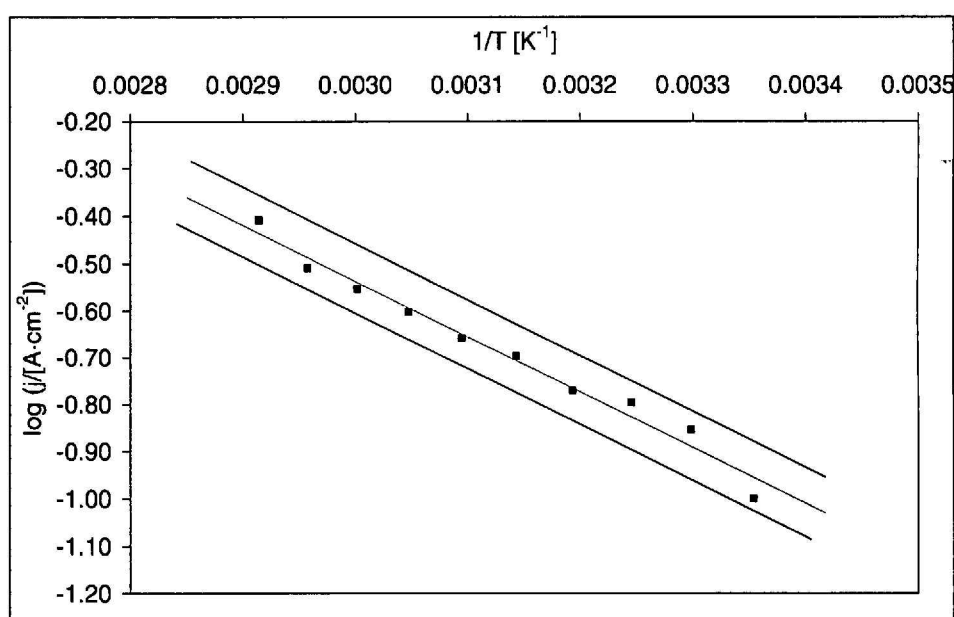


Fig. 4. Arrhenius plot including 95% confidential interval for determining the apparent activation energy ($E_A = -0.9$ V vs. Ag/AgCl 3 M).

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