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Electrocatalytic hydrogenation of vat dyes

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Abstract

Increasing eco-efficiency of textile wet processes has become an important topic. Reducing agents required for the application of vat dyes (i.e. indigo) cannot be recycled, and lead to problematic waste products. Therefore, modern economical and ecological requirements are not fullfilled. The application of electrocatalytic hydrogenation of vat dyes at electrodes comprising a thin grid coated with a layer of nickel in which fine particles of Raney nickel are dispersed has been investigated by spectrophotometric and voltammetric experiments in laboratory cells. Experiments show the feasibility of this new route which offers tremendous environmental benefits and has a vast potential in textile dyeing processes, because it does not require any reducing agent. © 2002 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Until now in most industrial processes vat dyes (i.e. indigo) are reduced by sodium dithionite. This procedure is necessary to attain a water soluble form of the dyestuff, the so-called leuco dye with affinity to the cellulosic fibre. After diffusion into the fibre it will remain fixed there after having been reoxidised to the water-insoluble form. The disposal of dyeing baths and rinsing water is causing various problems, because the necessary reducing agents will finally be oxidised into species that can hardly be regenerated. Thus, excess dithionite, sulphite, sulphate, thiosulphate and toxic sulphide heavily contaminate waste water from dyeing plants (Scheme 1).

Therefore, many attempts are being made to replace the environmentally unfavourable sodium dithionite by ecologically more attractive alternatives. Investigations were either focused on the replacement of sodium dithionite by an organic reducing agent (i.e. α-hydroxyketones) with biodegradable oxidation products [1], or on the use of ultrasound to accelerate the vatting procedure and increase the conversion [2,3]. Catalytic hydrogenation of indigo is also possible and a well known process [4,5]. However, it is impossible to use this technique directly in the dye house due to the high explosion and fire risk.

Electrochemistry would be an elegant way to reduce dye molecules, because it minimizes the consumption of chemicals. It is possible to reduce solid indigo microcrystals immobilised on the

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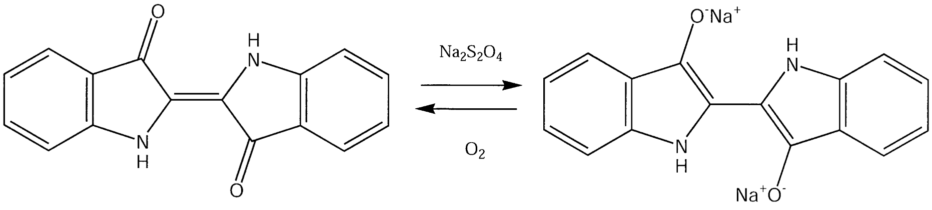


Scheme 1. Vatting of indigo.

electrode surface, and the results are very similar to those obtained for indigo dissolved in solvents [6,7]. However, if indigo is present in an aqueous suspension it shows a distinctly different behaviour, and cannot be reduced electrochemically. Therefore, an electrochemical reduction process employing a redox mediator (i.e. complexes of iron with triethanolamine or gluconic acid) [8,9], and a process based on the formation of a radical anion in a comproportionation reaction between the dye and the leuco dye and the subsequent electrochemical reduction of this radical have been developed [10–12]. However, in both cases the specific reactor performance is up to now low, and still some chemicals are necessary.

Therefore, in this communication we report a novel, environmentally friendly route to reduce vat dyes based on electrocatalytic hydrogenation (ECH). This “green” technology offers many advantages over conventional techniques including cost and energy efficiency, since it does not require any reducing agent. ECH involves the electrochemical reduction of water to produce adsorbed hydrogen that chemically reacts with an organic substrate on a low-hydrogen-overpotential, electrically conductive metal powder catalyst surface (i.e. Raney nickel or platinum black). The catalytic material serves both as an electrode (to generate the hydrogen) and as a catalyst for hydrogenation. Often, a portion of the electrochemically produced hydrogen does not react with the organic substrate, in which case molecular hydrogen gas is evolved from the cathode. ECH has been carried out successfully since years on various substrates and has several advantages over catalytic hydrogenation [13]. The kinetic barrier due to the splitting of the hydrogen molecule is completely bypassed, thus, elevated temperatures and pressures can be avoided. Furthermore, the electrochemical production of hydrogen directly at the catalyst surface circumvents the compression, transportation, and storage of hydrogen.

Recently this principle has been used in a precoat-layer-cell by bringing indigo into contact with a cathode, wherein the cathode is formed by a support of an electrically conductive material and a cathodically polarized layer formed thereon in situ by precoat filtration [14,15]. Unfortunately, during the process a great pressure drop is built up over the filtration layer and the reactor performance is low. Therefore, we report ECH of vat dyes on electrodes comprising a thin grid coated with a layer of metal in which fine particles of catalyst are embedded [16–18].

2. Experimental

2.1. Chemicals

All aqueous solutions were prepared with deionised water. Indigo was supplied from BASF, Ludwigshafen, Germany. C.I. Vat Red 10 and C.I. Vat Green 1 were supplied from DyStar Textilfarben, Frankfurt, Germany. C.I. Vat Orange 9, C.I. Vat Orange 17, C.I. Vat blue 21 and C.I. Vat Red 28 were supplied from BEZEMA AG, Montlingen, Switzerland. All other chemicals were analytical grade, purchased from Fluka, Buchs, Switzerland and used as received.

2.2. Electrodes

The high surface area cathodes with a geometric area of 30 cm^2 were prepared in two different ways on a 100 mesh stainless steel grid (G. Bopp + Co. AG, Switzerland). Noble metal-blacks were prepared by electrodeposition using literature procedures (Pt [19], Pd [20], and Rh [21]). The convenient Raney-type electrodes were prepared by codeposition of Raney alloy particles with the electrodeposited nickel metal on the mesh and an activation step by immersing the electrode in a 30% (w/v) NaOH solution at 70 °C for 10 h and washing with distilled water [16–18]. The cathodes were kept in a 5% (w/v) NaOH solution until used. Nickel was plated at a current density of 30 mA cm^{-2} (based on geometric electrode area) and 70 °C from a well stirred plating solution consisting of 300 g l^{-1} $NiCl_2 \cdot 6H_2O$, 45 g l^{-1} $NiSO_4 \cdot 6H_2O$ and 30 g l^{-1} H_3BO_3 and 5 g l^{-1} of dispersed Raney nickel alloy particles (Ni:Al 50:50 w/w). A piece of nickel was used as the anode. Both electrodes were mounted in parallel in a vertical position. The current was applied for 30 min with one rotation (180°) of the cathode every 5 min to get a homogeneous distribution of the electrodeposition on both sides of the electrode. The amount of codeposited Ni/Al-alloy before leaching was typically 8–12 mg cm^{-2} compared to 15.7 mg cm^{-2} for the electrodeposited nickel.

Devarda copper has been prepared by a similar procedure by plating copper at 15 mA cm^{-2} and 70 °C from a solution made of 200 g l^{-1} $CuSO_4 \cdot 5H_2O$ and 30 g l^{-1} H_3BO_3 with suspended 5 g l^{-1} Devarda copper alloy (Cu–Al–Zn 50:45:5 w/w) by using a copper anode. Raney cobalt was produced by electrocodeposition at 50 mA·cm^{-2} and 70 °C from a solution of 330 g l^{-1} $CoSO_4$ $7H_2O$ and 30 g l^{-1} H_3BO_3 with suspended 5 g l^{-1} Raney cobalt alloy (Co–Al 31:69 w/w) by using a cobalt anode.

2.3. Galvanostatic experiments

The electrohydrogenations were carried out at constant current density (based on geometric electrode area) in a two-chamber glass reactor in which the anode and cathode compartments were separated by a Nafion-324 cation-exchange membrane. In the 100 ml anodic cell compartment a Pt/Ru expanded mesh was used throughout the experiments as a counter electrode. The cathode compartment containing two glassfiber sensors for online spectrophotometric measurement (GMP, Jobin Yvon) had also a volume of 100 ml. Both cells were connected to a thermostat (Colora Messtechnik GmbH) and a potentiostat (Amel 549) was used for the electrolysis experiments. Cathodic solutions of indigo were composed of sodium hydroxide 1 M and 2 g l^{-1} of the vat dyes. They were deoxygenated for at least 2 h before the experiment and maintained under an argon atmosphere during measurements. Anodic solutions consisted of 1 M sodium hydroxide solution.

3. Results and discussion

3.1. Electrocatalytic hydrogenation of indigo

ECH of indigo (C.I. Vat blue 1) has been examined over various cathode materials, and leuco indigo was produced directly from the indigo suspension. The hydrogenation product was identified by spectrophotometric analysis ($\lambda_{max} = 410$ nm) and laboratory dyeing experiments prove in general a dyeing behavior of the electrohydrogenated indigo similar to that of conventional reduction methods. In addition, in the vast majority of cases a 95% mass balance for indigo was obtained after the experiment by reoxidation to the insoluble product and filtration of the electrolyte. Therefore, it is obvious that the reaction product is stable under the applied conditions and no other hydrogenation products are formed (i.e. by over-reduction).

Table 1 summarizes the results of the electrode material influence. Palladium and rhodium are less

Table 1
Electrohydrogenation of indigo using different catalysts

Catalyst	Conversion[a] (%)	Current efficiency (%)
Pt black	81.9	65.5
Rh black	61.1	48.9
Pd black	54.5	43.6
Raney nickel	4.4	3.5
Raney cobalt	2.9	2.3
Devarda copper	1.4	1.1

[a] Conversion or yield of leuco compound was determined by spectrophotometric analysis. $T = 50$ °C; $J = 20$ mA cm^{-2} (geometric area); charge passed (Q) = 5 F/mol. Material balance >95%.

Table 2
Effect of current density on the ECH of indigo at Raney Ni electrodes

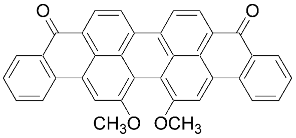
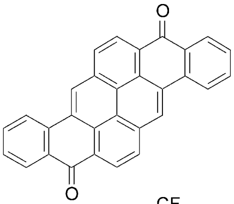
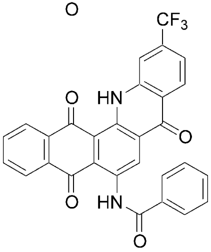
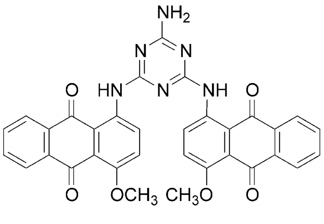
Current density[a] (mA cm^{-2})	Conversion[b] (%)	Current efficiency (%)
0.1	28.8	2.3
0.5	36.3	2.9
1	37.5	3.0
5	40.0	3.2
10	47.5	3.8
50	32.5	2.6
100	21.3	1.7

[a] Based on the geometric electrode area.

[b] Conversion or yield of leuco compound was determined by spectrophotometric analysis. $T = 60$ °C; charge passed (Q) = 50 F/mol. Material balance >95%.

active catalysts than platinum. In the case of Raney-type electrodes nickel is among the most active catalysts, but current efficiency of 3.5% is very low. These results follow, at least qualitatively, the sequence established from catalytic hydrogenation [22]. Platinum and rhodium are well known as catalysts to hydrogenate organic substrates at atmospheric pressure. Therefore, they are also effective under the applied electrochemical conditions. Palladium which requires usually increased pressure and temperature for normal hydrogenation, gives lower electrocatalytic conversion, and nickel, which normally requires very severe conditions, gives very low electrohydrogenation; instead a lot of hydrogen is

Table 3
ECH of different dye molecules at Raney Ni electrodes

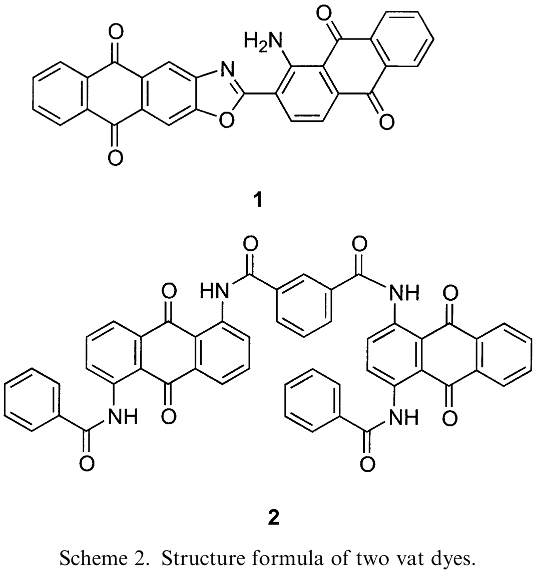
Substrate	Formula	Conversion[a] (%)	Current efficiency (%)
C.I. Vat Green 1		52.5	4.2
C.I. Vat Orange 9		24.3	3.9
C.I. Vat Blue 21		26.2	2.1
C.I. Vat Red 28		20.0	1.6

[a] Conversion or yield of leuco compound was determined by spectrophotometric analysis. $T = 50$ °C; $J = 20$ mA cm^{-2} (geometric area); charge passed (Q) = 50 F/mol. Material balance >90%.

evolved and both the current efficiency and the extent of hydrogenation decreases. In the case of this reaction, current efficiency is directly coupled to the conversion, because no side reaction (i.e. over-reduction) takes place with the dye.

Nevertheless, Raney nickel was chosen as the electrode material, because it is interesting from the standpoint of availability, costs and stability in alkaline medium. The stability of platinum black electrodes was shown to be poor, so that their industrial application is impossible. Usually, the Raney-type electrodes had a lifetime of 15–20 days in comparison to 1–2 days in case of noble metal blacks. However, activity was decreasing very fast after that time, because the Raney nickel particles become rather crumbly due to the hydrogen evolution.

A preliminary process optimization with Raney nickel electrodes has been performed by analyzing the effect of increasing current density from 0.1 to 100 mA cm^{-2} (Table 2). From 0.1 to 10 mA cm^{-2}, the small increase in cathodic polarization associated with the increase of current density favours hydrogenation over hydrogen evolution, which leads to an increase of both the current efficiency and the extent of hydrogenation. Further increase favours hydrogen evolution over hydrogenation as shown by the diminution of the current efficiency and of the extent of hydrogenation.



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2

Scheme 2. Structure formula of two vat dyes.

3.2. Electrocatalytic hydrogenation of other vat dyes

To show the versatility of the new method, electrocatalytic hydrogenation of various (the variety is based on the three classes of vat dyes: anthraquinone dyes, fused ring polycyclic dyes and indigoid dyes) dye molecules has been studied at Raney nickel electrodes (Table 3). It was possible to reduce C.I. Vat Green 1 (16,17-dimethoxyviolanthrone) with a current efficiency of 4.2%, all other dyes lead to lower values. This is probably based on the higher solubility of C.I. Vat Green 1. In the case of two other dyes (C.I. Vat red 10; **1** and C.I. Vat orange 17; **2**) (Scheme 2) no conversion has been observed. However, it is important to mention, that no decomposition of the dye molecules has been observed. This has also been proved by a mass balance after reoxidation to the insoluble product and filtration of the electrolyte. The drop in mass balance to 90% is due to the loss of material by adsorption on the catalyst [12].

4. Conclusions

In summary, we have shown the possibility of electrocatalytic hydrogenation as a new process for reducing vat dyes. Modern aspects of economical and ecological requirements are fulfilled, because this process does not require any reducing agent. Palladium and rhodium are less active catalysts than platinum. In case of Raney-type electrodes electrodes—which are interesting from the standpoint of availability, costs and stability in alkaline medium—nickel is among the most active catalysts, but current efficiency is much lower than with noble metal-black electrodes. The application has been investigated in small laboratory cells. The results obtained are the basis for further investigations on scale-up and optimisation.

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