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State of the art technologies and new electrochemical methods for the reduction of vat dyes

Albert Roessler*, Xiunan Jin

Institute for Chemical and Bioengineering, Swiss Federal Institute of Technology ETH Hoenggerberg, CH-8093 Zurich, Switzerland

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Dedicated to Professor Paul Rys on the occasion of his 65th birthday and his retirement

Abstract

Until now, in most industrial vat dyeing processes, vat dyes are reduced mainly using sodium dithionite. This process produces large amounts of sodium sulphate and sulphite as by-products which increase the costs for waste water treatment. Hence, many attempts are being made to replace the environmentally unfavourable sodium dithionite by ecologically more attractive alternatives, such as organic reducing agents or catalytic hydrogenation. In recent investigations to improve the biocompatibility of the vatting process even further, various electrochemical reducing methods have been described, such as indirect electrochemical reduction employing a redox mediator, direct electrochemical reduction of indigo via the indigo radical, electrocatalytic hydrogenation and direct electrochemical reduction of indigo itself on graphite. These methods offer tremendous environmental benefits, since they minimize the consumption of chemicals as well as effluent load. However, most of these electrochemical processes are still in the development stage. This article gives an overview of the processes most commonly used and the state of development of recent electrochemical innovations.

Keywords: Electrochemical processes; Indigo; Vat dyes; Electrochemical reduction; Dyeing

1. Introduction

In the coloration of cellulosic fibres, vat dyes (including indigo) hold a large part of the dyestuff market. About 33,000 tons of vat dyes (including indigo) are being used annually since 1992 (Fig. 1) [1,2]. The situation will remain constant in the near future mainly because vat dyes yield coloured fibres of excellent all-round fastness, particularly to light, washing and chlorine bleaching [1]. Reactive dyes have not yet achieved the popularity of anthraquinone vat dyes that were invented a century ago [3]. Thus, at present, there is no true alternative to this class of dye [1–5].

Nevertheless, vat dyes require a somewhat complicated application procedure because they are practically insoluble in water. The present use of this dye category is based on reduction to obtain the water-soluble form of the dye (*leuco* dye). In its reduced form, the vat dye has substantivity towards cellulosic fibres and, after absorption, is

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* Corresponding author. Tel.: +44-1-632-5381; fax: +41-1-632-1074.

E-mail address: roessler@tech.chem.ethz.ch (A. Roessler).

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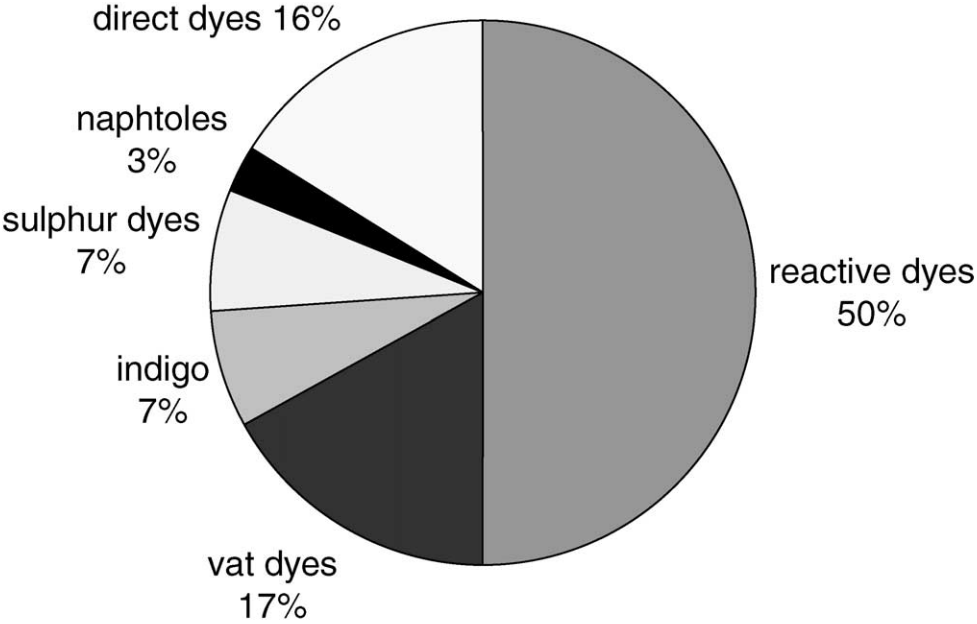


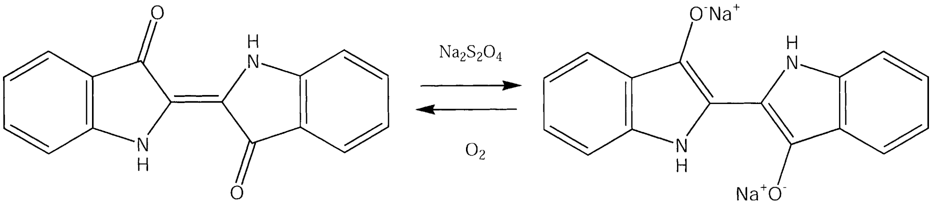
Fig. 1. Consumption of dyes for cellulosic fibres (in % on the base of the market value in 10^6 DM) [2].

reoxidised to the original water-insoluble form (Scheme 1) in situ in the fibre [6–8].

In modern textile dyeing processes, the reduction of vat dyes is carried out using powerful reducing agents among which sodium dithionite ($Na_2S_2O_4$) is of major importance. Unfortunately, the disposal of dye baths and rinse water causes problems, because the reducing agents will finally be oxidized into species that can hardly be regenerated. Thus, sulphite, sulphate, thiosulphate and, toxic sulphide [9], contaminate waste water from dyeing plants (worldwide approximately 180,000 t/a). In addition, as a result of the considerable excess of reducing agent required to stabilize oxidation-sensitive dye baths, the waste water may contain excess dithionite which affects aerobic processes in waste water treatment [10]. Therefore, many attempts are being made to replace the environmentally unfavourable sodium dithionite by ecologically more attractive alternatives. This article gives a summary of the processes most commonly used today as well as new electrochemical alternatives that are in the developmental stage in which the electric current assumes the role of the hydrosulphite.

2. State of the art reducing technologies

Previous investigations focused on the replacement of sodium dithionite by an organic reducing agent (i.e. α-hydroxyketones), which meets the requirements in terms of reductive efficiency and biodegradability. However, some substances are



Scheme 1. Vatting process.

expensive and the use of some α-hydroxyketones is restricted to closed systems because it forms strong-smelling condensation products in alkaline solution [11–14]. Some other reducing systems, based on sulphur containing substances, have also been recommended in recent years (i.e. hydroxyalkyl sulphinate, thiourea, etc.) [15–17]. The relatively low sulphur content and lower equivalent mass than that of hydrosulphite lead to lower amounts of sulphite and sulphate in the effluent. However, there is no reducing agent available today which can replace hydrosulphite in all areas. The dominant position of hydrosulphite is due to the particularly favourable relationship between its properties and its cost. Nevertheless, there is a continuing need for improving the eco-efficiency of this critical textile wet process.

2.1. Vat process with an ultrasonic reactor

Great opportunities exist for the conservation of dyes and chemicals through optimization of the concentration of chemicals used and by improvements in dye fixation. Recent developments in the field of indigo indicate that the consumption of sodium dithionite can be reduced to an almost stoichiometrical minimum of 1.1 (1.1 mol of dithionite used for 1 mol of indigo) [11,18]. Better dye fixation can be achieved by an almost oxygen-free dye bath, a high concentration of dye, a small amount of liquor (i.e. 200 l) and only a few number of dips of the yarn. In addition, a special fixation zone is used in front of the oxidation to enhance dye uptake by 10–15% [11]. Optimal concentrations and reaction conditions in the vatting reactor can be achieved by controlling the concentration of dye, reducing agents and NaOH by appropriate modern analytical methods [19–23]. In contrast, it could be demonstrated that 100% vatting can be accomplished in a few minutes in a completely oxygen free atmosphere and with the use of ultrasound [11,18]. Ultrasound enhances the vatting rate by disintegrating the dispersed water-insoluble dye aggregates into smaller particles. Owing to the increase of the dye surface, in addition to the simultaneous shortening of the diffusion interface, the probability for collisions between molecules of the reducing agent and the indigo molecules increases and finally the reaction rate will be faster [14,24]. An apparatus for carrying out the process described above comprises a mixing vessel and at least one reactor with ultrasonic resonators; the dyeing solution is subsequently drawn off (Fig. 2).

Since the degradation products of the excess dithionite can be acidic and have to be neutralized by alkali, the hydroxide in the vatting mixture is also consumed during the process. Thus, reduction of the necessary amount of sodium hydrosulphite leads also to a lowering of NaOH consumption. Due to the lower electrolyte load, the dye concentration in a stock solution can thereby be increased up to 130 g/l. Thus, the process and the apparatus have the great advantage that a high colour yield is achieved and less environmental pollution is produced. However, a further lowering of the electrolyte concentration which would increase the concentration of dissolved leuco dye can be effected only with electrochemical vatting or by hydrogenation.

2.2. Catalytic hydrogenation—pre-reduced dye

The catalytic hydrogenation of vat dyes was suggested a long time ago by Brochet [25]. Although there are many problems with several vat dyes (i.e. over-reduction, slow reduction rate), the preparation of leuco indigo solutions by catalytic hydrogenation of indigo can be effected in a generally known manner. In particular, by reducing an alkaline indigo paste (customarily from 10 to 35% by weight of indigo, from 2 to 10% by mass of NaOH) using Raney nickel as catalyst at a hydrogen pressure generally between 2 and 4 bar and at a temperature generally between 60 and 90 °C.

However, it is impossible to use this technique on-site in a dye house due to the high explosion and fire risk. Thus, pre-reduced indigo is produced as a commercial product in an indigo plant and shipped as a 40% aqueous solution. It can be used directly in a dye bath, which has only to be stabilized by reducing agents [26]. Therefore, this very young product offers the advantage that in the dyeing process, a considerable proportion of the chemical reducing agent, dithionite, can be dispensed with. Unfortunately, the eco-efficiency of this process is negatively affected by the high water content of the product (60%). However, transport costs are definitively influenced by the volume of the product. Due to the low bulk density of indigo powder, the transport volume based on unit mass of indigo for pre-reduced aqueous solution is approximately the same as in the case of indigo powder. Therefore, the concept of pre-reduced indigo has the potential to conquer the denim market. Some dye houses are already using the product even though they get completely reliant on the dye supplier, because at present only one company is offering this technology [26].

3. Electrochemical techniques

For ecological and economic reasons, electrochemical reduction is an attractive alternative to vatting techniques employing chemical reducing agents [27–29]. Grotthuss [30] was the first to discover that the electric current itself is capable of reducing indigo. Here, the most challenging engineering task is to achieve a dye reduction rate and a current efficiency which are high enough to make electrochemical reduction industrially feasible. Obviously, the rate-limiting step of electrochemical reduction is electron-transfer from the cathode surface to the surface of the microcrystal of the dispersed dye pigment. This is especially the case if the electrons have to be transferred directly between solid surfaces. It is possible to reduce solid indigo microcrystals immobilized on the surface of several electrode materials in aqueous solution, and the results are very similar to those obtained for indigo dissolved in various solvents [31,32]. However, if indigo is not immobilized but instead, is present as solid particles in aqueous suspension, it shows a distinctly different behaviour. Goppelsroeder published an extensive series of experiments on the electrochemical reduction of indigo suspended in water [33–39]. This work was substantiated by Wartha [40], Mullerus [41] and Nevyas [42]. Unfortunately, it must be conceded from these investigations that it is not industrially feasible to reduce indigo electrochemically under dye bath conditions on a planar electrode. The current efficiency was in all experiments below 20% [43,44]. Thus, the most limiting factor seems to be the poor contact between indigo particles and the electrode. It is therefore desirable to develop a reduction process by using a different

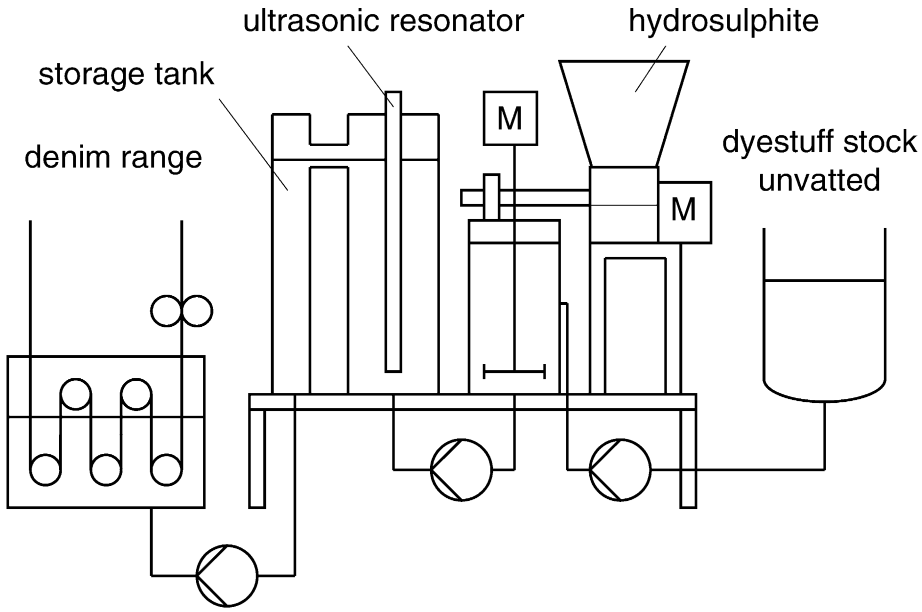
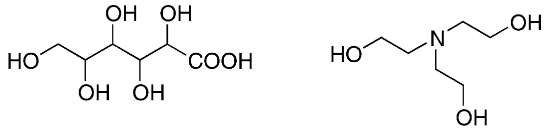


Fig. 2. Dye stock preparation for the denim technology (vatting reactor VR3, Tex-A-Tec AG, Wattwil/Switzerland [9]).



(a) (b)

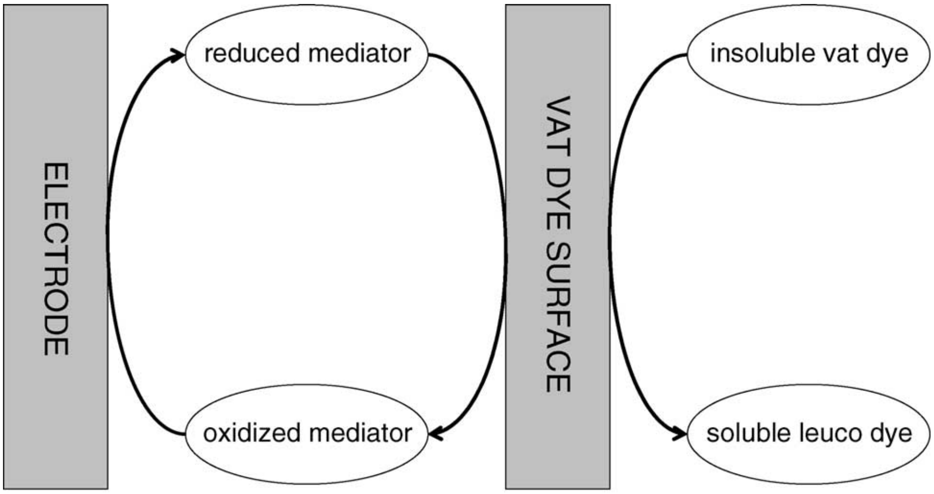
Scheme 2. Complexing agents used for the formation of the mediator: triethanolamine (a) and gluconic acid (b).

reactor and/or process design based on the intensification of the contact between the dye particles and the electrode. Hence, an indirect electrochemical reduction process employing a soluble redox mediator was developed to enhance the rate of the electron-transfer [46–63].

3.1. Mediator-enhanced electrochemical reduction

This process is mediated by an electron-carrier whereby reduction takes place between the separated surfaces of the electrode and the dye pigment instead of by direct contact between both surfaces (Scheme 2) [45]. The mediators employed in this process are regenerable iron complexes with triethanolamine or gluconic acid as ligands (Scheme 3). In a recent attempt complex mixtures of triethanolamine and D-gluconate have been investigated. They are of particular interest for the mediator process because it is possible to combine the advantages of both ligands [60,61]. These mediators, however, are expensive and not entirely harmless from a toxicological point of view [64].

A great advantage of this technique is the direct information about the state of reduction in the dye bath, which is available by redox potential measurement, and that control by adjustment of the cell current is possible. The reducing agents normally used cannot be monitored in a comparable manner [65]. Thus, often a surplus of reducing agents often has to be applied to guarantee stable dye bath conditions. An important property of the iron(II)–amine complex is the high rate of dye reduction, which is much faster than that with sodium dithionite [65]. However, as described in many publications, the cathodic reduction runs with low current density because electrochemical reduction of the complex is the rate-determining step and an increase in the concentration of the electrochemically active iron-complex is limited [46,65–67]. Therefore, to achieve a large cathode area with sufficient cell current, a novel electrochemical cell (especially a cathode construction) has been described [68]. In order to meet all requirements in an economical way, a multi-cathode cell with a large number of cathodes, electrically connected with one or two anodes, has been suggested [69]. This configuration allows the operation of the cell with a maximum cathode area and a minimum anode area [70,71]. The process was tested successfully for continuous dyeing



Scheme 3. Principle of the mediator technique.

of cotton yarn on a full scale indigo dyeing range using a 1000 A multicathode electrolyzer [71]. However, the huge electrode surface of 500 m^2 is still necessary to achieve a feasible reduction rate at an industrial scale. Thus, it is impossible to use this technique for the complete reduction of a stock solution in the case of continuous dyeing, because the operating costs and the return on investment are not attractive enough for an application in the denim industry [2]. Indirect electrochemical reduction can only be used in discontinuous exhaust dyeing processes [62] and to stabilize the dye bath in continuous dyeing by diminishing the amount of leuco indigo oxidized during dyeing by air contact (Fig. 4b) [26].

In addition, after reduction and prior to the dyeing process, the mediator has to be separated from the soluble leuco dye by ultrafiltration, and the concentration of the mediator in the filtrate is increased by nanofiltration. This offers the possibility to restore the reducing power and to recycle water, the mediator (with losses of 15% [65]) as well as textile auxiliaries. However, the filtration considerably increases the costs for this vatting process and introduces several technical problems (Fig. 3) [72,73]. Therefore, this mediator-technique remains under development even after many years and at present, production trials are performed only in one pilot plant [74,75]. Thus, there is still a continuing need for new alternatives improving the eco-efficiency of the application of vat dyes.

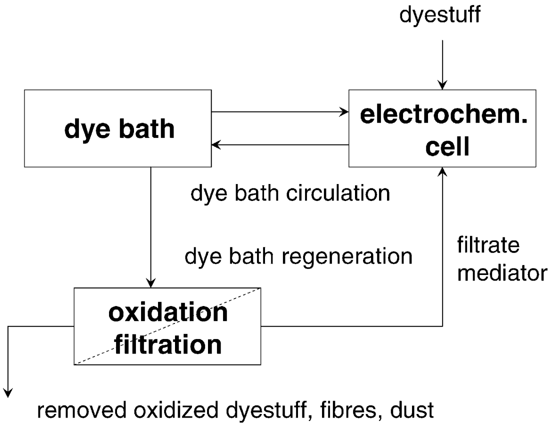


Fig. 3. Flow scheme for application of indirect electrochemical reduction of vat dyes in package dyeing [32].

3.2. Direct electrochemical reduction of indigo via the indigo radical

As an alternative to mediated electrochemical reduction, a novel electrochemical vatting process for vat and sulphur dyes has been described [76–78] which does not require the permanent presence of a redox mediator. It is based on a reaction mechanism in which a radical anion is formed by a comproportionation reaction between the dye and the leuco dye, followed by the electrochemical reduction of this radical. The leuco dye, acting as an electron-shuttle between the electrode and the surface of the dye pigment, has to be generated first in a small quantity to initiate the reduction. Further electrochemical reduction is self-sustaining, as shown in Scheme 4 for indigo.

The indigo radical anion occurs as an intermediate with maximum absorptions at 545 and 496 nm as identified by its EPR-spectrum [76]. From electrochemical investigations it has been concluded that the radical anion is easily reduced and that the reaction product (leuco indigo) is stable under the conditions used [77]. The effect of several parameters, such as current density, pH and temperature, on electrochemical kinetics have been analysed and were the basis for further work on scale-up and optimisation [78]. For future industrial application of the direct electrochemical

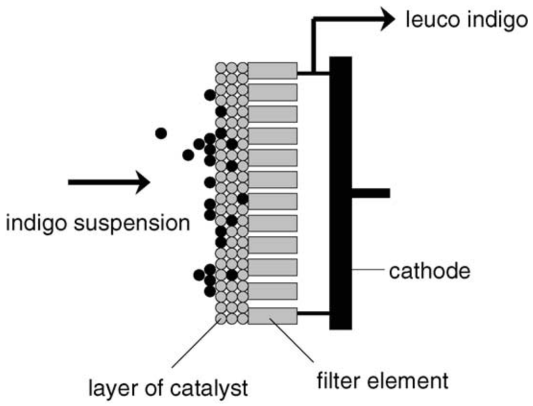
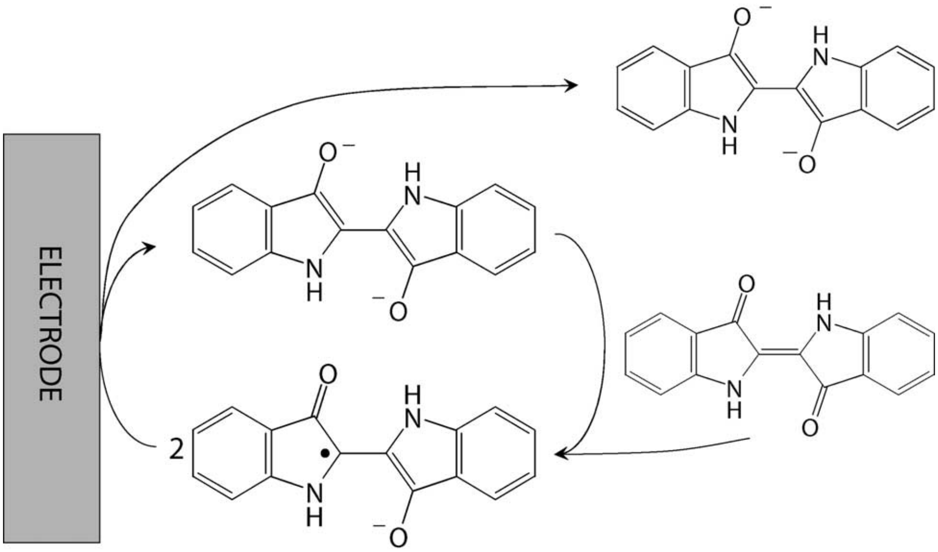


Fig. 4. Concept of the precoat-layer-cell.



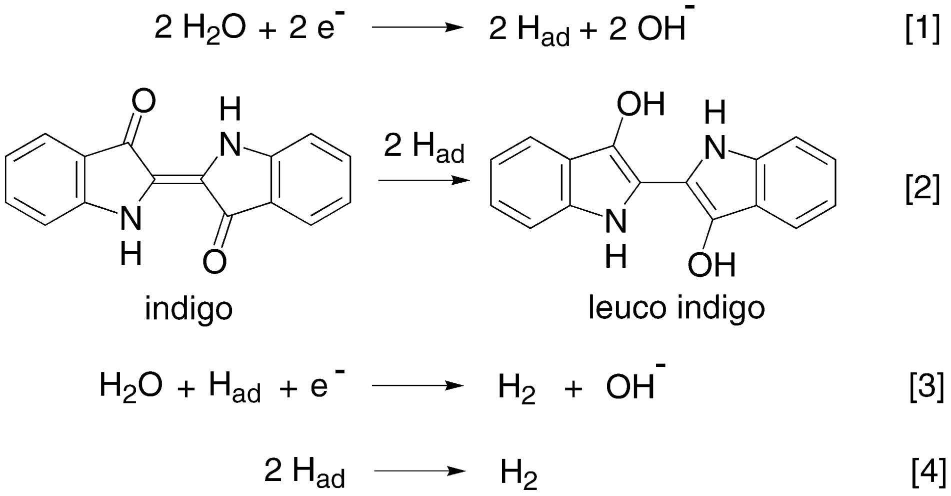
Scheme 4. Mechanism of the direct electrochemical reduction of indigo radical.

reduction of vat dyes, the reduction rate has to be increased considerably. All experimental data are in agreement with the diffusion-controlled reduction of the intermediate radical anion being the rate-limiting step of this electrochemical process. Because this limiting rate is critically depending on the thickness of the diffusion layer at the electrode surface, an increase of the catholyte flow could enhance significantly the reduction rate. Until now, however, reactor performance even for bath-stabilization is still too low. Further investigations focusing more on enhancing the radical concentration (i.e. by surfactants) will be necessary.

3.3. Electrocatalytic hydrogenation

Electrocatalytic hydrogenation is a recently introduced reduction method for vat and sulphur dyes and it proves to be a promising and attractive alternative in terms of economic and ecological aspects [79–82]. The process consists of a sequence of reduction steps which differ principally from those of the previously described indirect and direct electrochemical vatting processes via the dye radical. These involve electron-transfer from the cathode to either a mediator or the leuco radical anion of the vat dye. In contrast to this mechanism, electrochemical hydrogenation is a process in which adsorbed hydrogen, produced in situ by electrolysis of water, reacts with adsorbed organic substrates (i.e. vat dye) at the electrode surface (Scheme 5). The hydrogenation step is in competition with hydrogen evolution reaction and the efficiency of the electrocatalytic hydrogenation is determined by this competition. Electrocatalytic hydrogenation has been carried out successfully over the years on a lot of substrates and has several advantages over catalytic hydrogenation [83]. 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.

The industrial feasibility of this novel route has been studied recently in a divided flow cell using Raney-nickel electrodes. Several vat dyes could be reduced with this method. In the case of indigo, optimization of conditions in the system was attempted, and a scale-up in indigo concentration to 10 g/l was achieved. Unfortunately, using these optimized conditions, only a low current efficiency of 12.7% could be reached at 95% conversion. Thus, a huge electrode surface of more than several hundreds of square meters would be necessary



Scheme 5. Electrocatalytic hydrogenation of indigo.

to attain an industrially feasible reduction rate for stock solutions. Probably the method will be only powerful enough for dye bath stabilization. Nevertheless, Raney nickel was chosen as electrode material, because it is interesting from the standpoint of availability, costs and stability in alkaline medium. The stability of platinum-black electrodes—which are among the most active ones—was shown to be poor, so that their industrial application is impossible [81,82].

However, on the basis of these results, it should be possible to improve the efficiency of the process by using a different reactor design based on the intensification of the contact between the dye particles and the electrode. For this purpose the so-called precoat-layer-cell has been developed [79,80]. The reactor is based on the filtration principle, i.e. by bringing the indigo into contact with a cathode, where the cathode is formed by a support of an electrically conductive material (i.e. filter fabrics) and a cathodically polarized layer (i.e. Raney nickel) formed on the filter in situ by precoat filtration (Fig. 4). The severe drawback of this technique seems to be the big pressure drop built up during the filtration process and the persistent danger of blocking the reactor. In addition, the reactor performance is low. Thus, research and development has been abandoned.

Recently, in accordance with the above-mentioned problems, noble metal particles supported on graphite granules have been investigated as electrode material in a fixed- and fluidized bed reactor [84–86]. The pressure drop over the granular material was much lower than in case of fine Raney nickel powder and it was still possible to end up in fair and good electrogenolysis efficiencies. However, noble metals are very expensive and the long-time behaviour of the catalyst was shown to be poor [86].

3.4. Direct electrochemical reduction of indigo on graphite electrodes

Carbons and graphite are high-surface-area materials and are therefore extensively used in electrochemistry. Even for the reduction of indigo, these materials have been applied as described by Chaumat who used a specially prepared cathode of finely divided indigo and graphite powder in a solution of sodium carbonate [87,88]. Recently, it has been shown that graphite granules can act as electrode material for the direct electrochemical reduction of indigo in aqueous suspension. Optimized conditions were sought and a scale-up in indigo concentration to 10 g/l was achieved [84–86]. This is a really promising result, because graphite is a very cheap and stable material. In addition, an electrochemical fixed- or fluidized-bed reactor is a reasonable economic reactor design for this task.

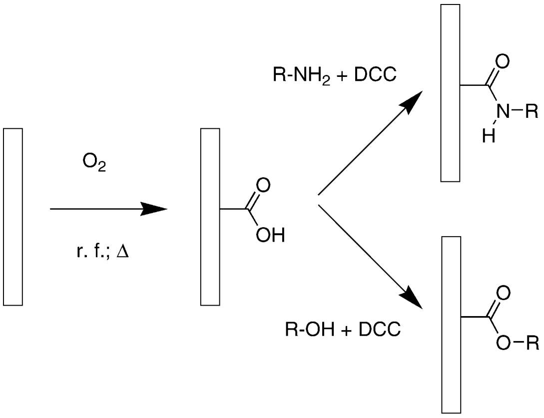
Due to the high hydrogen overvoltage on graphite [89] under the applied conditions, no chemisorption or only very weak, chemisorption of hydrogen is possible. Therefore, a normal electron transfer seems to be the relevant process for the reduction of indigo. Unfortunately, the reduction rate was very low. Therefore, a great deal of work has been focussed on the acceleration of the process [84]. There is at present little doubt that much of the chemical activity of the carbon surface is connected with quinone and hydroquinone groups, whether directly attached to the carbon black surface or part of more complex structures [89]. Therefore, it should be possible to accelerate the relevant processes (electron transfer kinetics and probably also the adsorption rate) by the selective generation of quinone-like functionalities on the surface of the used graphite electrode. In addition, it is well known that oxidative pre-treatment can increase the content of oxygen-containing groups on the surface of carbon [89]. Thus, special pretreatment of the graphite (i.e. soaking with hydrogen peroxide or pre-anodization) was investigated to enhance the reduction rate [84]. Another interesting approach to enhance the electrocatalytic properties is based on the covalent bounding of quinoid molecules onto the graphite surface [84,90,91]. Thus, electron transfer mediators, which can undergo fast electron transfer with the electrode and also with the substrate (indigo), are immobilized on the carbon electrode. Several immobilization concepts are thinkable and a suitable one depends upon the substrate (i.e. graphite) and the mediator molecules. In the particular case of indigo reduction, anthraquinones have been used as redox-active molecules. These substances are already well known from the mediator process [92]. Scheme 6 shows the possibility of immobilizing such species with an amine or hydroxyl functional group via the surface carboxylic groups.

Until now, it is possible to reduce an extensive range of vat dye (i.e. indanthrene dyes) and indigo suspensions up to 100 g/l without a blocking of the reactor. For example, in case of indigo the investigations end up in fair and good values of approximately 60% current efficiency, 1 kWh/kg power consumption and a reduction rate of 10 mg/min kg graphite (at 50 °C) [84]. Thus, this process can compete with the mediator technique from an economic point of view. Probably, the installation costs for the reactor are also lower. In addition, recycling of the mediator by ultra- and nanofiltration is not required.

These results are obviously basis for the further development of a cheap, continuously and ecologically working cell for the direct electrochemical reduction of dispersed vat dyes. Especially the introduction of surface functionalities by chemical reaction routes is at present an exciting research area. Hopefully, the immobilization of redox-active substances succeeds in a high and industrial feasible reduction rate. However, the next steps will be pilot-plant trials and a scale-up procedure. It is worth noting, that this won't be easy and an optimization of the cell construction will be a requirement for the successful realization of this method in textile dye houses.

3.5. *Stabilization or regeneration of dithionite by electrolysis*

It is obvious that another alternative could be based on the application of electrochemical techniques to the non-regenerable reducing agents. Daruwalla investigated the electrolysis of the dye bath [93–96]. He assumed that dithionite ions $S_2O_4^{2-}$ can be transformed to sulfoxylate ions SO_2^{2-} on an iron cathode. Thus, a very powerful reducing species with a redox potential higher than that of dithionite



Scheme 6. Covalent modification via the carboxylic surface group on carbon. DCC = dicyclohexylcarbodiimide. r.f. = radio frequency plasma. Δ = thermal. R = i.e. anthraquinone.

itself is generated which should reduce dithionite consumption by 30%. However, until now no commercial realisation of the proposed process is known. Nevertheless, an electrochemical regeneration of the reducing agent from SO_3^{2-} and SO_4^{2-} would be an environmentally friendly way to solve the problems in the application of vat dyes. Electrolysis of a suspension of indigo in a warm solution of sodium bisulfite, $NaHSO_3$ has been successful [97–99]. In addition, several papers have been published about the electrochemical regeneration of dithionite [100–102]. Olin Corp. has recently brought the electrosynthesis of dithionite to commercial scale. Unfortunately, the process is not feasible under normal dye bath conditions [101, 102]. As a consequence, during the last few years investigations have been focusing on the electrochemical reduction of vat dyes.

4. Conclusions

The current situation and suggested changes in the continuous vatting process are summarized in Fig. 5. After several decades of research and development there is still no commercial reducing technology (including electrochemical processes) available today that can replace sodium dithionite in all areas of vat dye application. However, it is possible to diminish the consumption of sodium dithionite for stock vatting and for the dye bath stabilization to a stoichiometrical minimum of 1.1 with state of the art technologies (Fig. 5a). Such efforts result in significant money savings for the manufacturers, with an associated reduction of the effluent load. Nevertheless, there is a continuing need for improving the eco-efficiency of this critical textile wet process. A further reduction of the necessary amount of reducing agent is only possible by the electrochemical vatting technique or hydrogenation.

Although there are many problems with several vat dyes, catalytic hydrogenation seems to be an interesting solution for indigo (Fig. 5a, b). Unfortunately, it is impossible to use this technique directly in the dye house due to the high explosion and fire risk (Fig. 5a). Therefore, dye suppliers offer concentrated pre-reduced leuco indigo solutions for shipping to the dye house (Fig. 5b). However, the eco-efficiency of this process is negatively affected by high water content of the product. In addition, the dye houses become completely reliant on the dye supplier, because only one company offers this technology at present.

Therefore, still the method of choice would be an electrochemical stock vatting technique (Fig. 5c). In recent attempts, various electrochemical reducing methods have been investigated, such as the indirect electrochemical reduction employing a redox mediator, the direct electrochemical reduction of indigo via the indigo radical, the electrocatalytic hydrogenation route and the direct electrochemical reduction on graphite.

All these methods offer tremendous environmental and economic benefits, since they minimize

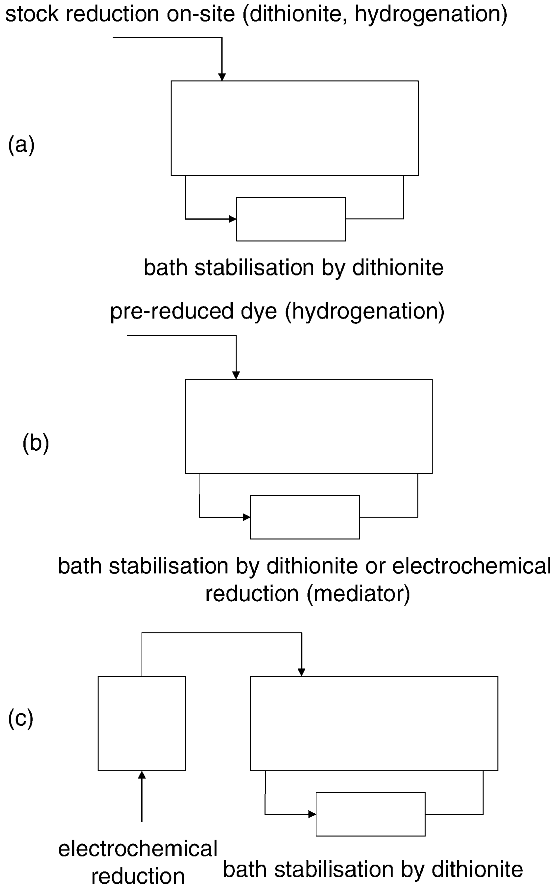


Fig. 5. Integration of electrochemistry in the vatting process: (a) current situation; (b) pre-reduced dye; (c) electrochemical techniques.

the consumption of chemicals as well as the effluent load. Until now, however, the electrochemical reactor performance is too low for the complete reduction of a stock solution in the case of continuous dyeing. As a consequence, the operating costs and the return on investment are not attractive enough for an application in the dyestuff industry. Therefore, in a particular embodiment of the dyeing process with pre-reduced indigo only the dye bath stabilization has been achieved by electrochemical reduction in the presence of a mediator (Fig. 5b).

On the other hand, an application of electrochemical vat dyeing in discontinuous exhaust dyeing processes might be possible, because the necessary reactor performance is much lower. Unfortunately, this concept is not suitable for indigo. Satisfying the needs of the customer (i.e. stone-washed look) skin dyeing is still in progress, which can only be achieved in continuous processes. However, in the extensive range of vat dyes (i.e. indanthrene dyes) usually core dyeing is realised. Thus, the combination of an electrolyzer and a discontinuous yarn-dyeing machine is a conceivable variation for electrochemical vat dyeing. In case of the mediator technique such a process is close to commercialization with a yarn-dyeing machine (X-cones).

From the point of stability, availability and costs, the latest development concerning direct electrochemical reduction on graphite granules seems to be the most attractive process and the results are obviously a promising basis for further development. However, the next step will be a scale-up procedure and it is worth noting that this requires a lot of investigations. Nevertheless, looking at the successful development of several processes in the last years it can be concluded, that a good degree of progress in the right direction has been made. The market introduction of the mediator process is imminent and the message is simple: electrochemistry in textile industry is coming our way.

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