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SCIENCE DIRECT®
Dyes and Pigments 63 (2004) 29–37
DYES and PIGMENTS
www.elsevier.com/locate/dyepig

Direct electrochemical reduction of vat dyes in a fixed bed of graphite granules

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Received 24 September 2003; received in revised form 6 January 2004; accepted 21 January 2004

Abstract

Reducing agents required in the dyeing process for vat and sulphur dyes cannot be recycled and lead to problematic waste products. The application of electrochemical reduction of several vat dyes and even mixtures of them on a fixed bed cathode consisting of graphite granules has been investigated by spectrophotometric experiments in a laboratory scale pilot plant. Experiments yield information about the kinetics and show the possibility and versatility of this environmentally friendly process for production of water soluble leuco dyes. In addition to singular dyes, even dyestuff mixtures were investigated. Regarding the effect of different molecular structures on the kinetics and a preliminary understanding of the reaction mechanism, relationships between computed molecular parameters and the reduction rate are presented.

Keywords: Electrochemical reduction; Indigo; Vat dyes; Graphite; Fixed bed; Hydrophobicity

1. Introduction

Dyestuffs such as sulphur and vat dyes, especially indigo, play an important role in today's dyeing industry (market about 120 000 t/a). In an attempt to increase the eco-efficiency of today's dyeing processes for vat dyes, in the last years alternative electrochemical techniques for vatting (=reduction) of such dyes, in particular indigo, were investigated [1]. The conventional, most used reducing agent, sodium dithionite, cannot be recycled and the disposal of dyeing baths and rinsing water is causing high costs and various problems with the effluent (high salt load, depletion of dissolved oxygen, problems with nasal nuisance, toxicity of sulphide, etc.). Therefore, modern economical and ecological requirements are not fulfilled. Electrochemical reducing methods would be a valuable alternative because they

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doi:10.1016/j.dyepig.2004.01.005

do not require any chemical reducing agent. Thus, they offer tremendous environmental and economical benefits and have a vast potential in textile dyeing processes [1].

The latest development concerning the direct electrochemical reduction on graphite granules [1,2] seems to be the most attractive process. Graphite is a very cheap and stable material. Hardly any decomposition of the granules has been observed throughout all experiments and there was no necessity to clean the electrode material over several months. In addition, the pressure drop over the granular material proved to be feasible. Until now, however, only the reduction of indigo has been investigated and the versatility of this method has not been tested yet. This is of vital importance for an industrial application because indigo is only one product in an extensive range of vat dyes (i.e. Indanthren® dyes). Thus, in this paper reduction experiments with different dyestuffs are presented. In addition, the vatting of dyestuff mixtures was investigated, which is of crucial interest in the application of vat dyes. Moreover, relationships between computed molecular parameters of different dyes and the reduction rate are discussed regarding the reaction mechanism.

2. Experimental

2.1. Chemicals

All aqueous solutions were prepared with deionised water. C.I. Vat Blue 1 (Indigo), C.I. Vat Red 10 (Indanthren® Red FFB), C.I. Vat Green 1 (Indanthren® Brilliant Green FFB), C.I. Vat Orange 17 (Indanthren® Orange GG), C.I. Vat Blue 5 (Brilliant Indigo 4B), C.I. Vat Blue 6 (Indanthren® Blue BC), and Indanthren® Gray 5607 were supplied by DyStar Textilfarben, Frankfurt, Germany. C.I. Vat Yellow 33, C.I. Vat Blue 14, and C.I. Vat Blue 43 (Hydron Blue) were supplied by BEZEMA AG, Montlingen, Switzerland. C.I. Sulphur Black 1 (Diresul® Liquid Black RDT) was supplied by Clariant, Switzerland. All dyes were used as received in technical grade quality. Setamol WS (lignin-sulfonate) from BASF, Ludwigshafen, Germany was used as dispersing agent. All other chemicals were of analytical grade, purchased from Fluka and used as received.

2.2. Electrochemical reactor

A small multipurpose plate and frame cell (EC Electro MP-Cell from ElectroCell AB, Sweden) was chosen for the experiments. 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 a working electrode configuration, a flat graphite plate electrode plus a porous three-dimensional bed ($10 \times 10 \times 5$ cm) made by graphite granules was used. The diameter of the granules was between 3 and 5 mm. The surface estimated from the porosity of the bed, the particle diameter and the bed volume is close to 0.3 m^2. The thickness of the bed has been optimized regarding the space time yield of the reactor. However, due to a limited penetration depth of the current density [3] only a maximum bed depth of 5 cm has been realized. Though, due to the high ionic conductivity of the ground-electrolyte most likely even thicker beds are possible. Nickel was used as anode material and the cell was divided into two compartments by a Nafion-324 membrane (DuPont). The set-up of this pilot plant used in the experiments is given in Fig. 1. The flow circuit is described in detail elsewhere [4,5]. Current supply was from a potentiostat (Radiometer Copenhagen DEA 332, Electrochemical Interface IMT102 and Software Voltamaster2).

2.3. Electrodes

Eleven different graphite granules (sieve fraction 3–5 mm) were used after washing with distilled water three times and wetting overnight in 1 M sodium hydroxide solution at room temperature: (A) enViro Gram, No. 00514, artificial graphite from electrode scrap, enViro Cell, Oberusel, Germany; (B) TIMREX T1000-8000, porous and flaky artificial graphite, Timcal group, Bodio, Switzerland; (C) Norit RX3 Extra, Lot. No. 510207, activated graphite, Norit Netherlands B.V., Amersfoord, Netherlands; (D) granular

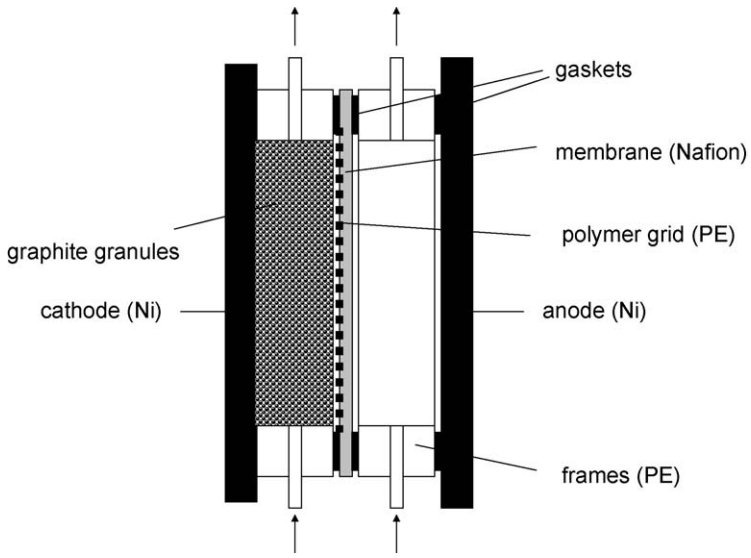


Fig. 1. Schematic figure of the plate and frame reactor (Electrocell AB).

carbon from coconut shells, Lot. No. 2840, PMC, Sevierville, USA; (E) artificial graphite from electrode scrap, NGS Naturgraphit GmbH, Leinburg, Germany; (F) calcinated petroleum coke, NGS Naturgraphit GmbH, Leinburg, Germany; (G) metallurgical coke, Coferal, Munich, Germany; (H) Novacarb #3003, activated graphite, MAST Carbon, Guildford, Surrey, UK; (I) #7B9 Graphite, Asbury Carbons/Cummings-Moore Graphite Co., Detroit, USA; (J) CC610 Petrol Coke, Asbury Carbons/Cummings-Moore Graphite Co., Detroit, USA; and (K) #5555 Activated Coal, Asbury Carbons/Cummings-Moore Graphite Co., Detroit, USA.

2.4. Procedure

Cathodic dispersions of the different vat dyes were composed of sodium hydroxide 1 M, 0.3 g/l of the dye and 5 wt.% (related to the dye) Setamol WS as dispersing agent. They were deoxygenated for at least 2 h before the experiment and maintained under a nitrogen atmosphere during measurements. In all experiments, the solutions were deoxygenated for at least 2 h before the experiment and maintained under a nitrogen atmosphere during measurements. Anodic solutions consisted of 1 M sodium hydroxide solution. Usually, the reduction experiments were performed at an electrode potential of −1000 mV vs. Ag/AgCl, 3 M, 50 °C and a fluid flow of 1.4 l/min.

2.5. MO calculations

Vat dye structures have been geometry optimized by molecular mechanics calculations (MM3 in CAChe WorkSystem Pro, Version 5.02, Fujitsu Ltd. 2002) in searching for global minima by varying the torsion angles available in each dye. The lipophilicity (log p) has been calculated according to the atom typing scheme of Ghose et al. ([6], see also [7]).

3. Results and discussion

3.1. Electrochemical reduction of different single vat dyes

From the graphite materials examined (enViro cell, Timcal, Norit, PMC, NGS, Coferal, Mast Carbon, Asbury Carbons), granular electrographite (artificial graphite from electrode scraps) or petroleum coke proved to be the most active

electrode materials with sufficient electronic conductivity. Much of the chemical activity of the carbon surface is connected with oxygen functionalities (i.e. quinone and hydroquinone groups [1,2]). However, the degree of surface oxidation should not be too high. For example, in the case of activated carbon the high surface area with numerous active sites seems to be beneficial to the electrode applications, but low conductivity is not. Activated products are made up of a poorly developed framework of sp^2-hybridized carbon atoms contaminated by insulating areas with sp^3-hybridized carbons, especially at the surface.

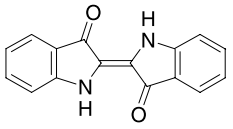
Thus, granular electrographite (enViro Cell) has been used for further investigations. A series of potentiostatic runs was carried out in order to assess the versatility of the method and the effect of different molecular structures on the kinetics (Scheme 1, Table 1), the variety based on the following three classes of vat dyes: anthraquinone dyes, fused ring polycyclic dyes and indigoid dyes.

All reduction experiments were performed at an electrode potential of −1000 mV vs. Ag/AgCl, 3 M. Thus, it was possible to compare the results. However, it is important to mention that there is still potential for further improvement. Each investigated vat dye has its own optimized electrode potential regarding reduction rate or current efficiency, which most probably differ from −1000 mV vs. Ag/AgCl, 3 M. Nevertheless, it was possible to reduce all of them and, moreover, the dye molecules did not decompose either, i.e. by overreduction or by dehalogenation under the applied conditions (Table 1). In the vast majority of cases, a 95% mass balance was obtained after the experiment by reoxidation to the insoluble product and filtration of the electrolyte. The diminished mass balance of 90% observed sometimes is probably due to the loss of material by adsorption on the graphite. In addition, laboratory exhaust dyeing experiments show in all cases a dyeing behaviour of the reduced vat dyes similar to that of conventional reduction methods. Thus, substances can even be reduced with this method, which are usually very sensitive against overreduction. For example, in the case of C.I. Vat Yellow 33, **8** a cleavage of the azo chromophore would be possible, because direct cathodic reduction of azo groups to the corresponding amines or hydrazo-groups is a well known process [8]. However, due to a reduction in the electrode potential it is very easy to avoid this unfavourable process and to optimize the production of the leuco species. The influence of the potential on the reduction of C.I. Vat Blue 14, **6** is shown in Fig. 2. Changing the electrode potential to values higher than −1000 mV vs. Ag/AgCl, 3 M at t_1, a well known overreduced brownish tetrahydro leuco dye, **11** of C.I. Vat Blue 14, **6** can be produced out of the dihydro leuco species, **10** [9,10] (Scheme 2).

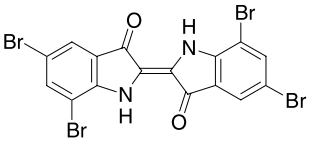
The application of sulphur dyes is similar to that of dyeing with vat dyes and indigo. However, the redox behaviour of sulphur dyes is quite different to the vat dyes and Bechtold et al. [11] published an extensive series of experiments on the direct electrochemical reduction of Sulphur Black 1. Thus, it is no surprise that even these substances can be reduced electrochemically in the fixed bed of graphite granules. Table 1 shows the result of the reduction of the sulphur vat dye Hydron Blue (C.I. Vat Blue 43, **9**), which can be reduced in an efficient way with an industrially feasible current efficiency. In addition, preliminary investigations with Sulphur Black 1 were also successful.

The leuco dyes were produced—in contrast to the process based on the electrochemical reduction of the dye radical [5,12]—directly from the dye suspension and were identified by their maximum of extinction (λ_{max}) in the UV/VIS-spectra [12]. Thus, direct electron transfer between the dye and the graphite seems to be the relevant process. However, it cannot be excluded that the electrochemical reduction of the dye radical occurs simultaneously to the direct reduction of the pigment. Nevertheless, it is impossible that the radical-mechanism is highly significant for this process. The concentration of the radical species is very low and, consequently, so is the reduction rate [2,12]. In addition, due to the high hydrogen overvoltage on graphite [13] 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 vat dyes. Nevertheless, the theoretical understanding of the process is still in its infancy and the rate-limiting step is unknown. On one

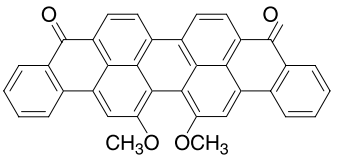
C.I. Vat Blue 1, **1**



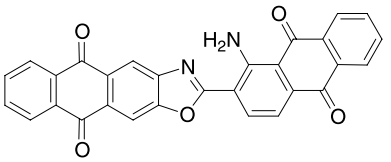
C.I. Vat Blue 5, **2**



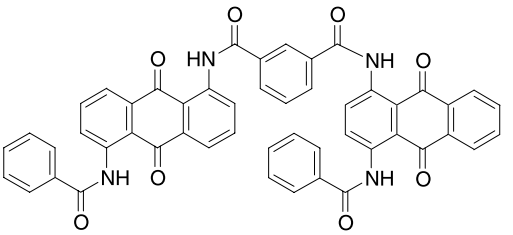
C.I. Vat Green 1, **3**



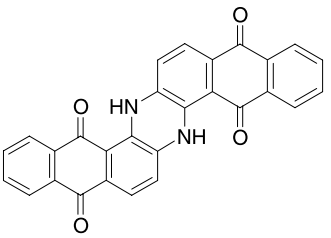
C.I. Vat Red 10, **4**



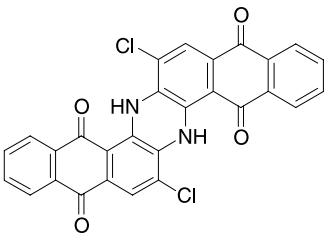
C.I. Vat Orange 17, **5**



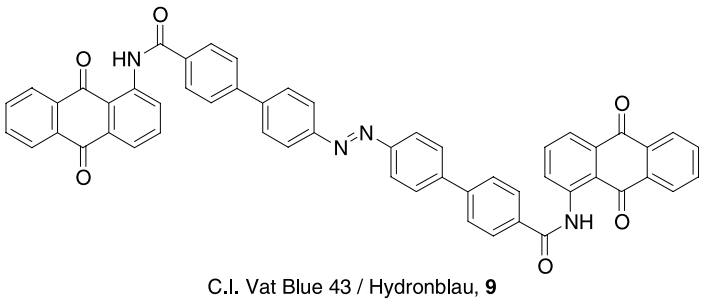
C.I. Vat Blue 14, **6**



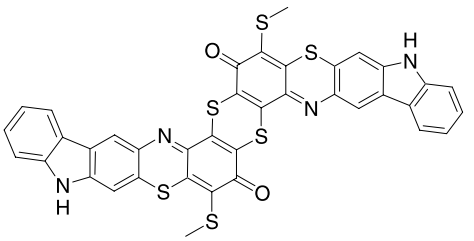
C.I. Vat Blue 6, **7**



C.I. Vat Yellow 33, **8**



C.I. Vat Blue 43 / Hydronblau, **9**



Scheme 1. Molecular structures of investigated vat dyes. The structure of **9** refers to [19].

Table 1
Reduction experiments with several vat dyes

Substance	r (μmol/min kg graphite)	Current efficiency (%)	Current density (mA/m^2)
C.I. Vat Blue 1	38.0	72.7	140.0
C.I. Vat Blue 14	30.8	72.3	93.3
C.I. Vat Blue 5	24.8	84.4	53.3
C.I. Vat Blue 6	28.0	65.2	58.3
C.I. Vat Green 1	22.8	86.7	76.7
C.I. Vat Orange 17	26.4	67.5	43.3
C.I. Vat Red 10	28.8	77.8	63.3
C.I. Vat Yellow 33	13.2	81.6	43.3
C.I. Vat Blue 43	30[a]	—[b]	126.7
Mixtures:			
C.I. Vat Blue 14	29.8	82.6	51.9
C.I. Vat Green 1	15.2		
Indanthren® Gray 5607	2.6[a,c]	—[b]	80.0

[a] Reduction rate r in mg/min kg graphite due to unknown molar mass.
[b] Calculation not possible due to unknown molar mass.
[c] Reduction rate r related to the rate determining component.

hand, an influence of the leuco dye concentration on the reduction rate has never been observed. Thus, desorption or dissolution of the leuco dye is probably not determining the reaction rate. On the other hand, due to the small apparent activation energy of 11.4 kJ/mol and only a limited influence of the electrode potential on the reduction rate, it is most likely also not the electron transfer [2]. In addition, there is no correlation between the reduction potential and the reduction rate (Table 2). Such an account of the investigation on the ease of reduction of vat dyes is reported elsewhere [14]. However, it can be seen from the results in Table 1 that substitution of hydrogen by the more electronegative bromine or chlorine diminished the reduction rate, although this shifts the potential to more positive values [15].

Thus, we have investigated the influence of the molecular structure on the kinetics (Table 1). This has been done together with modeling the lipophobicity (log p) and the van der Waals surface (S) (Table 2). The reduction rate correlates with the lipophilic properties (log p) with good results regarding the diversity of the dye molecules (Fig. 3):

$$r = (-2.942 \pm 0.364)\log p + (40.515 \pm 2.919)$$

$$n = 8, \quad R^2 = 0.92$$

where r is the reduction rate in μmol/min kg graphite. The significant decrease in the reduction

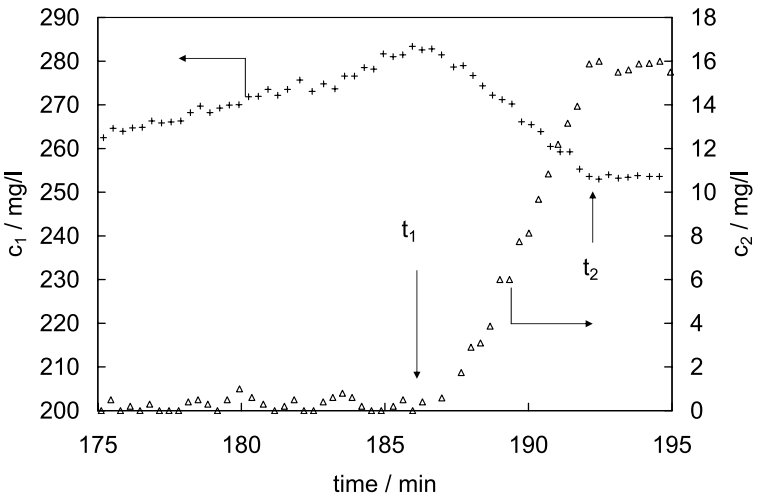
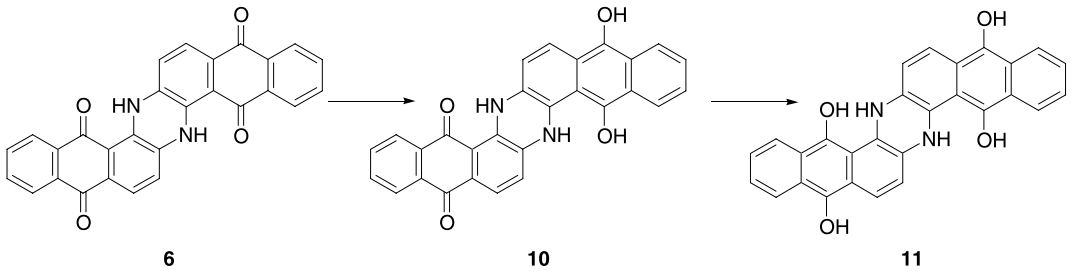


Fig. 2. Concentration c_1 of the dihydro leuco species, **10** (+) and concentration c_2 of the overreduced tetrahydro component, **11** (△) vs. time profile for the overreduction of C.I. Vat Blue 6, **7**. Electrode potential (vs. Ag/AgCl, 3 M): −1000 mV ($0 < t < t_1$), −1200 mV ($t_1 < t < t_2$), 0 mV ($t > t_2$). System parameters: enViro cell graphite granules, 1 M NaOH, 300 mg/l vat dye and 5 wt.% (related to the dye) Setamol WS, 50 °C, fluid flow 1.4 l/min.



Scheme 2. Overreduction of C.I. Vat Blue 6, **7** via the dihydro leuco species, **10** to the brownish tetrahydro component, **11** [9,10].

rate with rising lipophilicity indicates that the adsorption of the pigment on the lipophilic graphite surface is probably not rate determining. Though, the dependence of the lipophobicity (log p) on the extent of surface molecular area is evident and the contribution of steric effects could be important for the adsorption process. In fact, the reduction rate is a function of the surface area of the molecule (S) and drops down using larger dye molecules (Table 2). However, obviously other parameters also affect the reduction rate, because there is no clear correlation between these two physical values:

$$r = (-0.031 \pm 0.0092)S + (41.579 \pm 6.507)$$

$$n = 8, \quad R^2 = 0.56$$

where r is the reduction rate in μmol/min kg graphite and S is the van der Waals surface in $Å^2$. Therefore, in the case of highly hydrophobic dyes undesirable large agglomerates of the pigment probably negatively affect the reduction rate due to a diminished external surface. In aqueous media, hydrophobic dyes probably exist in the form of complexes consisting of many dye and dispersant molecules linked together by van der Waals hydrophobic–hydrophobic interactions. In addition, aggregation of the pigment is favoured with increasing lipophilicity [16]. Thus, the rate limitation of the dye adsorption cannot be finally excluded. However, the solubility of the pigment could be also important. For the vat dye reduction, two views of the mechanism are possible. Both, dissolution and transport to the electrode followed by electron transfer and electron hopping across the solid/solid boundary layer are plausible at a microscopic scale. Increasing solubility could promote the more efficient route via the dissolved species. Unfortunately, due to the very low solubility of vat dyes it was not possible to detect the soluble dye species.

Table 2
Molecular parameters and reduction rate of different vat dyes

Substance	log p	van der Waals surface ($Å^2$)	IP (eV)	r (μmol/min kg graphite)
C.I. Vat Blue 1	1.214	256.6	1.346	38.0
C.I. Vat Blue 14	3.329	416.2	1.572	30.8
C.I. Vat Blue 5	4.381	354.8	1.750	24.8
C.I. Vat Blue 6	4.365	414.2	1.595	28.0
C.I. Vat Green 1	6.603	463.6	2.013	22.8
C.I. Vat Orange 17	5.919	740.9	1.586	26.4
C.I. Vat Red 10	3.333	410.1	1.697	28.8
C.I. Vat Yellow 33	8.701	778.2	1.458	13.2

3.2. Electrochemical reduction of dyestuff mixtures

For the achievement of special requested color nuances, it is common to apply mixtures of several dyes in the vatting process [17,18]. Thus, we have investigated the possibility of the process for the reduction of dyestuff mixtures. In Table 1 also the results of reducing experiments performed with two different mixtures of vat dyes are shown. Both mixtures are based on the recommendation to mix only dyes of similar possible properties and nuances, which are close together [17,18]. However, Indanthren® Gray 5607 represents a commercially available mixture of unknown vat dyes, while the first experiment was performed with a 1:1 mixture of C.I. Vat Blue 14 and C.I. Vat Green 1. It is obvious from Fig. 4 that the reduction of both

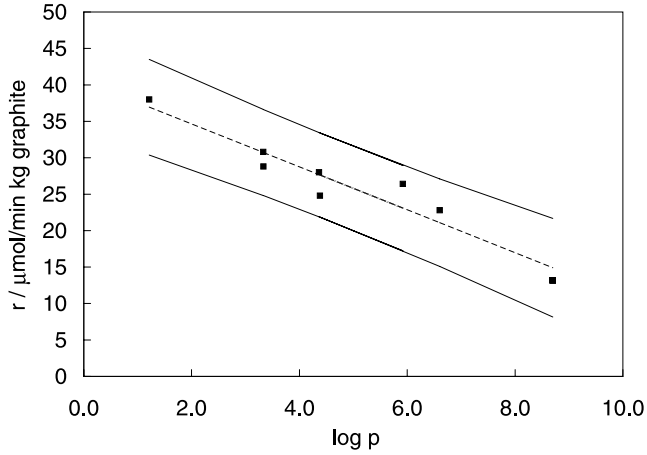


Fig. 3. Relationship between reduction rate r and calculated lipophilicity log p for several vat dye molecules.

dyes is taking place simultaneously and there is a lag of time between the starting of the reduction. Probably, the dye molecules compete in the adsorption on the graphite granules. This corresponds also with the slightly diminished reduction rates compared to the values obtained during single dye reduction.

4. Conclusions

Graphite granules have been used as electrode material in a fixed- and fluidized bed reactor to address the question of the industrial feasibility of this new direct electrochemical reduction method for vat dyes. Experiments yield information about the effect of different molecular structures on the kinetics and show the versatility of this process for production of water soluble leuco dyes, which offers environmental benefits. In addition to singular dyes even dyestuff mixtures were investigated.

The reduction rate correlates with the lipophilic properties (log p) with good results regarding the diversity of the dye molecules. The significant decrease in the reduction rate with rising lipophilicity could be based on the formation of larger pigment agglomerates, because the degree of aggregation increases with hydrophobicity. However, in addition, the solubility of the pigment could also be

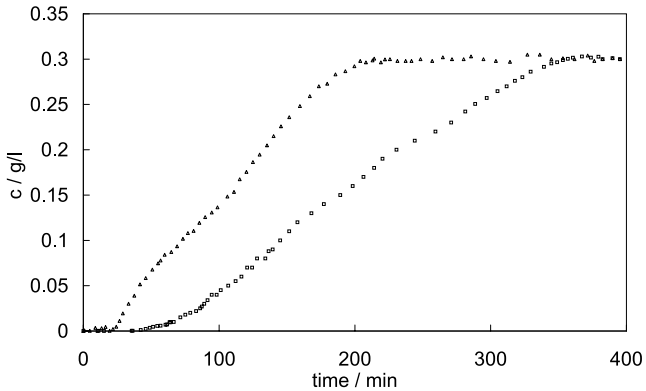


Fig. 4. Concentration vs. time profile for the reduction of the mixture C.I. Vat Blue 14, **6** (△) and C.I. Vat Green 1, **3** (□). System parameters: enViro cell graphite granules, 1 M NaOH, 300 mg/l vat dye mixture and 5 wt.% (related to the dye) Setamol WS, current density 51.6 mA/cm^2, 50 °C, fluid flow 1.4 l/min.

important. Still both, dissolution and transport to the electrode followed by electron transfer and electron hopping across the solid/solid boundary layer are plausible mechanisms at a microscopic scale. Increasing solubility could promote the more efficient route via the dissolved species. Thus, a certain reaction step cannot be finally determined as rate limiting, but the results indicate that adsorption and dispersion of the pigment are of paramount importance for the process.

The discovery seems to be of future interest both from an economical and an ecological point of view for the industrial application of an electrochemical vatting process. However, these results are a basis for the further development of a cheap, continuously and ecologically working cell for the direct electrochemical reduction of dispersed vat dyes.

Acknowledgements

The authors would like to acknowledge Prof. P. Rys, Prof. U. Meyer, O. Dossenbach, U. Meyer and P. Skrabal (ETH Zurich) for generous support and many inspiring and illuminating discussions. Many thanks especially to P. Skrabal for the MO calculations. The companies *Tex-A-Tec AG*, Wattwil, Switzerland (W. Marte), *ElectroCell AB*, Täby, Sweden (J. Bersier and P. Bersier, L. Carlsson), *enViro Cell*, Oberursel, Germany (W. Dietz), DyStar Textilfarben, Frankfurt, Germany (W. Schrott and H. Brunner), Bezema AG, Montlingen, Switzerland, NGS Naturgraphit GmbH, Leinburg, Germany (H. Meissner), MAST Carbon, Surrey, UK (S. Tennison) and *Asbury Carbons Inc./Cummings-Moore Graphite Co.*, Detroit, USA (L. Fish) are acknowledged for valuable support and discussion. We would like to thank Philippe Trüssel, LTC workshop, ETH Zurich for the excellent construction of the reactor and the flow circuit. ETH Zurich, Commission for Technology and Innovation (CTI) as well as the Hartmann-Müller-Fonds is acknowledged for financial support.

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