

Review of the process development aspects of electrochemical dyeing: its impact and commercial applications

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Society of Dyers and Colourists

This review discusses the recent progress made in both direct and indirect electrochemical dyeing processes and the parameters that control the dyeing process.

Introduction

A number of major dye classes can be used for the coloration of cotton/cellulosics including reactive, vat, sulphur, direct, azoic, solubilised vat dye, etc. The choice of dye depends on the required shade, its fastness and cost. The worldwide consumption of different dye classes is given in Table 1 [1,2]. From this table it can be seen that, although the consumption of reactive dyes is by far the greatest, vat and sulphur dyes also form important dye classes for the coloration of cotton and other cellulosic fibres. The growing consumption of reactive dyes is due to the fact they exhibit excellent levelling and fastness properties, high exhaustion, high fixation and exceptionally good results on various types of textile printing [3].

Vat and sulphur dyes are insoluble in water and, therefore before they can be used in any application, they need to be converted into a water-soluble form using suitable reducing agent and alkali. Different reducing agents used for vat and sulphur dyes are briefly reviewed in this paper, giving particular emphasis to the emerging technique of electrochemical reduction.

Table 1 Estimated annual worldwide consumption of cellulosic dyes

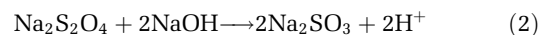
	Usage per annum (tonnes)		
	1988	1992	2004
Sulphur	90 000	70 000	70 000
Direct	74 000	60 000	68 000
Vat	36 000	21 000	22 000
Indigo	12 000	12 000	12 000
Azoic	28 000	18 000	13 000
Reactive	60 000	109 000	178 000
Total	300 000	290 000	354 000

Reducing agents for vat dyes

Conventional reducing agents

Sodium dithionite is the universally used reducing agent for vat dyes. Several other options were explored earlier such as fermentation methods, FeSO₄-lime method, zinc-lime method, bisulphite zinc-lime method, thiourea-dioxide, sodium borohydride, etc. However, owing to various problems, these reducing agents were not found to be commercially successful [4,5]. Therefore, at present, sodium dithionite is the only popular reducing agent used for the reduction of vat dyes and the dyes reoxidised to the original water-insoluble form in the fibre [6,7].

Interestingly, soon after the invention of synthesised vat dyes in 1901, sodium dithionate was identified as a reducing agent in 1904 [8,9]. It is also known as sodium hydrosulphite and has the chemical formula Na₂S₂O₄. It reduces all vat dyes at temperatures ranging from 30 to 60 °C and above. The reducing property of sodium dithionite is due to the evolution of hydrogen when dissolved in water or sodium hydroxide (NaOH) [10].



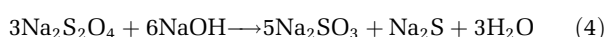
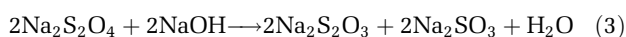
The amount of Na₂S₂O₄ and NaOH required for a specific vat dye to be reduced largely depends on the number of reducible C=O groups and how compact the dye structure is. Based on these criteria, all vat dyes have been classified into four classes, namely I_K, I_W, I_N and I_N special [7,10]. A specific class of vat dyes requires a specific amount of Na₂S₂O₄, NaOH, as well as a certain temperature range for vatting and dyeing. I_K dyes have relatively low substantivity for cellulose and so are dyed at room temperature. This group of dyes is not currently in use. I_W dyes have much higher substantivity and are dyed at 45–50 °C with little more NaOH than I_K dyes. I_N dyes require still little more NaOH and are dyed at 60 °C. Like I_N dyes, I_N special dyes are dyed at 60 °C only; however, they need the highest amount of NaOH and have a very high substantivity.

Optimal concentrations and reaction conditions in the vatting reactor can be achieved by controlling the concentration of dye, reducing agents and NaOH [11].

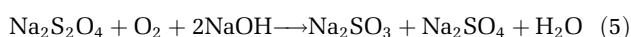
Sodium dithionite is very unstable, decomposing oxidatively and thermally into several byproducts. Some byproducts of $\text{Na}_2\text{S}_2\text{O}_4$ are acidic in nature and hence require higher quantities of NaOH than the stoichiometric requirement [12–14]. The stability of the alkaline solutions of $\text{Na}_2\text{S}_2\text{O}_4$ decreases with an increase in temperature, an increase in the surface area exposed to the air and a decrease in agitation of the bath. The ultimate result is that nearly three times the amounts of NaOH and $\text{Na}_2\text{S}_2\text{O}_4$ over the stoichiometric requirement are required for efficient dyeing. There are various routes through which decomposition of sodium dithionite and consumption of NaOH take place [15].

Decomposition of sodium dithionite in vat dye bath

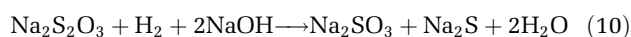
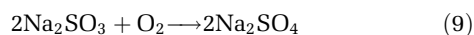
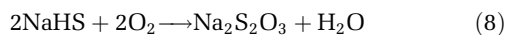
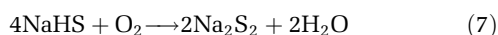
Thermal decomposition:



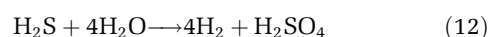
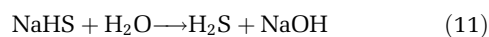
Oxidative decomposition:



Other possible reactions:



Some of the byproducts formed are sulphur compounds (Na_2S , NaHS, etc.) which pollute the air through the formation of H_2S . At the same time, salts of sulphur in the form of sulphates and sulphites (Na_2SO_3 , NaHSO_4 , Na_2SO_4 , $\text{Na}_2\text{S}_2\text{O}_3$) contaminate sewage, lower its pH and show corrosive action where sewage comes into contact with i.e. concrete works, iron structures, etc.



Because of the environmental problems associated with sodium dithionite, the use of alternative ecofriendly reducing agents has been explored.

Ecofriendly reducing agents

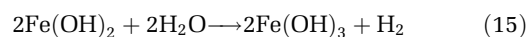
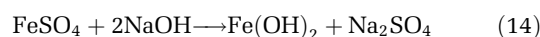
To overcome the effluent and ecology-related problems associated with sodium dithionite, attempts were made by several researchers to develop alternative reducing systems which were ecofriendly in nature. These new reducing systems include hydroxyacetone, Iron(II) salts along with a suitable ligand, etc.

Hydroxyacetone

A refined dyeing process has been developed in which hydroxyacetone is used as the reducing agent [9]. Hydroxyacetone provides a reduction potential of -810 mV vs Ag/AgCl/3 M KCl. The major advantage of this reducing agent is that the chemical oxygen demand (COD) of dyeing effluent can be reduced by biological degradation of pollutants, and the wastewater obtained is free of sulphides, sulphites and sulphate. In spite of its ecofriendliness, this reducing agent has not yet become commercially possible because of its high cost.

Iron(II) complexes

Iron(II) salts have been widely used since ancient times to reduce vat dyes through a technique known as the 'Copperas method', in which FeSO_4 and Ca(OH)_2 are used. But the dye bath produced by this method results in bulky sediments due to poor solubility of Fe(OH)_2 and precipitated CaSO_4 . It has been found that Fe(OH)_2 , produced via reaction of iron(II) salts with NaOH, can be complexed and brought into solution to get the desired reduction potential.



It is well known that Fe(OH)_2 is a strong reducing agent in alkaline medium. The reducing effect increases with an increase in pH. However, Fe(OH)_2 is poorly soluble in alkaline solution and gets precipitated out. Therefore, it shows low reduction potential, which is not adequate for the reduction of even indigo at 60°C . The true reduction potential of Fe(OH)_2 is stable when it is not allowed to precipitate. This is possible through coordinate complex formation between Fe(OH)_2 and a suitable ligand [16]. According to Werner's coordination theory, a complex could be formed between Fe(OH)_2 and weaker ligands. The weaker ligands could be compounds having groups with unshared electrons (i.e. COOH, OH, etc.) such as gluconic acid, triethanolamine, tartaric acid and citric acid. This complex formation improves the water solubility of Fe(OH)_2 , enabling it to act as a reducing agent. Based on this principle, Semet *et al.* [16] suggested the use of gluconic acid along with Fe^{II} salt (1:1 molar ratio) for the dyeing of cotton with vat dyes at 60°C . This reducing system is considered to be ecofriendly as the gluconic acid is neutralised during the balancing operation of the effluent treatment. Fe(OH)_2 formed in the presence of alkali during the dyeing operation gets converted into insoluble Fe(OH)_3 , which acts as a flocculent and settles down.

Studies with different ligands to keep Fe(OH)_2 in solution have been carried out by Chavan and Chakraborty [15,17]. They have established that a successful dyeing of cotton with indigo can be carried out using Fe^{II} salt complexed with suitable molar ratios of tartaric acid, citric acid or triethanolamine along with NaOH. Such a system is termed as a single ligand system. Although the single ligand system is suitable for dyeing cotton with indigo, it is not suitable for dyeing cotton with vat dyes other than indigo. For this reason, a two-ligand system consisting of Fe^{II} salt complexed with citric

acid and triethanolamine or Fe^{II} salt complexed with tartaric acid and triethanolamine has been suggested. Chavan and Chakraborty [17] established the suitability of two-ligand systems for the successful dyeing with a large number of vat dyes on the basis of an increase in $\text{Fe}(\text{OH})_2$ solubility compared with the single-ligand system.

Reducing agents for sulphur dyes

Conventional reducing agents (sulphide based)

An estimated 90% of sulphur dyes used worldwide are still reduced by means of sulphide compounds [18], such as sodium sulphide (Na_2S), sodium hydrosulphide (NaHS) and sodium polysulphide (Na_2S_x , where x can be from 1 to 6). The polysulphide variety is available as aqueous solution, while sulphide and hydrosulphide are available in both solid and liquid forms [19].

Some of the environmental problems associated with sulphide-based reducing agents are the contamination of effluent with sulphur, the liberation of H_2S gas and its toxicity. Unfortunately, the threshold limit of H_2S is very low (10 ppm). Attempts have been made to replace sulphide-based reducing agents for the dyeing of sulphur dyes [20].

Ecofriendly reducing agents

Glucose

Glucose has long been known as a reducing agent for sulphur dyes [21]. Sulphur black and indocarbon dyes are almost always reduced with glucose during the one-stage printing process. In exhaust dyeing, especially in open dyeing machines like jiggers and winches, glucose does not give satisfactory results, as the dye yield is highly dependent on temperature. Only at temperatures above 90 °C are reasonable results obtained. A considerable improvement is achieved when the dyeing is carried out under strongly alkaline conditions with the addition of stabilisol S liquid (stabilising agent from DyStar, Germany). Glucose, in combination with NaOH, provides a reduction potential in the range -550 to -600 mV vs $\text{Ag}/\text{AgCl}/3\text{ M KCl}$, which is normally sufficient for the reduction of sulphur dyes. Glucose and NaOH together with stabilisol S liquid have also proved successful in continuous dyeing. Good results are obtained with all solubilised sulphur dyes. In principle, water-insoluble sulphur dyes can also be applied using glucose, NaOH and stabilisol S liquid. This system can also be applied at the boil but the padded textile needs more time for oxidation requiring longer times in between two successive dips.

Laga *et al.* attempted to replace sodium sulphide with liquid jaggery during the dyeing of jute fabric with sulphur dyes [22]. It was found that for liquid jaggery, 2.5 times of the weight of the dyestuff was sufficient to reduce the dye completely. Also, it was found that the strength of the colour (K/S values) developed on fabric dyed with different sulphur dyes and liquid jaggery was comparable with that of sodium sulphide. Liquid jaggery (highly concentrated) was prepared by treating commercial jaggery with 0.04% citric acid for 24 h at room temperature.

One Study also proved that, on a commercial scale, sodium sulphide can be totally replaced with glucose obtained from the hydrolysis of starch. This option is found to provide a cost-effective substitution of sodium sulphide. Furthermore, no capital expenditure is required in this substitution [23].

Vhanbatte [20] used molasses, a byproduct of the sugar industry, as a source of reducing sugar. Molasses contains ca. 60% total sugar including glucose, fructose and sucrose.

Mercaptoethanol

Molleskal SF, marketed by BASF based on β -mercaptoethanol, can be used as a substitute for sodium sulphide [20]. Soluble sulphur dyes can be applied using mercaptoethanol and NaOH, both by exhaust method and by the one-bath pad-steam process. Yields are in some cases slightly poorer than the sulphide system, but are generally acceptable. The advantage of mercaptoethanol is the absence of sulphide in the effluent and obnoxious smell emission. Disadvantages include its restricted use excluding the ready-to-use liquid sulphur dyes and high expenses in overall dyeing. Moreover, many of the water-insoluble sulphur dyes do not dissolve completely, leaving behind a residue.

Electrochemical dyeing

As seen earlier, conventional reducing agents used for the reduction of dyestuffs result in non-regenerable oxidised byproducts that remain in the dyebath. Used dyebaths cannot be recycled because the reducing power of these chemicals cannot be regained. Disposal of the dyebaths and the wastewater causes a variety of problems due to the non-ecofriendly nature of the decomposition products (e.g. sulphite and sulphate from the use of dithionite, sulphides from sulphur dyes and a high COD from the use of organic reducing agents). Maximum attention from an ecological standpoint therefore has to be paid to the reducing agents generally used for these dyes. To a large extent, it is better to dispense with the reducing agents. This is the aim of the most recent development, i.e. electrochemical dyeing, which is still in the laboratory stage, but could become the dyeing process of the future for vat, indigo and sulphur dyes [24]. In the present review, the origin and development of electrochemical dyeing is discussed, in which chemical reducing agents are replaced by electrons from the electric current and effluent-contaminating substances are dispensed with altogether [8,24].

The first attempt in this direction, although not directly involving electrochemical dyeing, was made by Daruwalla over thirty years ago [25]. He attempted to reduce sodium dithionite in quantities needed for the reduction of vat dyes by the application of a direct voltage. This reduction can be attributed to the fact that sodium dithionite at the cathode is converted into a form that exhibits increased reducing power. By appropriate cathodic reduction under suitable conditions (cathode potential, sodium dithionite concentration, pH and temperature), it is possible to generate a powerful reducing species from sodium dithionite with redox potential higher than sodium

dithionite itself. This behaviour of sodium dithionite has been explained by Cermak [26] to be due to the decomposition of hydrosulphite according to Eqn 16 to produce a free radical ion SO_2^- .



However, these products after dyeing cannot be regenerated at an applied voltage at the cathode, making recycling of the bath liquor impossible. In the electrochemical dyeing technique, the same concept is adopted one step ahead making the liquor recycling possible. Electrochemical dyeing can be carried out by two methods such as direct and indirect electrochemical dyeing.

Direct electrochemical dyeing

In the case of direct electrochemical dyeing (Figure 1), organic dyestuffs are directly reduced by contact between the dye and the electrode surface [27]. However, in practice, the dyestuff is partially reduced by using a conventional reducing agent and then a complete dye reduction is achieved by the electrochemical process. This facilitates the improved stability to the reduced dye [28–30].

To start the process, an initial amount of the leuco dye has to be generated by a conventional reaction, i.e. by adding a small amount of a soluble reducing agent. Once the reaction has begun, the further process is self-sustaining. This system is found to be successful in case of sulphur dyes. However, concentration of the dye required to get a specific shade is higher than that for a conventional reduction process due to the limited cathode–dye particle interface.

In such a system, a dyestuff particle has to come into contact with the electrode surface to get reduced as the dyebath has to productive capacity, the atmospheric oxygen present in the dye solution reoxidises the dyestuff molecule reduced in this way. Also, as the dye itself has to be reduced on the surface of the cathode, the area of the cathode must be large, which itself is a constraint.

Rosler *et al.* have used graphite granules as an electrode material to increase the surface area in a fixed and fluidised bed reactor to address the question of industrial feasibility of a direct electrochemical reduction method for vat dyes [1,31,32]. They have optimised the conditions for the system using an indigo concentration of 10 g/l, and to achieve higher concentrations of vat and

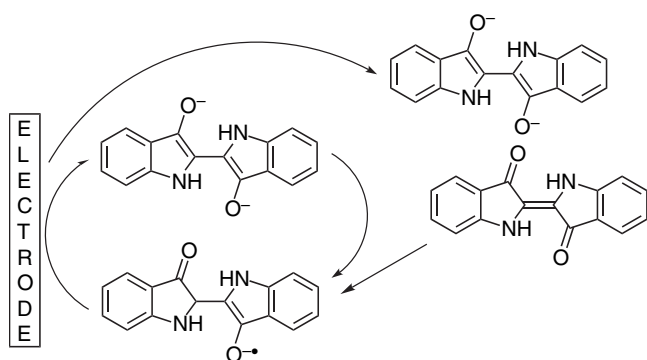


Figure 1 Direct electrochemical indigo reduction

other types of dyes, a special treatment is suggested by introducing quinine-like functional groups on the graphite surface.

Indirect electrochemical dyeing

Bechtold [33,34] patented the indirect electrochemical dye reduction method in 1993 and has published a number of other related patents since then [35–37]. In this method, the dye is not directly reduced at the electrode surface (Figure 2). Rather, a reducing agent that reduces the dye in the conventional manner is added, which in turn gets oxidised after dye reduction. The oxidised reducing agent is subsequently reduced at the cathode surface, which is then further available for dye reduction. This cycle is continuously repeated during the dyeing operation. In electrochemistry, the agent that undergoes both reduction and oxidation cycles is known as reversible redox system and is called a mediator [38–42].

Thus, in this system, the dye reduction does not take place due to direct contact of dyestuff with the cathode, as in direct electrochemical reduction, but it takes place through the mediator that gets reduced by contact with the cathode. Therefore, this system is known as indirect electrochemical dyeing.

The object of the reversible redox system primarily is to generate a constant reduction potential in the dye liquor. Therefore, the addition of conventional reducing agent is not essential and no accumulation of decomposition products of the reducing agents takes place. This electrochemical dyeing process appears to be simple because, after the dyeing cycle, the unexhausted dye gets precipitated by air oxidation and can be removed by filtration. After the dye removal, the liquor containing mediator, ligand and alkali can be recycled for subsequent dyeing operations. This appears to be the most important feature in terms of cost and the environmental friendliness of the process.

Therefore, the use of indirect electrochemical reduction not only lowers the cost of reduction chemicals but it also enables, for the first time, the closed cycling of the dye liquor following the removal of the residual dye. Therefore, disposal of the dyebath with the exception of the rinse water is thus possible.

Mediator systems

In theory as per the Nernst equation, any desired reduction/oxidation potential (up to the liberation of hydrogen gas) can be achieved in solution by combining

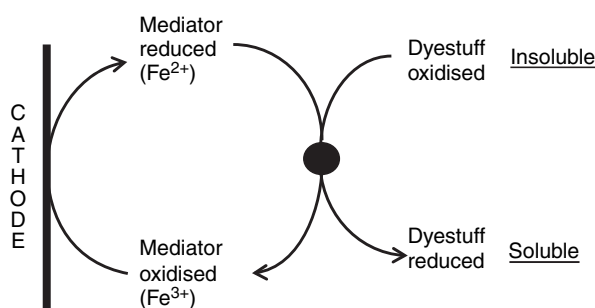


Figure 2 Indirect electrochemical dye reduction

an appropriate proportion of reduced and oxidised species [41]. At any given time in an electrochemical system, both oxidised and reduced forms of the redox pair are available in the solution. By varying the voltage provided, the concentration of these oxidised or reduced species can be adjusted, as well as the potential prevailing in the solution.

However, for mediator systems to be used in industry, there must be sufficient 'capacity' of the mediator system (stability of the potential achieved in solution). The reduction potential, which can be realised industrially in solution, is therefore always close to the normal potential of the redox pair used at normal rates of conversion at the electrode and the mediator capacity is expressed in terms of maximum cathodic potential achieved.

Some of the mediator systems, which can be used as reversible redox systems for the indirect electrochemical dyeing, are discussed in the following sections.

Organic redox system

As organic compounds with an anthraquinonoid basic structure were investigated by Bechtold *et al.* [41,43] for their suitability as a mediator in indirect electrochemical dyeing, experiments with anthraquinone monosulphonic acid, anthraquinone disulphonic acid, hydroxyl-anthraquinones and various substituted products enabled the reduction of sulphur and vat dyes with soluble 'leuco form' formation potential below the cathodic potential of the mediator system.

Anthraquinoid systems investigated by Bechtold *et al.*, have cathodic peak potentials up to -850 mV vs Ag/AgCl/3 M KCl. The alkali content of 4 g/l NaOH and a concentration of 1 g/l of anthraquinone derivative are found to be sufficient to achieve dye reduction. The cathode peak potential with this system, using different anthraquinones, is given in Table 2.

In evaluating the mandatory quantity of mediator, the introduction of oxygen from the air must also be taken into consideration. The required quantity of catalyst can be reduced using a closed apparatus. However, with these organic redox systems, the relatively low rate of conversion at the electrodes is a disadvantage.

Inorganic redox system

Inorganic compounds, which can be used as mediators, are primarily based on metal complex salts. The reducing action of metal salts of low valency levels, such as the one used in the Copperas method and the zinc dust method, was used during the earlier stages of application of vat dyes on cotton. However, these reducing agents have several drawbacks such as precipitation in the dye bath and heavy metal content of the effluent due to large quantities employed. The use of heavy metal complexes (Ni and Co complexes), to accelerate reduction operations using conventional reducing agents, has also been tried [39], but other problems have been faced in practice with these systems.

A wide variety of complex salts were investigated by Bechtold *et al.* with the aim of discovering redox systems with a high negative reduction potential under homogeneous conditions, i.e. without precipitation.

Table 2 Cathode peak potential of different anthraquinone systems with 4 g/l NaOH [41]

Compounds	Cathode peak potential (mV vs Ag/AgCl/3 M KCl)
1,2-Dihydroxyanthraquinone	-880
1,4-Dihydroxyanthraquinone	-760
1,8-Dihydroxyanthraquinone	-770
Anthraquinone-2-sulphonic acid	-640
Anthraquinone-1,5-sulphonic acid	-750
Anthraquinone-2,6-sulphonic acid	-560
1,2-Dihydroxyanthraquinone-3-sulphonic acid	-870
1,2,5,8-Tetrahydroxyanthraquinone	-885
1-Amino-2-carboxyanthraquinone	-750
1-Aminoanthraquinone-2-sulphonic acid	-720

Various experimental aspects need to be taken into consideration when choosing a complex salt as a mediator [39]:

- Normal reduction potential of the mediator system has to be slightly higher than the reduction potential of the dye. For the widest possible applicability, the normal potential should therefore be at least -950 mV vs Ag/AgCl/3 M KCl.
- The operating potential of the electrode has to be considerably greater than the reduction potential in solution. Therefore, the conversion from oxidised form to reduced form of the mediator should take place at the electrode without a marked over-voltage (i.e. without the hydrogen gas evolution) with respect to the mediator, as hydrogen gas evolution will then be the easiest possible reaction and all supplied energy will be utilised for it.
- The operating electrode should have the maximum possible over-voltage towards hydrogen evolution. Thus, maximum possible cathodic peak potential can be achieved.

Currently, the most suitable iron complex system [iron(II) salt/triethanolamine (TEA)] allows potentials up to -1050 mV vs Ag/AgCl/3 M KCl to be achieved under dyeing conditions in a homogeneous solution. This iron complex can be prepared either from Fe^{II} salts or from Fe^{III} salts. The potential which can be attained allows a reduction of all the usual vat dyestuffs without the additional use of reducing agents.

Suitable ligands for iron(II) complexes

In another study, Bechtold *et al.* [41] carried out experiments on an Fe^{II} complex system using various other ligands. General requirements for a ligand to form coordination iron compound that is suitable as a mediator are:

- it should form a stable coordination compounds with Fe^{II} and Fe^{III} in an alkaline medium;
- reversible charge transfer from Fe^{III} to Fe^{II}, whereby minimum dissociation of the complex should take place;
- maximum current density or maximum cathode potential in alkaline solution should be provided; at least -600 mV for indigo, or better -1000 mV vs Ag/AgCl/3 M KCl, to reduce all vat dyestuffs;

- a high rate of electron transfer from the cathode to the oxidised Fe^{III} complex should take place;
- multiple reuse of dyeing liquor should be possible; and
- rapid electron transfer from the reduced form of the mediator to the oxidised dyestuff should take place.

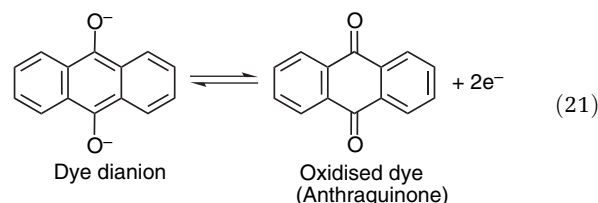
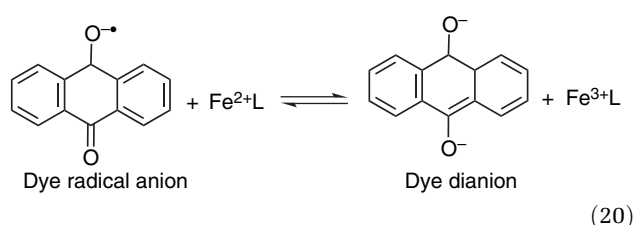
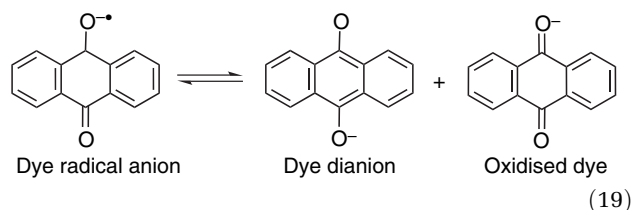
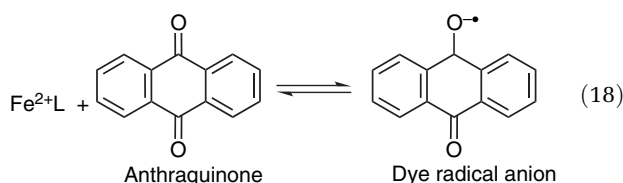
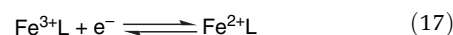
The main criteria to find suitable ligands for Fe^{II} complexes are the stability of the coordination compound in alkaline medium and the maximum attainable redox potential. Values obtained for different ligands are shown in Table 3. Cathodic peak potential values are mentioned for suitable ligands only (which will not precipitate) [44].

However, Triplex VII (HEDTA), bicine, diethanolamine and TEA have only shown good stability of Fe^{II} complex in alkaline solution. The reduced form of these complexes, especially the more stable complex with TEA as ligand, is well suited to reduce vat dyestuffs. The potentials of Fe^{II} complexes up to –1050 mV vs Ag/AgCl/3 M KCl with TEA as a ligand in an alkaline solution enable the reduction of all current vat dyes, indigoid dyes, sulphur dyes and azo dyes without the addition of other reducing substances.

Recently, Bechtold *et al.* have demonstrated that mediator systems prepared by mixing one or more salts of a metal capable of forming a plurality of valence states with at least one amino-containing complexing agent and at least one hydroxyl-containing but amino-devoid complexing agent in an alkaline medium has an improved capacity to reduce the vat dyes [45–50]. Galvanostatic batch reduction experiments with use of a laboratory multicathode cell confirmed the favourable properties of the Fe^{III}-D-gluconate complex in comparison with the binuclear Ca^{II}-Fe^{III}-D-gluconate complex towards dyestuff reduction [45–47]. Bechtold *et al.* have also proved that in an alkaline aqueous solution cellulose fibres, e.g. cotton, viscose, model and lyocell fibres, showed a distinct tendency to complex Fe^{III}-ions by ligand-exchange reactions with Fe^{III}-D-gluconate and Fe^{III}-hepta-D-gluconate complexes. They have also proved that these complexes with Fe-triethanolamine complex make ligand-exchange reactions and give good efficiency for the vat dye reduction [49,50].

Indirect electrochemical reduction mechanism

A general reaction for the indirect electrochemical dyeing process using Fe^{II}-TEA complex is established [2,40,44] as follows:



In the first reduction step, the iron complex is cathodically reduced (Eqn 17) in a reversible electrochemical process. The reduced complexes diffuse from the electrode towards the dyestuff particles. At the surface of the dispersed particle, charge transfer involving one electron occurs (Eqn 18) and a dye radical anion gets formed, which is an intermediate step to form a

Table 3 Suitability of different ligands to form stable Fe^{II} complex [44]

Ligand ^a	Cathodic peak potential (mV vs Ag/AgCl/3 M KCl)	Iron-binding capacity (stability) of Fe ^{II} -ligand complex in alkaline solution
NTA	Precipitated	No binding capacity
EDTA	Precipitated	No binding capacity
DTPA (Triplex V)	Precipitated	No binding capacity
EGTA (Triplex VI)	Precipitated	No binding capacity
HEDTA (Triplex VII)	–650	High
Bicine	–850	High
Glycine	Precipitated	No binding capacity
Triethanolamine	–1050	High
Diethanolamine	–1000	Low
Triethylenetetramine	Precipitated	No binding capacity

^a EDTA, ethylenediaminetetraacetic acid; DTPA, diethylenetriamine pentaacetate; EGTA, ethylene glycol-bis-(b-aminoethylethertetraacetic acid; HEDTA, hydroxyethylethylenediaminetriacetic acids; NTA, nitrilotriacetate

completely reduced dye dianion. Here, the anthraquinone dye and the oxidised dye are the same.

A completely reduced dye dianion can be formed by two routes. As most of the dyes require two electrons for the reduction of each molecule, two dye radical anions are assumed to give one fully reduced dye dianion molecule and to regenerate one dye molecule in its oxidised form (Eqn 19). Another possible reaction mechanism for the formation of a reduced dye molecule is such that, a one-electron transfer may take place to form a reduced mediator to a dye radical anion and form a fully reduced dye dianion molecule as a reaction product (Eqn 20). In an additional reaction, equilibrium between the fully reduced dye dianion molecule and the insoluble oxidised form of the dye is built up (Eqn 21).

Difficulties to establish indirect electrochemical dyeing process

Several problems [40] must be considered in the scale-up of this indirect electrochemical reduction process. They are given below.

- The actual reduction of the dye should be carried out separately in an electrochemical cell and the reduced dye is then circulated separately into a conventional dyeing unit, e.g. jigger.
- To keep the dye in the reduced form, it is necessary to reduce the oxidised mediator at the cathode. This is possible only when there is a continuous circulation of the dye liquor from the dyeing equipment to the electrochemical cell.
- The design of the cell should be such that the cathode should have the maximum surface area available for the reduction of the mediator.
- Three-dimensional electrodes with large surface area occupying small space in the electrochemical cell should be designed. This kind of cell will have the advantage of carrying out dye reduction with minimum volume of mediator.
- A cell with minimum area of separator (semipermeable membrane, separating anolyte from catholyte) is necessary. It will ensure the minimum cost of the separator and will not allow the reoxidation processes to take place due to bleeding of the separator, diffusion of oxygen. The reoxidation at separator may cause a chemical short circuit, thus requiring further enlargement of the cathode area.

Electrochemical cell system for dye reduction

In electrochemical dyeing, the chemical reducing agent is replaced by electrons from the electric current introduced into the dyebath via special cathodes [51,52]. One of the reduction electrochemical systems [33,34] used by Bechtold comprised a vessel containing the reduction system made up of triethanolamine, ferric sulphate and alkali in a fixed proportion. This was subjected to stirring with the help of a magnetic stirrer. This facilitated a uniform distribution of the ferric sulphate in the system. At the bottom of the vessel, there was a working cathode made of copper. This cathode provided the electrons as the power supply unit was operated. The extent of electron generation liberated at the cathode (known as cathode potential) was measured with reference to a

reference electrode (Ag/AgCl/3 M KCl) with the help of the voltmeter. The actual reduction potential of the dyeing system was measured between the copper cathode and the reference electrode. It is important that the working cathode is shielded by a diaphragm in order to avoid a reoxidation at the anode.

At the beginning of the process, the dye is not added into the reduction system. Before dye addition, it is necessary to convert ferric ion into ferrous ion and also expel the dissolved oxygen from the system. This is achieved by providing voltage to the cathode for the first 15–20 min. By this time, the stabilisation of the reduction potential in the system also takes place. After this, the dye is added to the system and the application of the voltage to the cathode is continued for the liberation of electrons. It is envisaged that the electrons liberated at the cathode will convert the ferric ion to ferrous ion. The ferrous ions, in turn, interact with the sodium hydroxide to form ferrous hydroxide, which is a potential reducing agent. However, in order to exploit the reducing property of ferrous hydroxide, it is necessary to keep it in solution with the help of a suitable ligand. This role is played by TEA present in the system. Once the liberation of ferrous ions from the ferric salt is initiated, the dye is then added to the system. As the reduction potential is already developed in an aqueous solution consisting of TEA, ferric sulphate and NaOH, the reduction of dye takes place immediately [53].

The actual dyeing is carried out in a dyeing compartment where the fabric sample is placed. The compartment is provided with a perforated bottom and the reduced dye solution is circulated through this compartment with the help of circulation pump. The oxidation and after treatment of the dyed fabric are carried out separately. The dyeing cycle is illustrated in Figure 3.

When using cathode material having a higher hydrogen overvoltage, a working potential of up to -1200 mV vs Ag/AgCl/3 M KCl can be realised at the cathode with a power supply unit, depending on the liquor content, without generating hydrogen.

Figure 4 shows a potential–time diagram for typical dyeing experiments, including a curve with sodium dithionite as reducing agent [53]. In electrochemical dyeing, in the beginning, a build up of the reducing species in the dyebath takes place, and hence a build up of the potential can be observed. After the desired potential in the dyebath is reached, the dye can be added. Only a small change in the dyebath at the point of dye

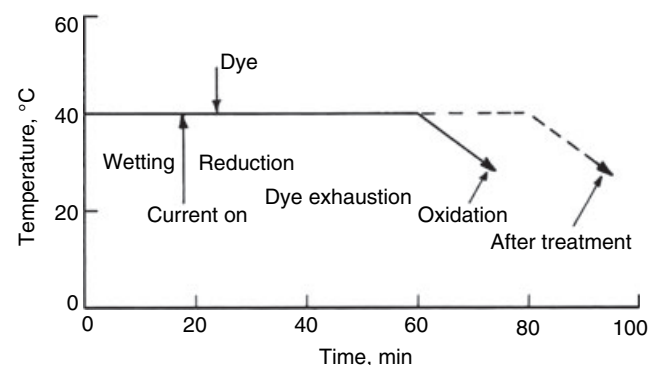


Figure 3 Electrochemical dyeing cycle

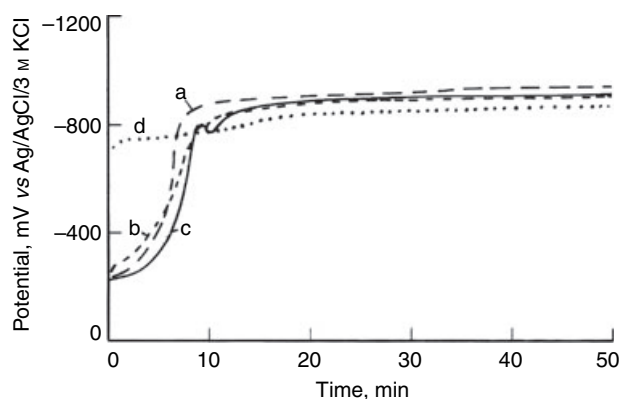


Figure 4 Potential–time curves: (a) Indanthrene Blue GC (55 °C), (b) Indanthrene Brilliant Green FFB (40–47 °C), (c) Indanthrene Blue BC (20 °C), (d) Indanthrene Brilliant Green FFB with sodium dithionite (55–60 °C)

addition is noticeable. Afterwards, the potential in the dyebath remains stable mostly.

But in the case of sodium dithionite as a reducing agent, it shows a slow build up of the reduction potential and is maintained throughout the dye reduction process [53]. This behaviour is due to a significantly lower reactivity of sodium dithionite at temperatures below 60 °C. It is a fact that with the conventional reducing agents the dyebath potential depends on the type and concentration of the reducing agent used, and the dyebath temperature. The indirect electrochemical reduction technique using mediators permits direct control of the dyebath potential without the undesirable connection between temperature and reduction potential.

Liquor recycling in electrochemical dyeing

The possibility of restoring the reducing power of a used dyebath is an attractive process in these days of concern over dyehouse effluent [2]. Naturally, if reuse of the mediator system with different dyes is intended, the residual dye has to be removed from the dye liquor. This is more a straightforward proposition with vat dyes, because of the insolubility of their oxidised form in aqueous solutions, and their ability to form suspensions, which can be removed by a filtration process from the oxidised dye liquor.

After completing the dyeing procedure, the remaining dye and the reduced mediator can be oxidised by bubbling air through the solution to form the insoluble form of the dye. Recycling the dyeing liquor is then achieved by pressure filtration through a polytetrafluoroethylene (PTFE) membrane with a pore size of 0.45 or 1.2 μm at a pressure of 1–2 MPa (10–20 bar). However, the dyebath has to be circulated through the electrochemical cell at a rate that must follow the threshold conversion rate in the cell. A complete filtration should be ensured to avoid contamination of the cell by impurities released from the goods.

In an electrochemical dyeing experiment carried out by Bechtold, the liquor recycling loop was repeated nine times. Dyeing experiments showed good reproducibility in the colour of the dyed goods, confirming that electrochemical regeneration of the reducing agent can be

achieved for many cycles without a measurable loss in the electrochemical activity.

Two process engineering concepts for continuous electrochemical dyeing, namely the closed circuit and the mediator concentrate technique, have made liquor recycling viable.

Closed circuit technique

Mass balance for the electrochemical dyeing of 15 000 kg goods with a closed circuit technique is so-called because the contents of the dyebath are circulated through the electrochemical cell in this technique. With this method, the mediator and vat dyes like indigo can be recovered from the wastewater. This is passed through the ultrafiltration unit to remove the insoluble dye. The filtrate of the ultrafiltration is then subjected to nanofiltration where the concentration of the mediator is increased to a final value of 0.6 M of Fe^{III} complex. The Fe^{III} salt concentrate is also metered into the electrochemical cell so that the $\text{Fe}^{\text{II}}/\text{Fe}^{\text{III}}$ ratio in the dyebath is maintained and the prevailing solution potential is maintained. The advantage of this system is that it allows almost any desired amount of reduction equivalents to be admitted into the dyebath at constant concentration ratios [54].

Conclusions

Iron–amine complexes, e.g. $\text{Fe}^{\text{III}}\text{-TEA}$ complexes, show a sufficiently high negative redox potential in alkaline solutions and therefore these are considered suitable agents for the indirect electrochemical reduction.

Electrochemical dyeing experiments have established good reproducibility and results almost similar to that of conventional vat dyeing with sodium dithionite.

Indirect electrochemical reduction technique using mediators permits direct control of the dyebath potential without the undesirable connection between temperature and reduction potential.

Iron–amine system allows the dyebath to be recycled after the removal of the oxidised dyes by filtration. Closed circuit technique of dyebath recycling allows process control activities to adopt and also avoids tailing effect in dyeing.

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