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Review

Ecological alternatives to the reduction and oxidation processes in dyeing with vat and sulphur dyes

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Abstract

This article gives a summary of the most commonly used ecologically unfriendly processes for the reduction and oxidation of vat and sulphur dyes. It also describes the new alternatives that are in the development stage and could be important in the near future. Sodium dithionite as the dominant reducing agent produces large amounts of sodium sulphate, and also toxic sulphite and thiosulphate as by-products. Consequently, high amounts of hydrogen peroxide and alkali are required for the treatment of effluents, which add to the cost of the process. Attempts have been made to use organic biodegradable reducing agents, enzymes, catalytic hydrogenation, and also indirect or direct, electrochemical reductive methods that employ a redox mediator (electron-carrier). The reduction has also been carried out via the dye radical molecule or, in the case of indigo, by direct electrochemical reduction using graphite as the electrode material. Physical techniques, for example using ultrasound, magnetic fields or UV have been shown to be effective only when used to accelerate methods using classical reduction and oxidation processes. However, although these methods offer some environmental benefits, there is still no satisfactory alternative reducing and/or oxidising agent available today.

Keywords: Vat and sulphur dyes; Dyeing; Reduction; Oxidation; Ecology; Catalysis; Organic agents; Electrochemistry; Ultrasound; Magnetic field; UV application; Biotechnology

1. Introduction

According to data from 2005 [1], cotton and other cellulose fibres are still very important textile fibres. They are used worldwide (Table 1) and their consumption is increasing.

In the colouration of cellulose fibres, vat (including indigo) and sulphur dyes still represent a relatively large part of the dyestuff market (about 31%, Fig. 1); among them about 120 000 tons of vat dyes are being used annually [2]. It seems that the situation will remain constant also in the near future mainly because vat dyes yield coloured fibres of excellent all-round fastness, particularly to light, washing and chlorine bleaching.

However, vat and sulphur dyes require a complicated application procedure (reduction and oxidation mechanisms) because they are practically insoluble in water and have no affinity for cellulose fibres in such a state. Thus, these dyes have to be reduced (vatted) before dyeing to be converted into the water-soluble form (*leuco* enolate dye form) (Scheme 1) which have substantivity towards fibres and which, after absorption into the fibres to be dyed, should be re-oxidised to the original water-insoluble dye pigment form in situ in the fibres [4,5]. The leuco-vat anion may be compared with water-soluble direct dye anions, for it is the anion which is responsible for vat dyeing. Incidentally, the word *leuco* comes from the Greek word *leucos*, meaning white, which is the colour of the vat-acid of indigo. In conventional vat-dyeing processes, the dye is reduced in a high alkaline medium (pH 11−14) using powerful reducing agents among which sodium dithionite ($Na_2S_2O_4$) is of major importance. Because of the individual molecular structures of different dyes, concentrations of reducing agents and alkali, temperature and timing, each dye requires an individual procedure. The reducing agent either

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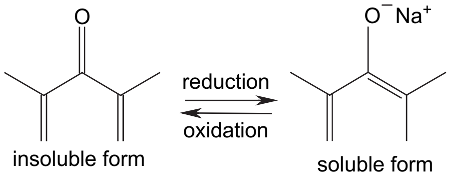
Table 1
Cotton consumption [1]

Cotton consumption (million 480-pound bales)								
	World total	United States	Other Americas	China	India	Pakistan	Turkey	Others
1985	76.3	6.4	6.1	18.8	7.1	2.4	2.1	33.4
1990	85.4	8.7	6.6	19.4	9.0	6.2	2.6	32.9
1995	85.5	10.6	7.0	19.8	11.4	7.2	4.1	25.4
2000	90.5	8.9	8.5	24.7	13.3	7.9	5.1	22.1
2004	100.6	6.2	8.0	34.9	13.7	10.0	6.1	21.7

Source: Fibre Economics Bureau and authors' estimates.



Scheme 1.

donates hydrogen to subtract oxygen from or add electrons to other chemicals; the affected chemicals/dyes are said to be reduced. During the reduction process, the reducing agent itself is oxidised, often irreversibly. To be practically useful, solutions of a vat dye reducing agent must have a level of reducing power (reduction potential) sufficient to reduce all commercial vat dyes to their water-soluble forms, economically and quickly [6]. The quantity of reducing agent is determined by the chemical structure and nature of the particular dye (number of reducible groups, relative molecular mass, content of the pure dye), the specific surface area of the dye liquor, the temperature of the dye liquor, the agitation of the liquor, and the amount of air present in the dyeing process. The conversion of the vat dye into the leuco form is a heterogeneous reaction that comprises the following stages: diffusion of molecules of the reducing agent to the surface of dye particles, sorption of the reducing agent, chemical reaction between the dye and reducing agent on the surface with the formation of a leuco compound [7]. The aqueous alkaline solutions in which the dyeings are carried out are generally set by sodium hydroxide, aqueous alkali metal salt, or potassium hydroxide solutions. Depending on dyebath pH, the reduced form of the dye molecule exists in unionized, mono-/di-ionized, multi-ionized form, or as mixtures of the forms. High dyebath pH values (such as 12–13 or more), result in a high level of ionization of both, the vat dyes and the cotton. The soluble form of the dye (Scheme 1) is fully ionized to give a negatively charged dye anion with associated positively charged sodium cations. High pH also ionises the hydroxyl groups on cotton, thus giving it a negative charge. Mutual repulsion of the negatively charged dye and cotton results in decreased substantivity and aggravated penetration of the dye into the fibre with associated lower colour yield. On the other hand, moderate dyebath pH values (of the order of 11) produce a lower degree of ionization of the dye and the fibre, resulting in increased colour yield [8]. The control of the reduction process is carried out by measuring the redox potential [9], while the kinetics and thermodynamics of the reduction–oxidation of vat dyes on cellulose material can be controlled by cyclic voltammetry [10–13]. After dyeing, follows removal of the excess of reducing agents and sodium salts, and conversion of the reduced dyes back to the insoluble pigment by an oxidation reaction. Commonly used oxidising agents are hydrogen peroxide or atmospheric oxygen under harsh conditions (high pH or temperature) and/or expensive and hazardous catalysts (metavanadate). Oxidising agents either add oxygen to, subtract hydrogen from, or take electrons away from other chemical/dye compounds; the dye structure loses at least 2 electrons from the anion and reverts to the original pigmentary form with the double bonded oxygen. The pigment or molecular aggregate thus produced becomes trapped mechanically within the fibre and its insolubility gives rise to excellent wash and light fastness properties of the so-dyed textile material. After oxidation, all vat dyeings are subjected to heat treatment in the presence of water, generally in a weakly alkaline detergent liquor at boiling temperature in order to obtain the final shade and improve the fastness ratings (e.g., light- and chlorine-fastness). The processes occurring during soaping are unknown. Crystallization of amorphous dye particles or coarsening primary particles by aggregation is assumed to occur. If soaping takes too long, migration of the aggregates to the surface of the textile can cause deterioration of the rub-fastness. [6].

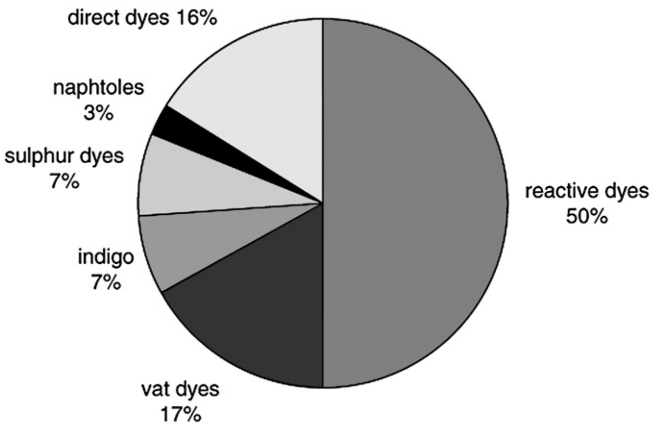
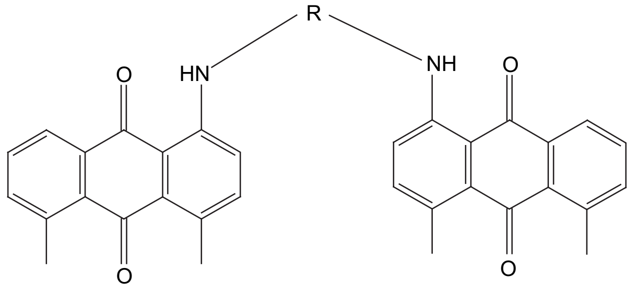


Fig. 1. Worldwide consumption of dyes for dyeing of cellulose fibres [3].

1.1. Basic characteristics of vat and sulphur dyestuffs and their reduction–oxidation mechanism

With very few exceptions, vat dyes fall into two clearly defined groups, anthraquinonoid including heterocyclic quinones and indigoid, containing two or more keto (=O) groups separated by a conjugated system of double bonds. The most important vat dyes are based upon acylamino-anthraquinone **1**, indanthrone **2**, flavanthrone **3**, pyranthrone **4**, dibenzanthrone **5**, isodibenzanthrone **6**, carbazole **7**, benzanthrone acridone **8**, anthraquinone oxazole **9**, indigoid **10** and thioindigoid



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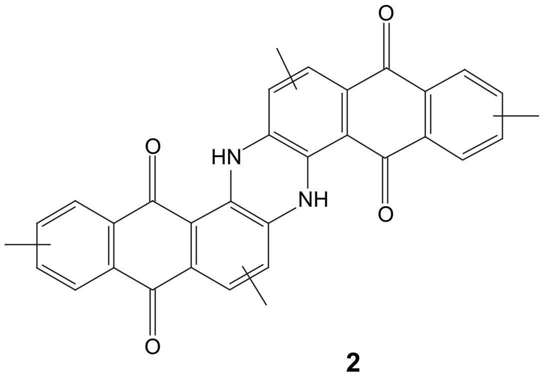

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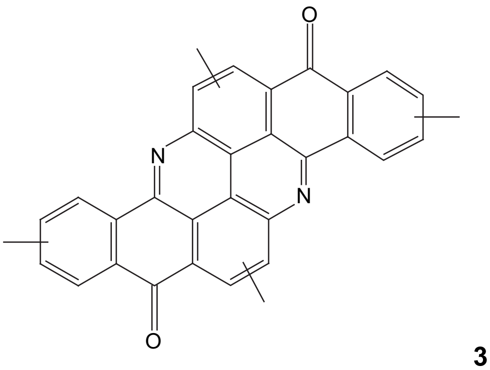

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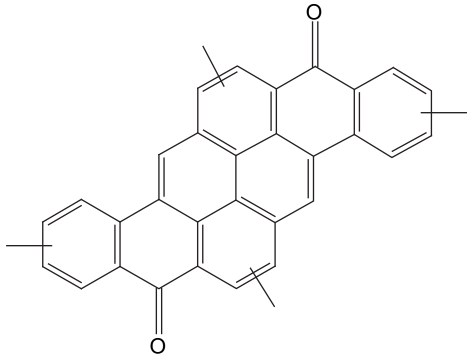

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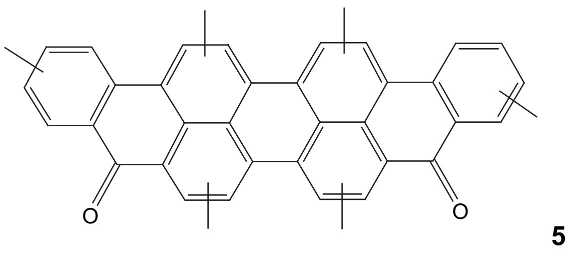

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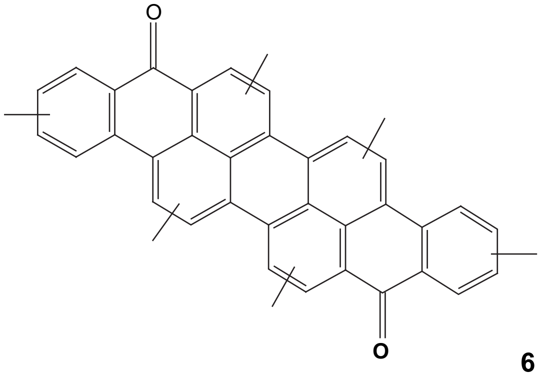

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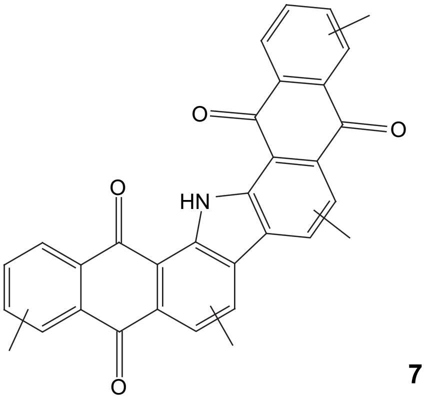

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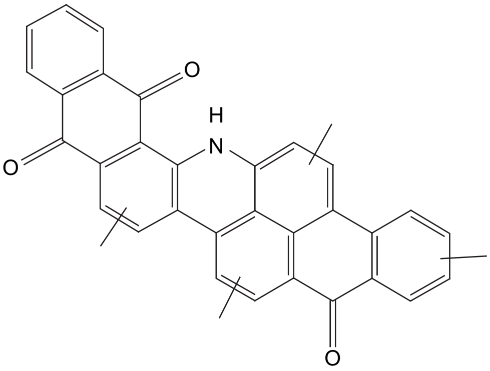

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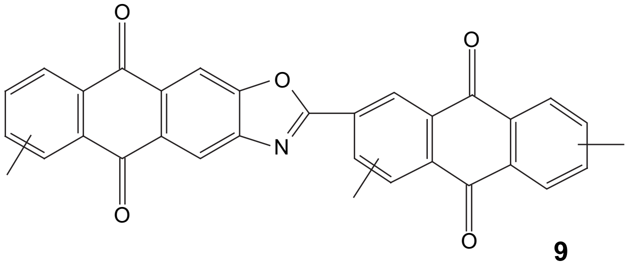

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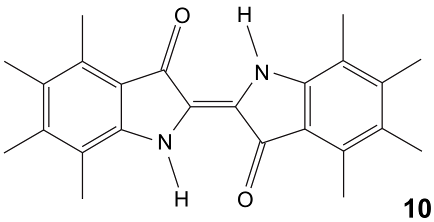

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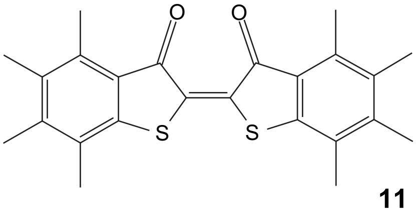

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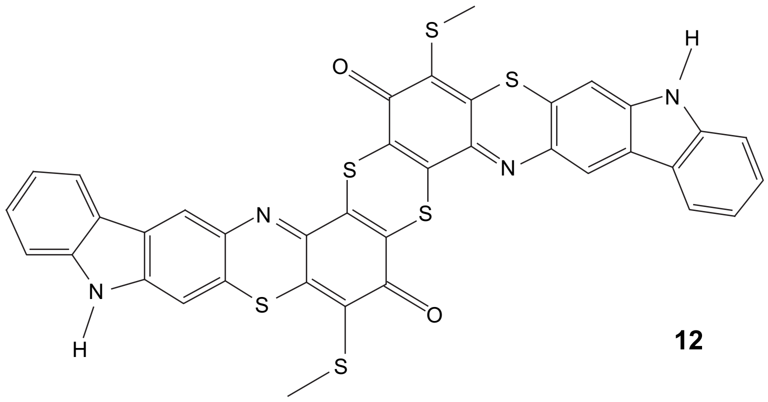

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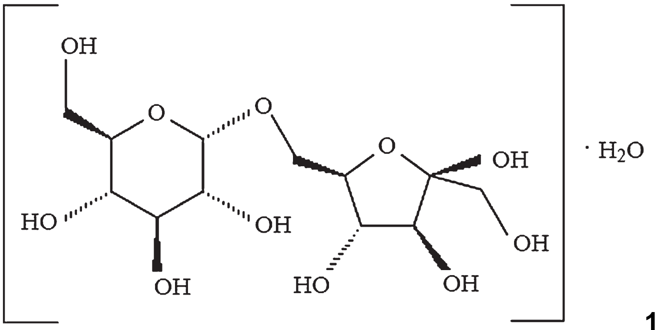

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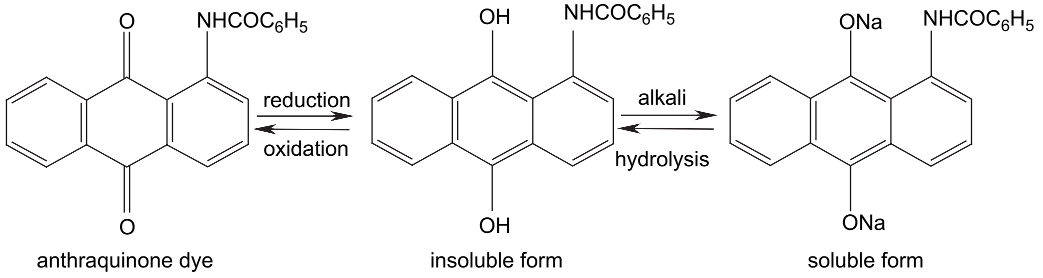
11 structures, and so may be of any colour [4,14–16]. The vat dyes may be homogeneous dyes or mixtures. Since the leuco reduction potential (enolate dye form potential) of vat dyes lies between −650 mV and −1000 mV, it is important that the reducing agent has a reduction potential in the same range or even more negative, and so harsh reducing agents are applied. However, the chemical constitution of a vat dye (especially the number of keto groups) influences the properties of the leuco enolate form in the dyeing process, e.g., thermal stability, substantivity, rate of absorption, diffusion into the fibre and levelling, colour and fastness properties. The dyes are commercially available in the form of liquids, granules, or powders as well as pastes.

Anthraquinone dyes are based on 9,10-anthraquinone, which is produced by oxidation of anthracene. As 9,10-anthraquinone is essentially colourless, in order to produce commercially useful dyes, strongly electron donating groups such as amino or hydroxyls are introduced into one or more of the four positions. Appropriate selection of donor groups (OH, NH_2, NHR, HNAr) and substitution pattern positions, produces a wide variety of colours, although the range is lesser than with azo dye structures. The reduction–oxidation mechanism steps (i.e. changing the dye between insoluble and soluble forms and vice versa) of an anthraquinone dye are presented in Scheme 2.

Another important group inside the class of vat dyes is indigo. The indigo was discovered years ago during treatment of the plant *Indigofera tinctoria*, which was used both for painting and dyeing textiles such as wool and linen [14]. The indigo, also known as indigotin (CI Vat Blue 1) (**10**), exists as blue-violet needles or prisms with a pronounced coppery lustre. Intra- and inter-molecular hydrogen bonding are responsible for indigo's extremely low solubility in water, dilute acids and dilute alkalis, as well as its high melting point. Indigo is readily reduced by various reagents, such as sodium dithionite, hydroxyacetone and hydrogen, or by electrochemical methods. In an alkaline medium the yellow-brown sodium salt of leuco indigo is produced, which can be converted by acids to the



Scheme 2.

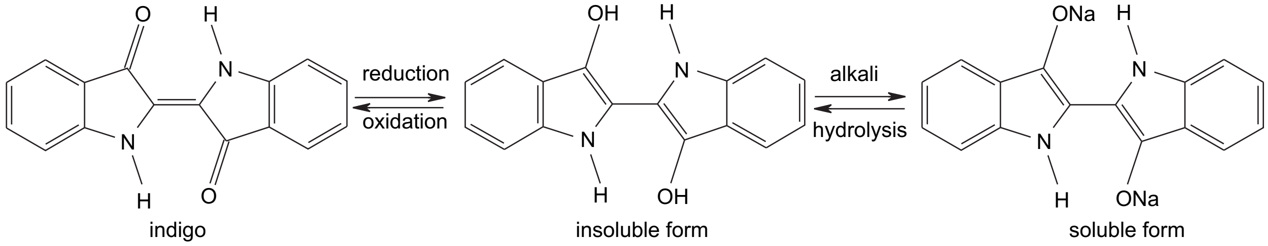
so-called white indigo. The requisite reduction potential (approx. −600 mV) of indigo lies between that of vat dyes and sulphur dyes. The mechanism of reduction–oxidation in this dyeing is presented in Scheme 3.

Another class of dyes that require reduction–oxidation steps for their application is sulphur dyes. The first sulphur dye was developed by Croissant and Bretonniere in 1873 [4]. Sulphur dyes are particularly important for the production of inexpensive products having average fastness requirements. The colour fastness depends greatly on the reduction conditions since over-reduction of the dye may result in low colour yields and/or off-shades. The dyes are very fast to light and washing, but not to chlorine. Since the reduction potential of sulphur dyes lies between −400 mV and −500 mV, milder reducing agents than those used in vat dyeing may be used. However, they are used mainly to dye cotton and other plant fibres in a sodium sulphide bath. A subsequent treatment with metal salts can improve the quality of dyeing. The sulphur dyes are macromolecular compounds which in their final form are characterised by di- and polysulphide bonds ($-S_n-$) between aromatic residues (Scheme 4). They are prepared by treating aromatic amines, phenols and aminophenols with sulphur or sodium polysulphide or both. The starting materials are sulphuretted with sulphur or sodium polysulphide either by heating at 180–350 °C, by boiling under reflux in a solvent, or under pressure at temperatures up to about 130 °C. The commercially available sulphur dyes can be divided into three groups [4,14]: (1) dyes which are polymeric and water insoluble, so their di- and polysulphide bonds have to be reduced by normally using sodium dithionite and alkaline medium ($pH > 10$); (2) pre-reduced, ready-to-use, but highly concentrated solutions of leuco sulphur dyes containing additional reducing agents for stabilization. They are prepared by reduction of base dyes with caustic and glucose; (3) water-soluble dyes containing thiosulphate groups and being applied with sodium dithionite.

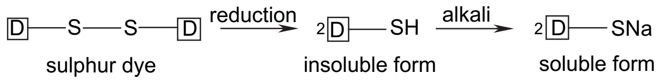
There is another class of dyes that seems to have features in common with both, vat and sulphur dyes, i.e. polysulphide melt dyes or sulphurised vat dyes [4]. Sulphurised vat dyes are produced from dye intermediates by a thionation process similar to that used in the preparation of sulphur dyes. They are similar to vat dyes by virtue of the quinoneimine structure. Reducing agents also convert them to leuco form with a change of hue. The agent not only reduces the quinoneimine group but also transforms the disulphide groups of the dye molecule to sodium thiolate groups. The reduction and the associated cleavage of the disulphide groups render the molecule considerably smaller. Sulphurised vat dyes are applied chiefly with dithionite and show a higher degree of fastness. CI Vat Blue 43 (**12**) is an example of a sulphurised vat dye [17].

1.2. Reducing agents used in classical dyeing processes and ecological problems

Sodium dithionite [5,18] is normally used as the reducing agent in the dyeing of textile material with vat dyes. For sulphur dyes sodium dithionite is used in combination with glucose, although in some cases sulphur dyes are still being reduced using sulphides (Na_2S, NaHS) and polysulphides (Na_2S_8). The advantage of sodium dithionite is that it effects extremely rapid reduction of the vat dye, particularly at high temperature, and therefore, in some dyeing methods it makes possible an extremely short fixing time, which is important in continuous dyeing requiring levelness dyeing without spot formation. On the other hand, sodium dithionite is very easily oxidised by atmospheric oxygen and its stability in aqueous alkaline solution declines very rapidly with increasing temperatures even in the absence of oxygen, so it is necessary to use an



Scheme 3.



Scheme 4.

excess of sodium dithionite (up to 70% of the total required) to compensate their loss for dye re-vatting. In some cases the very great reductive power of sodium dithionite may lead to excessive reduction and to destruction of the dye, so an approach using a mixture of sodium dithionite with a derivative of ammonia containing the radical of an alkali metal salt or ammonium salt of an alkylsulphinic acid having 1–4 C atoms or a hydroxyalkylsulphinic acid having 2–4 C atoms, attached via nitrogen, has been proposed. The addition of sulphinic acid derivates to sodium dithionite not only increases the stability at elevated temperature but also increases the stability of sodium dithionite with respect to oxidative influences of atmospheric oxygen. The dyeings obtainable according to the new process are distinguished from dyeings developed with sodium dithionite alone by improved levelness, higher brilliance and improved purity of shade [19].

The generation of non-regenerable oxidation products causes various problems in the disposal of the dyeing bath and the washing water, because the sodium dithionite is finally oxidised into compounds (sodium sulphate (Na_2SO_4), sulphite ions (SO_3^{2-}) and thiosulphate ions ($S_2O_3^{2-}$)) whose release affect the environment detrimentally due to their toxicity. In addition, the wastewater may contain considerable excess of the reducing agent ($Na_2S_2O_4$), which classified it in some countries among the most hazardous class of waters [18]. Besides, sodium dithionite affects the aerobic processes in water treatment, so addition of an oxidation agent is required for water stabilization. Wastewaters having a high sulphate/sulphite content are highly corrosive and can, for example, destroy waste lines (concrete pipes), so they present real technological problems. In addition, the formed sulphate deposits can form toxic hydrogen sulphide ions (HS^-) by anaerobic degradation. However, although vat dyes in the non-soluble form do not represent an environmental risk as regards their toxicity and biodegradability, they still colour the wastewater.

A further group of reducing agents [20] was discovered in the class of iron(II) complexes with triethanolamine, triisopropanolamine and also aliphatic hydroxy compounds containing a number of hydroxyl groups. The reducing effect of iron(II) complex is the result of a negative redox potential in an alkaline solution at a molar ratio of iron(II) and iron(III) from 0.8:1 to 2:1. One mole of oxidised dye which takes up two electrons per molecule to convert into the leuco form requires 2 mol of a mediator iron complex system, based on the redox-active metal ion supplying one electron [21]. However, all the mentioned mediator systems have certain disadvantages, like not having a sufficiently negative redox potential for dye reduction, not being sufficiently stable in the more weakly alkaline region, or having a relatively too large fraction of iron(II) complex to achieve the redox potential required. Furthermore, the large fraction of iron(II) complex required is a particular problem in producing indigo-dyed denim, because the textile material is dyed layer by layer by repeated immersion in the dyebath and subsequently oxidised in air. With this method, the mediator in the dyebath is completely oxidised with every air passage and first has to be reduced again for the next dyeing cycle. Additional problem presents wastewaters with high content of metal ions.

2. Ecological alternatives of reduction and oxidation mechanisms

In the last decade, many attempts have been made to replace the environmentally unfriendly reduction and/or oxidation agents by ecologically more attractive alternatives using advanced chemical, electrochemical, electrocatalytic hydrogenation and biological methods.

2.1. Upgraded chemical approaches

In order to reduce the use of environmentally unfavourable reducing agents, a research was focused on improving dyeing with vat dyes in 1990. BASF has developed Compress C plus, a process which applies special Caledon SF dyes in conjunction with a newly developed auxiliary system (Zetex CCP_1, Zetex CCP_2, sodium sulphate decahydrate and catalyst) without using sodium dithionite. The process is suitable for dyeing with vat dyes on dry-span as well as on thermo-sol machine with drying at 100–140 °C, and thermo-fixing for 20–30 s at 170–190 °C. The process is economical, easy, without essential loading of the wastewaters, and suitable for dyeing cotton fabrics and blends with polyester. The limitation of the process is that it allows dyeing only of pale shades [5,22]. Another attempt to achieve optimal application of chemicals for reduction and oxidation was made in 1999 in cooperation of companies Thies GmbH and DyStar [5]. The developed system pro VAT plus enables the measuring of the smallest quantity of chemicals. The regulation of the whole dyeing system is entirely automated and is based on continuous on-line measurement of redox potential changes in the vat dye reduction system.

2.2. Electrochemical techniques

Different electrochemical reduction techniques, especially for indigo dyes, have been investigated. Electrochemistry seems to offer a reduction method that could minimise the consumption of chemicals [23–25].

2.2.1. Indirect electrochemical process using a mediator [26–31]

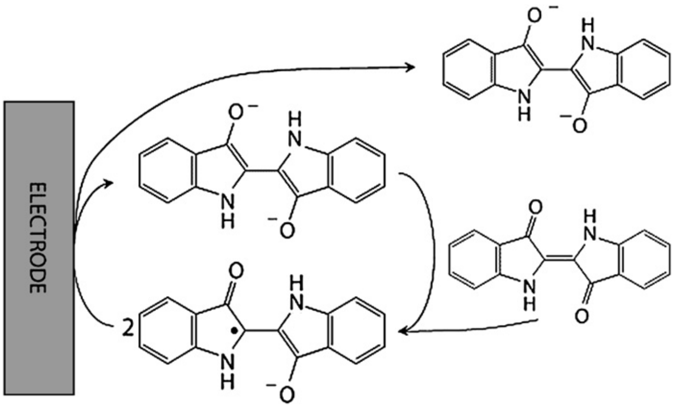
The process is mediated by an electron-carrier whereby reduction takes place between the separated surfaces of the electrode and the insoluble dye molecules and not by direct contact between both surfaces [20]. Mediators are reversible redox systems which reduce the dye and are themselves oxidised in the process. After conversion back to the reduced form at the cathode, they are then available for further dye reduction. However, reduction of the total amount of indigo necessary for dyeing requires enormous amounts of electrical energy and large electrode surfaces [32]. Among the already mentioned transition regenerable metal complexes (i.e. iron(II/III) complex), iron–saccharic acid complexes, selected anthraquinone compounds such as anthraquinonesulphonic acids and hydroxyanthraquinones are of important interest [33,34]. A great advantage of this technique is that the process can be monitored by measuring the redox potential [35]. 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. Such filtration considerably increases the costs for this vatting process and introduces several technical problems like big pressure drop built up during the filtration and the persistent danger of blocking the reactor (electrochemical cell).

2.2.2. Direct electrochemical reduction of dye pigment via the radical process [2,36]

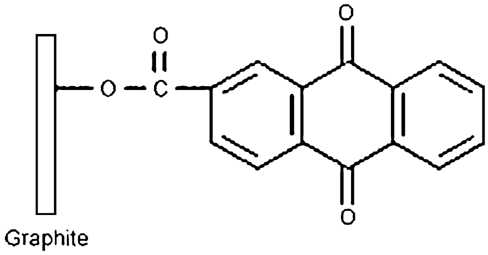
This reduction process is based on a reaction mechanism in which an indigo anion radical is formed by a comproportionation reaction between the dye and the leuco dye, followed by the electrochemical reduction of this radical. The leuco dye is acting as an electron-shuttle between the electrode and the surface of the dye pigment, as shown in Scheme 5. Anyhow, the electrochemical reaction rate is limited by the diffusion transport of the intermediate radical anion and at potentials more negative than −1100 mV the current density increases due to the cathodic liberation of hydrogen. In order to start the process an initial amount of the leuco dye is generated by a conventional reaction, i.e. by adding a small amount of a soluble reducing agent (sodium dithionite).

2.2.3. Direct electrochemical reduction of dye pigment on graphite electrodes [17]

Graphite as a cheap and stable high-surface-area material (working cell) can act as electrode material for the direct electrochemical reduction of indigo/vat dyes in aqueous suspension. The leuco dye is produced (in contrast to the process based on the electrochemical reduction of the dye radical) directly from the dye suspension, thus direct electron transfer between the dye and the graphite is obtained. Much of the chemical activity of the carbon surface is connected with oxygen functionalities (i.e. quinone and hydroquinone). To enhance the chemical activity of the carbon surface (i.e. increase the content of oxygen-containing groups on the surface of carbon), an oxidative pre-treatment approach or an approach based on the covalent bonding of quinoid molecules onto the graphite surface are proposed. In the particular case of indigo reduction, anthraquinones have been used as redox-active molecules. Scheme 6 shows the resulting material: covalently modified with redox-active quinones, which are attached to the carbons particles through the −OH groups on the surface [37].



Scheme 5.



Scheme 6.

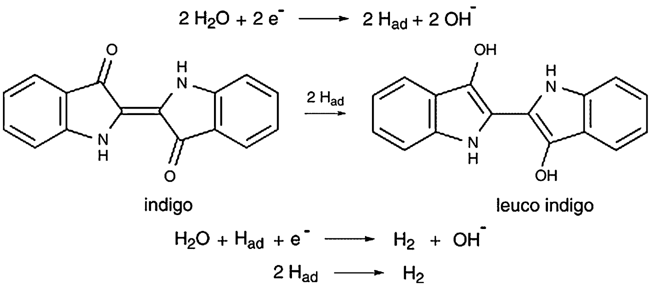
2.2.4. Electrocatalytic hydrogenation

The process consists of a sequence of reduction steps involving electron transfer from the cathode to either a mediator or the leuco radical anion of the vat dye [38]; adsorbed hydrogen, produced in situ by electrolysis of water, reacts with adsorbed organic substrates (i.e. vat dye) at the electrode surface (Scheme 7). The leuco dye prepared by catalytic hydrogenation is converted back into the pigment form in a conventional manner by air oxidation [39]. There are severe drawbacks in this technique, such as the big pressure drop built up, the persistent danger of blocking the reactor and low performance [3].

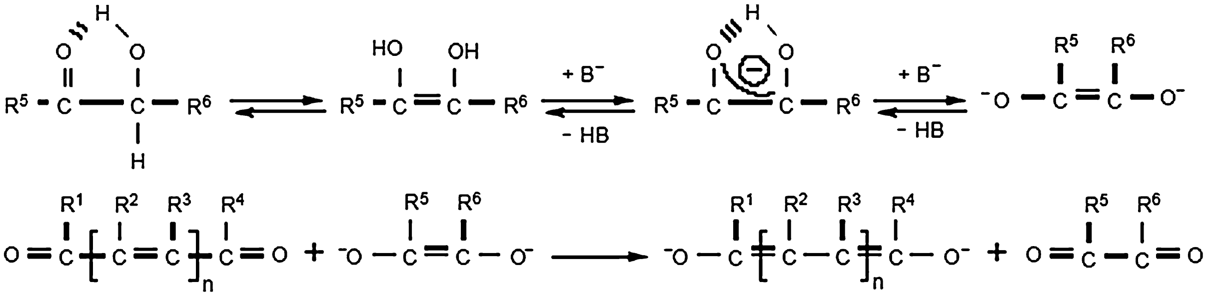
It has been reported recently that vat and sulphur dyes can be reduced in alkaline media by H_2 using an appropriate system involving the production of environmentally safe water [40]:

$$\text{dye} + H_2 \xrightarrow{\text{catalyst}} \text{leuco form} + H_2O$$

The low reactivity of hydrogen as reducing agent was resolved by using a hydrogenation metal catalyst (Pd) which, predictably, induces homolytic ($H_2 \rightarrow 2H^\bullet$) or heterolytic



Scheme 7.



Scheme 8.

splitting of the H–H bond ($H_2 \rightarrow H^+ + H^-$). The potential risk of fire and explosion because of the gaseous hydrogen was solved by Pd catalyst where Pd adsorbs hydrogen and forms a bulk hydride phase with an H/Pd. The bulk hydride guarantees constant surface activity of hydrogen and therefore the maintenance of catalytic activity even when the hydrogen is diluted within an inert gas carrier that it loses its inflammability. Different behaviour of vat and sulphur dyes towards the same reducing agent comes from electrolytic hydrogenation of organic substances. Some organic functions are easily reduced by hydrogen, whereas the others, e.g. quinones, can only be reduced by electrons. Leuco indigo prepared by catalytic hydrogenation as a product of dyestuff manufacturers is used in the patent for the process of dyeing cellulose-containing textile material with hydrogenated indigo [41].

Besides, it seems that the electrochemical techniques can be used also for *stabilization or regeneration of sodium dithionite.* By appropriate cathodic reduction, it is possible to generate from sodium hydrosulphite a powerful reducing species with a redox potential higher than that of hydrosulphite itself, which should reduce dithionite consumption by 30% [3,42].

2.3. Biodegradable organic compounds as reducing agent

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 applications. There have been previous attempts to replace sodium dithionite as a reducing agent for dyeing with vat dyes wholly or partly by small amounts of organic water-miscible (hydrophilic) solvents, i.e. enediols [43]. The enediols are in general α-hydroxycarbonyl compounds having a strongly reducing action (negative redox potentials) in an alkaline medium. Typical compounds which form enediols (enediolates) in an alkaline medium are in particular low molecular weight (C2–C6)-α-hydroxyketones and α-hydroxyaldehydes. The standard potential for 2,3-butanedione is −1718 mV in acetonitrile with 0.1 M tetraethylammonium perchlorate measured with a mercury working electrode, whereas the corresponding value for 2,2,5,5-tetramethylcylohexane-1,3-dione is −2903 mV; the standard potential of 1,2-cyclohexanedione lies between these two values [44]. The ability of α-hydroxyketones to reduce vat dyes is demonstrated in Scheme 8 [45]. Replacement of sodium dithionite in the vat-dyeing process by α-hydroxyketones seems to meet the requirements in terms of reductive efficiency and biodegradability. However, work on the reduction of vat dyes, in particular indigo, with enediols gave unsatisfactory results, since the reduction process was incomplete and the dyeings obtained were unable to meet the high requirements, for example with respect to constancy of shade and levelness. Besides, some substances are expensive and the use of some α-hydroxyketones is restricted to closed systems because they form strong-smelling condensation products in alkaline solution.

Some other reducing systems, based on sulphur containing substances, have also been recommended (i.e. hydroxyalkyl sulphinate, thiourea, etc.) [46]. The relatively low sulphur content and lower equivalent mass than that of hydrosulphite lead to lower amounts of sodium sulphates and toxic sulphide in the effluent. Another proposal has used thiourea dioxide (−1000 mV) in vat dyeing, it recommends continuous application with a mixing pump that combines dye dispersion with liquor containing thiourea dioxide, sodium dithionite, formaldehyde and caustic soda. Another system uses thiourea dioxide in combination with aliphatic ketones or alicyclic ketones or ketocarboxylic acids. Solid, pasty formulations of leuco indigo, in which oxidation to indigo is prevented by a mixture of alkali and a stabilizer based on sugar-derived polyhydroxy compounds, have also been used. When these formulations are used for dyeing, the sodium sulphate content of the dyehouse wastewater can be effectively lowered, but the wastewater contains high concentrations of dissolved organic hydroxyl compounds, measured as TOC (total organic carbon), COD (chemical oxygen demand) or BOD (biochemical oxygen demand). For the delicate dyestuffs, where over-reduction can occur, the use of isomaltulose [47] (α-D-glucopyranosyl-(1,6)-D-fructofuranose monohydrate) **13**, particularly of an isomaltulose mixture containing also trehalulose (α-D-glucopyranosyl-(1,1)-D-fructofuranose), as the reducing agent in the reduction of sulphur and vat dyestuffs has the advantage since the redox potential equilibrium of isomaltulose is reached considerably more rapidly than with the conventionally used sugars (fructose, mannose or glucose) [48]. Isomaltulose is a naturally occurring disaccharide composed of α-1,6-linked glucose and fructose [49]. When used as a reducing agent, it has the advantage that the detrimental environmental effects, which result from the release of sulphide (S^{2-}) ions, are avoided.

2.4. Biotechnological (enzymatic) approaches

The replacement of the existing chemical reduction and oxidation processes with enzymatic technologies could be a very attractive alternative from the ecological point of view. It is also economically attractive because of the possible reduction in the cost of treating the effluent. The main advantages of enzyme-catalyzed reactions are mild temperatures of processing, absence of by-products, and most of the enzyme processes are claimed to be environment-friendly [50]. The main disadvantage of the enzyme process is the dependence of enzyme activity on the temperature and pH, and the toxicity of some of them [51].

Before the introduction of chemical methods, indigo was reduced in a woad vat, by the anaerobic fermentation of treated (couched) woad leaves. Recent findings show *Clostridium isatidis* to be a unique indigo-reducing bacterium isolated from a woad dye vat that could be employed in a biotechnological indigo-reduction process [52,53] *C. isatidis* cultures generate redox potentials from −476 mV to −602 mV, which is about 100 mV more negative than those of the other bacteria examined [54]. The mechanism of bacterial indigo reduction remains unknown, but the unique features of the indigo-reducing *C. isatidis* indicate possible mechanisms for biotechnological indigo-reduction process.

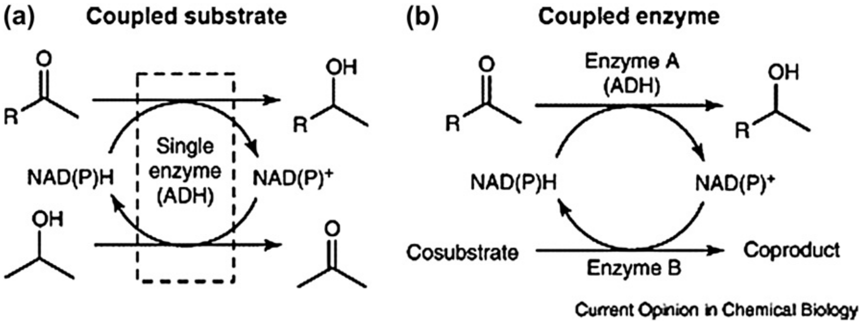
Dehydrogenases are another class of the enzymes that could be used for the reduction of vat dyes [55]. Dehydrogenases are enzymes that catalyze the reduction of carbonyl groups. To exhibit catalytic activities, the enzymes require a coenzyme such as nicotinamide adenine dinucleotide phosphate (NAD(P)H) from which a hydride is transferred to the substrate with carbonyl group (Scheme 9). The most elegant and simple approach makes use of a single enzyme, which simultaneously transforms the substrate with carbonyl group plus co-substrate with hydroxyl group (Scheme 9(a)). Scheme 9(b) shows the more complex ‘coupled-enzyme’ approach where cofactor-recycling is performed by using a second (and preferably irreversible) enzymatic reaction. The most advanced regeneration systems use innocuous hydrogen and oxygen as reductant and oxidant, respectively. In addition, the coupled-substrate system may be used in the oxidation and reduction mode, whereas separate cofactor-recycling systems are required for the coupled-enzyme approach [55].

Matsuda [56] reviewed the use of alcohol dehydrogenases (cells of fungus, *Geotrichum candidum*) in supercritical CO_2 for the reduction of various ketones. Supercritical fluids have the unique properties to present a grand opportunity to discover a range of novel chemical processes. They differ from ordinary solvents in having both their gas-like low viscosities and high diffusivities and their liquid-like solubilizing power. Instead of employing an isolated enzyme, the whole resting cell was used for reduction, thus avoiding the need for an expensive coenzyme. The use of dehydrogenases in supercritical CO_2 is also under intensive investigation [56].

However, there is still no method for replacing the reduction process in vat dyeing by a system that uses a biological approach, but there is enzymatic re-oxidation process that is already patented [57]. Oxidoreductases are enzymes that catalyze the oxidation of various aromatic compounds, specifically phenols and anilines [58]. Two classes of oxireductases are proposed for oxidation of vat and sulphur dyes: (1) laccases, multicopper containing enzymes (with a redox potential of 780 mV), that catalyze the oxidation of phenols and related compounds, and (2) peroxidases which oxidise compounds in the presence of hydrogen peroxide. The reduced vat or sulphur dye, adsorbed onto the treated material, is oxidised with laccase or peroxidase. To enhance the activity of laccase, a chemical redox mediator agent (e.g. ABTS (2,2′-azino-bis(3-ethylbenzthiazoline-6-sulphonic acid) diammonium salt) is added, which represents effective shuttle electrons between the enzymes and the dye. The enzymatic re-oxidation process has lot of advantages, like the mild process conditions resulting in less damage of the fibres, lower energy consumption due to lower temperature and shorter time of treatment needed.

2.5. Ultrasonic energy

Ultrasound has been shown to improve the dyeing vat processes by increasing the dye uptake of the substrate and reducing the amount of the reducing agent and other components used, as well as by reducing the time and energy required to obtain a desired colour [59–61]. The effect of cavitation energy of the ultrasound is attributed to the production of intensive movement of molecules in the liquor, which considerably accelerates fibre wetting, the rapid diffusion of dye molecules inside the fibre structure as well as the promotion of dye molecules’ de-aggregation. Influence of ultrasound on the vatting degree of indigo with α-hydroxyacetone has shown to increase the vatting degree by a factor of approximately 4–5 [62]. It is



Scheme 9.

well known that ultrasound enhances the degree of reduction by disintegrating dispersed water-insoluble dye aggregates into smaller particles and by forming significantly more homogenous and stabile dispersion of dye molecules in the dyebath or printing paste (especially at higher concentration of vatted/soluble dyes) leading to higher dye yield on the substrate [63]. Besides, the increase of the dye surface and simultaneous shortening of the dye diffusion interfaces, the probability for collisions between reducing agent and dye molecules increases resulting to the faster reaction rate [3]. The dissolving and vatting processes can thus be significantly shortened making the possibility to carry out the dyeing process in a continuous procedure.

2.6. Magnetic field [63–66]

The application of magnetic field is another promising physico-chemical method influencing the textile materials and/or the treating solution components. The use of permanent magnetic fields has shown to be importantly advantageous over other physical methods of intensification: besides low material and energy consumption as well as ecological safety of the method, a variety of resulting effects due to the selectivity influence of magnetic field on different substances and processes have been proposed. The influence of the magnetic field on the processes of quinone–hydroquinone transitions of vat dyes was determined [67]. It has been established that the magnetic field increases the rate of sodium dithionite oxidation and quinone-transformation of vat dyes and stabilizes the sodium dithionite composition when dyeing with vat dyes. Besides, the magnetic treatment during soaking increases the sorption and depth of dye penetration into the fibre. It is advisable to activate the interactions between the molecules of dye and the reducer in the solution penetrating into the pores of the fibres.

2.7. UV application

Modern universal equipment makes it possible to treat textile materials by UV and IR irradiations ranging in the wavelength from 300 to 1200 nm. Research work proves that it is possible to carry out photochemical colouration of fabrics by vat dyes and the thermal treatment in conventional dyeing and finishing [68]. Pobedinskij [69] presented an ambient, friendly photochemical technology of dyeing with leuco ethers of vat dye using UV irradiation.

3. Conclusions

Chemical, ecological and economical advantages of the latest research inventions related to the dyeing of vat and sulphur dyes applying reduction and oxidation mechanisms at dyeing processes are reviewed in the article. Special intention is paid to methods not using sodium dithionite as the most appropriate reducing agent, which would ideally give complete vatting and lead to dyeings with the stated high requirements. Electrochemical reduction methods offer tremendous environmental and economic benefits by minimising the consumption of chemicals and effluent load.

The physical activation of processes and/or fibres employing ultrasound, magnetic field or UV applications has shown to be practical (parallel) application enabling to solve ecological problems due to the reduction in consumption of chemicals. The economical benefit shows in the time reduction of technological processes and the increased rate of absorption and diffusion of the dye molecules into the fibre.

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