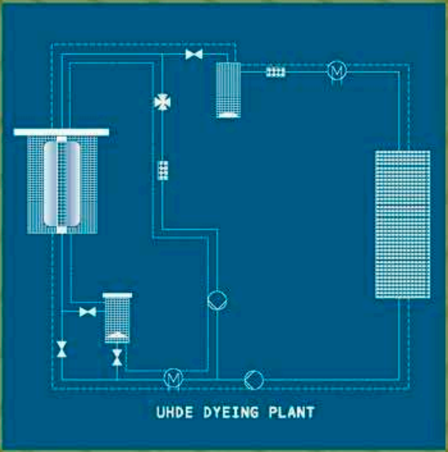
WOODHEAD PUBLISHING IN TEXTILES



Environmental aspects of textile dyeing

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European legislation relating to textile dyeing

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1.1 Introduction

European Union (EU) environmental legislation has developed over the last 30 years and comprises today some 300 legal acts and a large number of other policy documents of relevance for EU environmental policy. Section 1.2.1 of this chapter gives a general introduction to the EU forms of legislation and the principles of the EU environmental policy. The legislation related to the environmental aspects of textile processes in general, primarily the emissions to water and air, is discussed in sections 1.2 to 1.6.

The EU introduced in 1996 an integrated approach on the environmental performance of (large) textile facilities with wet processes, and industrial processes in general. The 'Integrated Pollution Prevention and Control', or so-called IPPC Directive is in essence about minimising pollution from various industrial point sources throughout the European Union by means of environmental permits (see section 1.3). These permits are based on the principle of using Best Available Techniques (BAT) and the BAT Reference documents (BREF) for the Textiles Industry.

A number of chemicals that may be used in textile processes are worth mentioning for their potential negative effects on the environment and human health and are therefore regulated (see section 1.4). To identify textiles meeting these requirements more easily, ecolabels are developed. Since the textile industry uses water as the principal medium for removing impurities, applying dyes and finishing agents, the main concern is therefore about the water discharged and the chemical load it carries. EU legislation regarding (waste) water is set out in section 1.5.

Improving air pollution is a world priority. To achieve a significant reduction in air pollution, national and international measures must be combined to reduce emissions of the gases responsible (see section 1.6). Future trends worth mentioning are the integrated product policy (IPP) and the new chemicals policy, REACH and GHS (see section 1.7). IPP aims to develop a more ecological product market by making products more environmentally sustainable throughout their life cycle. REACH is a single integrated system for the registration, evaluation and authorisation of chemicals.

1.2 Legislation relating to textile dyeing in Europe

1.2.1 Principles of EU environmental policy

Environmental policy is one of the greatest social challenges facing the public authorities and all sectors of the economy today. It is also a subject of which the public is acutely aware, since it directly affects its welfare and health. From the 1970s on, the concern to conserve the environment started to give birth to a series of Community initiatives. The Treaty on European Union upgraded the environment to a Community policy and no longer simply an action by the Community.

Community policy on the environment is set out in Article 174 of the Treaty establishing the European Community:

> Community policy on the environment shall contribute to pursuit of the following objectives:
>
> - preserving, protecting and improving the quality of the environment,
> - protecting human health,
> - prudent and rational utilisation of natural resources,
> - promoting measures at international level to deal with regional or worldwide environmental problems.
>
> Community policy on the environment shall aim at a high level of protection taking into account the diversity of situations in the various regions of the Community. It shall be based on the precautionary principle and on the principles that preventive action should be taken, that environmental damage should as a priority be rectified at source and that the polluter should pay.

The broad objectives of EU environmental policy as set out in Articles 174–176 provide the Community with legal competence to act in all areas of environmental policy. However, it is clear from the Treaty that this competence is not exclusive and that it is shared with the Member States.

The European Communities' core objective of achieving European unification is based exclusively on the rule of law. Community law is an independent legal system which takes precedence over national legal provisions. A number of key players (Commission, Council and Parliament) are involved in the process of implementing, monitoring and further developing this legal system for which a variety of procedures apply.

1.2.2 Forms of EU environmental legislation

European Union environmental legislation includes mainly directives, regulations and decisions.

Most EU environmental laws are *directives*. This is a form of law peculiar to the European Union. They are designed to impose obligations on Member States and to be sufficiently flexible to take into account differing legal and administrative traditions. The choice and method of aligning the national legal and administrative system is left to the discretion of the Member State. Directives are binding on all Member States but may contain differing requirements which take into account the different environmental and economic conditions in each Member State.

Framework directives set out general principles, procedures and requirements for legislation in different sectors. So far they have been adopted for the air, water and waste sectors. Other 'daughter' directives in each sector must conform to the general requirements of the framework directive.

About 10% of EU environmental laws take the form of *regulations*. Regulations are directly binding in Member States and supersede any conflicting national laws. Member states may not transpose the provisions of regulations into national law, even if the national law is identical to the regulation. Nevertheless, environmental regulations require further national measures for implementation.

Regulations usually have a precise purpose and are used where it is important that, in the Member States, precisely the same requirements are applied. In some sectors such as waste and chemicals, EU law is a mixture of regulations and directives.

Decisions are individual legislative acts which are binding in their entirety upon the parties to whom they are addressed. They differ from regulations or directives in that they are usually very specific in nature. They are less common in the environmental field. Environmental regulations or directives often give the Commission the power to take decisions to implement them. Table 1.1 summarises these three major forms of binding EU legislation.

1.3 Integrated pollution prevention and control (IPPC)

The European Union defines obligations with which highly polluting industrial and agricultural activities must comply. It establishes a procedure for authorising these activities and sets minimum requirements to be included in all permits, particularly in terms of pollutants released. The aim is to prevent or reduce pollution of the atmosphere, water and soil, as well as the quantities of waste arising from industrial and agricultural installations to ensure a high level of environmental protection. These rules are set out in the so-called IPPC Directive

Table 1.1 Three forms of binding EU legislation

Directives	Regulations	Decisions
Enter into force upon the date specified in the directive or on the 20th day after publication in the *Official Journal*: this obliges Member States to approximate	Enter into force upon the date specified in the directive or on the 20th day after publication in the *Official Journal*	Enter into force upon notification to the party to whom they are addressed.
Are the most frequently used of EU environmental laws	Are used when a unified system is needed: Funds, institutions; EU voluntary schemes such as eco-label; product or trade regulation (endangered species, transport of wastes)	Are used to specify detailed administrative requirements or update technical aspects of Regulations or Directives
Member States must adopt laws, regulations and procedures to give effect to the directive by the date of transposition; this is typically two years after the date of entry into force.	Member States must establish institutions and procedures; they should repeal conflicting national provisions	Focused in scope and application
Come into effect on the date of practical application, the same as the date of transposition unless other date(s) is(are) indicated in the directive itself for specific actions. Some directives can have direct effect if the Member State fail to transpose into national legislation.	Are directly binding on the date they come into force	Are binding on the parties to whom they are addressed on the date they come into force

96/61/EC of 24 September 1996. IPPC stands for Integrated Pollution Prevention and Control. The IPPC Directive is based on several principles, namely (1) an integrated approach, (2) best available techniques (BAT), (3) flexibility and (4) public participation.

1.3.1 Implementation of the IPPC Directive

All installations covered by Annex I of the Directive are required to obtain an authorisation (permit) from the authorities in the EU member states. Unless they have a permit, they are not allowed to operate. This Annex I section 6.2 includes '*Plants for the pre-treatment (operations such as washing,* *bleaching, mercerisation) or dyeing of fibres or textiles where the treatment capacity exceeds 10 tonnes per day*'. In 2001, 130 textile facilities exceding 10 tonnes treatment capacity were reported, emitting some 24 different pollutants above the EPER thresholds (see Table 1.2).

Since 30 October 1999 for the EU-15, and 1 May 2004 for the ten new Member States, the IPPC Directive has applied to new installations as well as to those 'existing' installations (i.e. those built before 2000) where the operators intend to carry out changes that may have significant negative effects on human health and the environment. Member States have been given an eight-year transitional period until October 2007 to ensure that all other existing installations fully comply with the Directive. Four new Member States – Latvia, Poland, Slovakia and Slovenia – were granted transitional periods for certain installations until the end of 2010.

The Commission has recently launched a review process of the IPPC Directive and related legislation on industrial emissions. While not altering its main underlying principles and level of ambition, the review will evaluate the scope to improve the functioning of the Directive, its coherence and complementarity with other industrial emissions-related legislation and the effectiveness of market-based-instruments in this context. The deadline of 30 October 2007 for the full implementation of the Directive remains valid.

1.3.2 Permits based on best available techniques (BAT)

'Integrated' means that the permits must take into account the whole environmental performance of the plant, including emissions to air, water

Table 1.2 Number of reported textile IPPC facilities and pollutants by country in 2001

Country	Facilities	Pollutants
Austria	3	5
Belgium	27	11
Finland	1	4
France	20	10
Germany	26	11
Greece	1	1
Ireland	1	1
Italy	18	10
The Netherlands	1	4
Portugal	8	11
Spain	15	14
Sweden	1	1
United Kingdom	8	3
EU total	130	24

and land, generation of waste, use of raw materials, energy efficiency, noise, prevention of accidents, risk management. The Member States have chosen various approaches to implement the IPPC Directive, such as case-by-case permitting or use of General Binding Rules for industry sectors.

Competent authorities responsible for issuing permits are required to take account of the general principles set out in article 3 when determining the conditions of the permit. These conditions must include emission limit values, supplemented or replaced where appropriate by equivalent parameters or technical measures. According to article 9(4) of the Directive, these emission limit values, equivalent parameters and technical measures must, without prejudice to compliance with environmental quality standards, be based on the best available techniques, without prescribing the use of any technique or specific technology, but taking into account (1) the technical characteristics of the installation concerned, (2) its geographical location and (3) the local environmental conditions. In all circumstances, the conditions of the permit must include provisions on the minimisation of long-distance or transboundary pollution and must ensure a high level of protection for the environment as a whole.

The permits must be based on the concept of 'best available techniques' (or BAT), which is defined in article 2(11) of the Directive:

> 'best available techniques' shall mean the most effective and advanced stage in the development of activities and their methods of operation which indicate the practical suitability of particular techniques for providing in principle the basis for emission limit values designed to prevent and, where that is not practicable, generally to reduce emissions and the impact on the environment as a whole:
>
> - 'techniques' shall include both the technology used and the way in which the installation is designed, built, maintained, operated and decommissioned,
> - 'available' techniques shall mean those developed on a scale which allows implementation in the relevant industrial sector, under economically and technically viable conditions, taking into consideration the costs and advantages, whether or not the techniques are used or produced inside the Member State in question, as long as they are reasonably accessible to the operator,
> - 'best' shall mean most effective in achieving a high general level of protection of the environment as a whole.

Annex IV lists the considerations to be taken into account when determining best available techniques, bearing in mind the likely costs and benefits of a measure and the principles of precaution and prevention: the use of low-waste technology, the use of less hazardous substances, the nature, effects and volume of the emissions concerned, the consumption and nature of raw materials (including water) used in the process and their energy efficiency, and the need to prevent accidents and to minimise the consequences for the environment.

1.3.3 Best available techniques for the textiles industry (BREF document)

Since the permits must be based on BAT, the licensing authorities need some assistance to find out which techniques are BAT. Therefore, the European Commission organises an exchange of information between experts from the EU Member States, industry and environmental organisations. This work is co-ordinated by the European IPPC Bureau and results in a BAT reference document, a so-called BREF document, for some 30 sectors. The 'Reference Document on Best Available Techniques for the Textiles Industry' was formally adopted by the Commission in July 2003. This document covers the industrial activities specified in Section 6.2 of Annex 1 of Directive 96/61/EC, namely: 'Plants for the pretreatment (operations such as washing, bleaching, mercerisation) or dyeing of fibres or textiles where the treatment capacity exceeds 10 tonnes per day'.

The BREF document contains a thorough description of the applied processes and techniques in the textiles industry (fibre preparation, pretreatment, dyeing, printing and finishing) as well as a description of environmental aspects of different process steps in textile processing. Upstream processes, which may have a significant influence on the environmental impact of the subsequent wet processing activities are also briefly described. Furthermore, some emission levels of environmental aspects and consumption of levels of energy, water and some chemicals are also presented. The main part of the BREF is a thorough description of different techniques to consider in the determination of the best available technique (BAT) for each textile process. It should be stressed, however, that this document does not propose emission limit values. Finally, the document lists the best available technique for each step of textile processing. In the Annex to the document different textile auxiliaries are described and possible substitutes for problematic substances are suggested.

1.3.4 European Pollutant Emission Register (EPER)

The IPPC Directive ensures that the public has a right to participate in the decision-making process, and to be informed of its consequences, by having access to (a) permit applications in order to give opinions, (b) permits, (c) results of the monitoring of releases and (d) the European Pollutant Emission Register (EPER).

EPER is the European Pollutant Emission Register of industrial emissions into air and water, which was established by a Commission Decision of 17

July 2000 to have better and public information about the amount of pollution that different installations are responsible for. The EPER Decision is based on Article 15(3) of the IPPC Directive 96/61/EC.

According to the EPER Decision, Member States have to produce a triennial report on the emissions of industrial facilities into the air and waters. The report covers 50 pollutants which must be included if the threshold values indicated in Annex A1 of the EPER Decision are exceeded. The first reporting year was 2001. The 130 textile IPPC facilities reported some 24 different pollutants, mainly emissions to water (see Table 1.3).

EPER will be replaced by the European Pollutant Release and Transfer Register (E-PRTR) from 2007 reporting period onwards. The E-PRTR will report on more substances and will also have information on what the industrial installations do with their waste and waste water. The reporting cycle will be annual instead of every three years.

1.4 EU legislation on chemical substances

A number of chemicals that may be used in textile processes are worth mentioning for their potential negative effects on the environment and human health and are therefore regulated. It is reported that more than 90% of the organic chemicals and auxiliaries in pretreatment and dyeing operations do not stay on the fibre, whereas the reverse is true in the finishing treatment. In order to protect the general public and the environment from certain dangerous substances and preparations and to ensure the proper functioning of the internal market, the European Union has drawn up a list of substances and preparations to which restrictions on marketing and use apply. In an increasingly health- and environment-conscious world, a product that is able to prove that it is better for the environment and health by a trustworthy label can help to make a difference in the eyes of customers.

1.4.1 Evaluation and control of the risk of substances

The European Union has laid down common rules to ensure the systematic evaluation and better management of the risks linked to existing substances as well as, where appropriate, new protective measures in Council Regulation 793/93/EEC of 23 March 1993 on the evaluation and control of the risks of existing substances. The purpose of these rules is, as part of the internal market, to protect humans and all parts of the environment from the possible effects of exposure to dangerous chemical products. The Regulation does not provide directly for risk reduction measures, although it may give rise to such measures being taken. If the risk reduction strategy contained in the Recommendation proposes limiting the marketing and use of a substance, the Commission may decide to propose measures under Directive 76/769/

Table 1.3 Aggregated emissions of all reported pollutants of textile IPPC activity in 2001 (in tonne $year^{-1}$)

Pollutant	To air (t y^{-1})	Direct to water (t y^{-1})	Indirect to water (transfer to off-site waste water treatment) (t y^{-1})
Ammonia (NH_3)	27.40	–	–
Arsenic and its compounds (As)	–	–	0.0337
Benzene, toluene, ethylbenzene, xylenes (as BTEX)	–	–	0.707
Brominated diphenylethers	–	–	1.40
Cadmium and its compounds (Cd)	–	0.0333	0.0476
Carbon dioxide (CO_2)	187 000.00	–	–
Carbon monoxide (CO)	1 230.00	–	–
Chlorides (Cl^-)	–	–	363 000.00
Chromium and its compounds (Cr)	–	0.7837	1.41
Copper and its compounds (Cu)	–	4.54	2.62
Hydrogen cyanide (HCN)	0.541	–	–
Lead and its compounds (Pb)	–	0.4839	0.2224
Mercury and its compounds (Hg)	–	0.00904	0.0079
Nickel and its compounds (Ni)	–	0.8146	0.992
Nitrogen oxides (NO_x)	941.00	–	–
Non-methane volatile organic compounds (NMVOC)	188.00	–	–
Phenols	–	0.0721	79.41
Phosphorus, total (P)	–	47.18	58.28
Polycyclic aromatic hydrocarbons (PAH)	–	–	12.28
Sulphur oxides (SO_x)	1 485.00	–	–
Tetrachloromethane (TCM)	0.8	–	–
Total organic carbon (TOC)	–	1 523.20	10 607.80
Trichloroethylene (TRI)	39.06	–	–
Zinc and its compounds (Zn)	–	2.27	2.05

EEC on restrictions on the marketing and use of certain dangerous substances and preparations. Furthermore, other Community instruments may be used with a view to reducing the threats posed by the substance under examination.

The criteria which define a substance as dangerous are harmonised at European level, as are the packaging and labelling criteria designed to ensure that these substances are easily identifiable in order to protect public health and the environment and ensure the free movement of such products.

Classification, packaging and labelling of chemicals is provided for by two directives and their subsequent amendments: Directive 1967/548/EEC of 27 June 1967 for dangerous substances and Directive 1999/45/EC of 31 May 1999 for dangerous preparations. Characteristics and parameters for assessment of dangers for the environment, and a new danger symbol 'dangerous for the environment' was added by Directive 92/32/EEC of 30 April 1992, amending Directive 67/548/EEC for the seventh time. The most recent proposal to amend the legislation will establish a single integrated registration system (REACH) and a Globally Harmonized System of Classification and Labelling of Chemicals (GHS) (see section 1.3).

Due to the large number of substances covered by the Regulation, a priority-setting approach has been adopted. The *lists of priority substances* are drawn up and published each year by the Commission. Four priority lists have been adopted under the regulation to date, resulting in 141 substances. The substances included are those that require priority attention because of their possible effects on man and the environment. Special attention is accorded to substances with potentially chronic effects, such as carcinogens. A number of criteria may be taken into account when deciding whether to include a substance, such as the effects on man and the environment, the absence of data on the effects of the substance and the work already carried out in other international fora. A substance already evaluated under other Community legislation may only be placed on the list if the evaluation in question fails to take account of risks to man and the environment.

To have an indication of the potential danger and information regarding the protection of health and the environment, Directive 91/155 defines the detailed arrangements for the information system for dangerous preparations. This information system in the form of safety data sheets (SDS) is principally intended for industrial and professional users and must enable them to take the measures necessary to ensure the protection of health and safety at the workplace and the environment. Any person, whether the manufacturer, importer or distributor, established within the Community, who is responsible for placing a dangerous substance or preparation on the market, shall supply the recipient who is an industrial user of the substance or preparation with a safety data sheet containing the information set out in the Directive. The information shall be provided free of charge at the latest when the substance or preparation is first supplied and thereafter following any revision due to any significant new information regarding safety and protection of health and the environment.

1.4.2 Restrictions on marketing and use of certain dangerous substances and preparations

Annex I of Council Directive 76/769/EEC of 27 July 1976 and its subsequent amendments on the approximation of the laws, regulations and administrative provisions of the Member States relating to restrictions on the marketing and use of certain *dangerous substances and preparations* contains the list of substances and preparations covered by the measures provided for in this Directive as well as the conditions governing their placing on the market. The list in Annex I has been amended several times introducing new substances and preparations. An overview of these directives relevant for substances and preparations used in textile processing is listed in Table 1.4. Among these chemicals there are also certain biocides.

Biocidal products are used during textile production as preservatives, but also in finishing treatment, for example insecticides and acaricides. Directive 98/8/EC of 16 February 1998 concerning the placing of biocidal products on the market establishes a regulatory framework for the placing of biocidal products on the market, with a view to ensuring a high level of protection for man and the environment and the proper functioning of the common market. The time limit for transposition of the Directive in the Member States was 14 May 2000. Active substances, introduced on the market after this date, are subject to the provisions of the Directive. At this same date, a 10-year review program of active substances already on the market (so-called existing active substances) was started. The aim of the programme is to assess all active substances that were already on the market before 14 May 2000. During this transitional phase, Member States may continue to apply their national rules on biocidal products containing existing active substances until the decision on the inclusion of the particular substances has been made.

Currently, some biocidally active substances are subject to restrictions under Directive 76/769/EEC on restrictions of the marketing and use of chemicals: arsenic (Directive 2003/2/EC), creosote (Directive 2001/90/EC), organic tin compounds (Directive 2002/62/EC), mercury (Directive 89/677/EEC), pentachlorophenol (Directive 1999/51/EC).

Existing active substances within product type 18, i.e. products used for the control of arthropods (e.g. insects, acarids), will be evaluated during the second phase of the review programme. Existing active substance within products used for the preservation of fibrous or polymerised materials, such as leather, rubber or paper or textile products, by the control of microbiological deterioration, i.e. product-type 9, will be evaluated during the fourth phase of the review programme.

Table 1.4 Overview of legislation related to restrictions on marketing and use of certain dangerous substances of relevance for the textile industry

Directive	Subject	Summary
76/769/EC	Restriction on marketing and use of dangerous substances	The Annex contains the list of products covered by the measures provided for in this Directive as well as the conditions governing their placing on the market.
1979/663/EEC	Tris [2,3-dibromopropyl] phosphate	May not be used in textile articles, such as garments, undergarments and linen, intended to come into contact with the skin.
1982/806/EEC 1989/677/EEC	Benzene	Not permitted in toys or parts of toys as placed on the market where the concentration of benzene in the free state is in excess of 5 mg kg^{-1} of the weight of the toy or part of toy (e.g. textiles). May not be used in concentrations equal to, or greater than, 0.1% by mass in substances or preparations placed on the market.
1983/264/EEC	Tris-aziridinyl phosphinoxide, polybrominated biphenyl (PBB)	May not be used in textile articles, such as garments, undergarments and linen, intended to come into contact with the skin.
89/677/EEC	Mercury compounds	May not be used as substances and constituents of preparations intended for use in the impregnation of heavy-duty industrial textiles and yarn intended for their manufacture.
1991/338/EEC	Cadmium and its compounds	This Directive prohibits the use of cadmium and its compounds in three areas: 'to give colour', stabiliser for finished products manufactured from vinylchloride and cadmium plating. Furthermore, it provides for a general exemption clause where justification exists on the grounds of safety or reliability and where the use of cadmium is unavoidable. In any case, whatever their use or intended final purpose, finished products or components of products listed in the Directive may not be placed on the market if their cadmium content expressed as Cd metal) exceeds 0.01% by mass of the plastic material.
94/27/EC	Nickel and its compounds	May not be used in jewellery and personal objects, including buttons and zippers, which may come into contact with the skin if the rate of nickel release from the parts of these products coming into direct and prolonged contact with the skin is greater than 0.5 $\mu g\ cm^{-2}/week^{-1}$;

Table 1.4 Cont'd

Directive	Subject	Summary
1999/51/EC	Pentachlorophenol and its salts and esters	Shall not be used in a concentration equal to or greater than 0.1% by mass in substances or preparations placed on the market. By way of derogation until 31 December 2008, France, Ireland, Portugal, Spain and the United Kingdom may choose not to apply this provision to substances and preparations intended for use in industrial installations not permitting the emission and/or discharge of pentachlorophenol (PCP) in quantities greater than those prescribed by existing legislation: (b) in the impregnation of fibres and heavy-duty textiles not intended in any case for clothing or for decorative furnishings.
1999/77/EEC	Asbestos fibres	Ban on the marketing and use of asbestos fibres; crocidolite, chrysotile, amosite, anthophyllite, actinolite and tremolite, and products containing these substances.
97/10/EC 97/56/EC 1999/43/EC 2001/41/EC 2003/34/EC 2003/36/EC	Substances classified as carcinogenic, mutagenic or toxic to reproduction (CMR)	Ban on the marketing to the general public of substances classified as carcinogenic, mutagenic or toxic to reproduction, and of preparations containing these substances.
2002/45	Short-chain chlorinated paraffins (SCCPs)	Ban on the use and marketing of substances or preparations containing more than 1% SCCPs in metalworking and leather finishing. By 1 January 2003, all remaining uses of SCCPs were to undergo a risk-assessment review.
2002/61/EC 2003/3/EC	Azoic colouring agents	Azo dyes which, by reductive cleavage of one or more azo groups, may release one or more of the aromatic amines listed in the Appendix, in detectable concentrations, i.e. above 30 ppm in the finished articles or in the dyed parts thereof, may not be used in textile and leather articles which may come into direct and prolonged contact with the human skin or oral cavity.
2003/11/EC	Pentabromodiphenyl ether (pentaBDE), octabromodiphenyl ether (octaBDE)	Ban on the marketing and use of pentaBDE and octaBDE as a substance, in preparations and in articles containing concentrations in excess of 0.1% by mass of pentaBDE and octaBDE.

Table 1.4 Cont'd

Directive	Subject	Summary
2003/53/EC	Nonylphenol, nonylphenol ethoxylate	May not be placed on the market or used as a substance or constituent of preparations in concentrations equal or higher than 0.1% by mass for, amongst others, textiles and leather processing except processing with no release into wastewater or systems with special treatment where the process water is pre-treated to remove the organic fraction completely before biological waste water treatment (degreasing of sheepskin).
98/8/EC*	Biocidal products	Regulatory framework for the placing of biocidal products (i.e. active substances and preparations containing one or more active substances, put up in the form in which they are supplied to the user, intended to destroy, deter, render harmless, prevent the action of, or otherwise exert a controlling effect on any harmful organism by chemical or biological means) on the market, with a view to ensuring a high level of protection for man and the environment and the proper functioning of the common market.
648/2004/EC*	Surfactants in detergents	Surfactants in detergents shall be considered as biodegradable if the level of biodegradability (mineralisation) measured is at least 60% within 28 days according to tests in Annex III A, or at least 70% according to tests in Annex III B.

Acts marked* are not amending acts of Directive 76/769/EEC.

The combination of an article (e.g. textiles) and an active substance, has to comply with the requirements of the Directive if the active substance is placed on the market as an inseparable ingredient of the article and if it is intended that the biocidally active substance is released from the treated article to control harmful organisms outside the treated article (external effect) or if it is intended to control only organisms that are not harmful to the treated article itself. In such cases, the article has the function of a delivery system and shall be considered as a biocidal product that must be authorised. Examples of such delivery systems are: mosquito nets containing insect repellents, mattress covers that are labelled as anti-mite for use in prevention of the action of house mites outside the cover (i.e. within the mattress), sleeping bag treated with an insect repellent, socks treated with a biocidally active substance intended to have a biocidal action on the foot, treated textiles to be used for pets that release substances with a lethal effect on fleas and flea eggs.

When an article (e.g. textiles) has been treated with a biocidally active substance with the intention to control organisms harmful to the treated article/material itself (on the surface or inside), then the treated article shall not be considered as a biocidal product (so-called internal effect). Examples of such articles might be treated materials like wood, leather and most water-based paints. However, the active substance that (by itself or in a formulation) has been used to treat the article is a biocidal product requiring authorisation.

Regulation 648/2004/EC of 31 March 2004 on *detergents* harmonises the rules of the biodegradability of surfactants in detergents and restrictions for the placing on the market of detergents and surfactants for detergents. This Regulation will permit improved protection of the aquatic environment against surfactants. These surfactants – also called tensides – are included in detergents and other cleaning products in order to reduce the surface tension of liquids so that they can wet surfaces and clean them more effectively. Thus, the surfactants in auxiliaries and the detergents used by textile companies in Europe must fulfil the criteria as set out in this Regulation.

1.4.3 Elimination and minimisation of persistent organic pollutants (POPs)

The Stockholm Convention on persistent organic pollutants (POPs) forms a framework, based on the precautionary principle, which seeks to guarantee the safe elimination of these substances, which are harmful to human health and the environment, as well as reductions in their production and use. Persistent organic pollutants are chemical substances that possess certain toxic properties and, unlike other pollutants, resist degradation, which makes them particularly harmful for human health and the environment. POPs accumulate in living organisms, are transported by air, water and migratory species and accumulate in terrestrial and aquatic ecosystems. They are, therefore, a cross-border problem on which international action is indispensable. The Convention covers 12 priority POPs, although the eventual long-term objective is to cover other substances. These 12 priority POPs are aldrin, chlordane, dichlorodiphenyltrichlorethane (DDT), dieldrin, endrin, heptachlor, mirex, toxaphene, polychlorobiphenyls (PCBs), hexachlorobenzene, dioxins and furanes. Some pesticides can still be found on imported natural raw material like cotton.

1.4.4 Ecolabelling

Labels allow consumers to make comparisons among products and give consumers the ability to reduce the environmental impacts of their daily activities by purchasing environmentally preferable and healthy products and minimising their consequences during use and disposal. Depending on the label, the criteria aim more at environmental aspects or harmful substances. Ecolabelling schemes are voluntary and mostly set up by private organisations. However, the EU eco-label scheme is regulated by law.

The Öko-Tex standard 100 is the world's leading eco-label for textiles. Products carrying this label have been tested and certified by internationally renowned textile institutes. Since 1992, the Öko-Tex standard 100 has grown into an international standard on safety of textiles, applied in the entire textile production chain. More than 6000 companies world-wide active in textiles and clothing are involved in the Öko-Tex certification network. With over 50 000 certificates granted to millions of textile products, Öko-Tex standard 100 has become the world's leading eco label for textiles. Other textile labels worth mentioning include Nordic Swan, Blue Angel, Toxproof.

The EU Flower is the EU regulated eco–label. The first criteria for textiles were established in 1999. Regulation 880/92/EEC on a EU eco-label award scheme seeks to promote the design, production, marketing and use of products which have reduced environmental impacts during their life cycles. The regulation also seeks to provide consumers with better information on the environmental impact of products. It does not apply to food, drink or pharmaceuticals, dangerous substances under Directives 67/548/EEC or 88/379/EEC, or to products manufactured using processes which are likely to cause significant harm to man or the environment. Conditions for the awards for each product group are to be determined by a Committee of Member State representatives after a consultation process involving interested groups from industry, commerce, consumer and environmental organisations. Product group eco-label criteria last three years and are determined according to life cycle assessments of product groups based on the maintenance of a high level of environmental protection. So far, eco-label criteria have been determined for several product groups, including bed linen and T-shirts. The current eco-label criteria for textile products for the EU flower were established by the Commission on 15 May 2002 (2002/371/EC) and are valid until 31 May 2007. At present (March 2006) 69 companies hold EU Flower licences for some 113 textile products.

1.5 EU legislation on water quality

The textile industry uses water as the principal medium for removing impurities, applying dyes and finishing agents and for the generation of steam. The main concern is therefore about the water (quantity and quality) supplied and discharged and the chemical load and pollutants it carries.

Water is one of the most comprehensively regulated area of EU environmental legislation. There are a number of measures taken at Community level to tackle particular pollution problems. Community policy concerning dangerous or hazardous substances in European waters was introduced more than two decades ago by Council Directive on Pollution Caused by Discharges of Certain Dangerous Substances (76/464/EEC). Several substances have been regulated in specific directives (also called 'daughter' directives) in the 1980s by defining Community-wide emission limit values and quality objectives in the surface and coastal waters. Other examples are the Urban Waste Water Treatment Directive and the Nitrates Directive (91/676/EC), which together tackle the problem of eutrophication (as well as health effects such as microbial pollution in bathing water areas and nitrates in drinking water); and the IPPC Directive, which deals with chemical pollution.

1.5.1 Water Framework Directive (WFD)

Historically, there has been a dichotomy in approach to pollution control at European level, with some controls concentrating on what is achievable at source, through the application of technology; and some dealing with the needs of the receiving environment in the form of quality objectives. Source controls alone can allow a cumulative pollution load, which is severely detrimental to the environment, where there is a concentration of pollution sources. Also quality standards can underestimate the effect of a particular substance on the ecosystem, due to the limitations in scientific knowledge regarding dose-response relationships and the mechanics of transport within the environment.

For this reason, a consensus has developed that both emission limit value legislation as well as water quality standards legislation are needed to have an efficient protection, i.e. a so-called 'combined approach'. This combined approach is also in accordance with the precautionary principle and the principle that environmental damage should, as a priority, be rectified at the source, as well as the principle that environmental conditions in the various regions shall be taken into consideration.

The Water Framework Directive (WFD) formalises this. On 23 October 2000, the Directive 2000/60/EC of the European Parliament and of the Council establishing a framework for the Community action in the field of water policy was adopted.

The aim is long-term sustainable water management based on a high level of protection of the aquatic environment. Article 4.1 defines the WFD general objective to be achieved in all surface and groundwater bodies, i.e. good status by 2015, and introduces the principle of preventing any further deterioration of status.

To fulfil this aim, it requires that, as part of the basic measures to be taken on the source side in the river basin, all existing technology-driven source-based controls must be implemented as a first step. But, over and above this, it also sets out a framework for developing further such controls. The framework comprises the development of a list of priority substances for action at EU level, prioritised on the basis of risk; and then the design of the most cost-effective set of measures to achieve load reduction of those substances, taking into account both product and process sources. On the effects side, it co-ordinates all the environmental objectives in existing legislation, and provides a new overall objective of good status for all waters, and requires that, where the measures taken on the source side are not sufficient to achieve these objectives, additional ones are required.

The WFD establishes river basin management based on an assessment of the characteristics of the river basin; monitoring of the status of its surface and groundwaters; definition of quality objectives; establishment of programmes of measures to achieve the defined objective. However, the administrative structure to achieve this river basin management is left to the discretion of Member States. The programme of measures will have to follow the above-mentioned combined approach, using the setting of emission limit values and of water quality standards. In this context, the full implementation of existing EU emission limit value legislation has to be provided, i.e. Urban Waste Water Treatment Directive, IPPC Directive, Nitrates Directive, Plant Protection Products Directive, Dangerous Substances Directives and its daughter directives (1976). In addition, the water quality standards established under the Water Framework Directive and other relevant EU water legislation (e.g. Bathing Water Directive) have to be complied with. These general EU provisions need to be transposed into national legislation. Thus, emission limit values for waste water of textile dyeing companies can be subject to different approaches depending on the Member States. Either the approach of an individual permit or authorisation system is used to set emission limit values for a single company, or emission limit values are defined for an industrial sector, or a combination of both. The WFD obliges Member States to set maximum emission limit values. However, as an alternative, Member States are allowed to control pollution by complying with water quality standards established in the same Directive and thus derived emission limit values. Furthermore, Member States will have to ensure that services to water users are paid at full cost-recovery prices (basically prices for water supply and waste water collection and treatment).

Article 16 of the WFD sets out a ‘Strategy against pollution of water’. The first step of the strategy was the establishment of a list of ‘priority substances’ to become Annex X of the Directive. The Commission will prepare Community-wide emission controls and quality standards for the priority substances.

The preparation of the priority list, included a procedure called COMMPS which was developed to identify the substances of highest concern at Community level. The Decision (2455/2001/EC) was adopted on 20 November

2001 and identifies 33 substances or group of substances (see Table 1.5), which have been shown to be of major concern for European Waters. Within this list, 11 substances have been identified as 'priority hazardous substances' which are of particular concern for the inland, transitional, coastal and territorial waters. 'Hazardous substances' are defined in Article 2(29) of the WFD as 'substances or groups of substances that are toxic, persistent and liable to bio-accumulate, and other substances or groups of substances which give rise to an equivalent level of concern'. These substances will be subject to cessation or phasing out of discharges, emissions and losses by 2020. A further 14 substances are identified as being subject to review for identification as possible 'priority hazardous substances'.

In accordance with Article 1(c) of Directive 2000/60/EC, the future reviews of the list of priority substances under Article 16(4) of that Directive will contribute to the cessation of emissions, discharges and losses of all hazardous substances by 2020 by progressively adding further substances to the list.

The list of priority substances adopted under this Decision is to replace the list of substances in the Commission Communication to the Council of 22 June 1982 on dangerous substances which might be included in List I of Council Directive 76/464/EEC. The Directive 76/464/EEC of 4 May 1976 on pollution caused by certain dangerous substances discharged into the aquatic environment of the Community was one of the first water-related Directives to be adopted. It had the ambitious objective of regulating potential aquatic pollution by thousands of chemicals already produced in Europe at that time. The Directive covered discharges to inland surface waters, territorial waters, inland coastal waters and groundwater. In 1980, the protection of groundwater was taken out of 76/464/EEC and regulated under the separate Council Directive 80/68/EEC on the Protection of Groundwater Against Pollution Caused by Certain Dangerous Substances. This Directive introduced the concept of list I and list II substances, the so-called Europe's Black List and Grey List of dangerous substances, which were listed in the Annex to the Directive, to eliminate pollution from list I substances and to reduce pollution from list II substances, but are now integrated in the WFD.

1.5.2 Protection of the maritime waters against pollution

The Community and Member States are party to various international agreements containing important obligations to prevent and eliminate pollution and to protect the maritime area against the adverse effects of human activities. Europe's seas may be divided into three regions (with possible subregions): the Baltic Sea, the North-East Atlantic and the Mediterranean, resulting in three conventions, Convention on the Protection of the Marine Environment of the Baltic Sea Area, signed in Helsinki on 9 April 1992 and approved by Council Decision 94/157/EC (the Helsinki Convention), the Convention for

Table 1.5 List of priority substances in the field of water policy (2455/2001/EC)

	CAS number†	EU number‡	Name of priority substance*	Identified as priority hazardous substance
1	15972-60-8	240-110-8	Alachlor	
2	120-12-7	204-371-1	Anthracene	(X)***
3	1912-24-9	217-617-8	Atrazine	(X)***
4	71-43-2	200-753-7	Benzene	
5	Not applicable	Not applicable	Brominated diphenylethers**	X****
6	7440-43-9	231-152-8	Cadmium and its compounds	X
7	85535-84-8	287-476-5	C_{10-13}-chloroalkanes (**)	X
8	470-90-6	207-432-0	Chlorfenvinphos	
9	2921-88-2	220-864-4	Chlorpyriphos	(X)***
10	107-06-2	203-458-1	1,2-Dichloroethane	
11	75-09-2	200-838-9	Dichloromethane	
12	117-81-7	204-211-0	Di-(2-ethylhexyl)phthalate (DEHP)	(X)***
13	330-54-1	206-354-4	Diuron	(X)***
14	115-29-7	204-079-4	Endosulfan	(X)***
	959-98-8	Not applicable	(alpha-endosulfan)	
15	206-44-0	205-912-4	Fluoranthene*****	
16	118-74-1	204-273-9	Hexachlorobenzene	X
17	87-68-3	201-765-5	Hexachlorobutadiene	X
18	608-73-1	210-158-9	Hexachlorocyclohexane	X
	58-89-9	200-401-2	(gamma-Lindane)	
19	34123-59-6	251-835-4	Isoproturon	(X)***
20	7439-92-1	231-100-4	Lead and its compounds	(X)***
21	7439-97-6	231-106-7	Mercury and its compounds	X
22	91-20-3	202-049-5	Naphthalene	(X)***
23	7440-02-0	231-111-4	Nickel and its compounds	
24	25154-52-3	246-672-0	Nonylphenols	X
	104-40-5	203-199-4	(4-nonylphenol)	

25	1806-26-4	217-302-5	Octylphenols	(X)***
	140-66-9	Not applicable	(4-t-octylphenol)	
26	608-93-5	210-172-5	Pentachlorobenzene	X
27	87-86-5	201-778-6	Pentachlorophenol	(X)***
28	Not applicable	Not applicable	Polyaromatic hydrocarbons	X
	50-32-8	200-028-5	(Benzo[*a*]pyrene)	
	205-99-2	205-911-9	(Benzo[*b*]fluoranthene)	
	191-24-2	205-883-8	(Benzo[*ghi*]perylene)	
	207-08-9	205-916-6	(Benzo[*k*]fluoranthene)	
	193-39-5	205-893-2	(Indeno[1,2,3-*cd*]pyrene)	
29	122-34-9	204-535-2	Simazine	(X)***
30	688-73-3	211-704-4	Tributyltin compounds	X
	36643-28-4	Not applicable	(Tributyltin cation)	
31	12002-48-1	234-413-4	Trichlorobenzenes	(X)***
	120-82-1	204-428-0	(1,2,4-Trichlorobenzene)	
32	67-66-3	200-663-8	Trichloromethane (chloroform)	
33	1582-09-8	216-428-8	Trifluralin	(X)***

*Where groups of substances have been selected, typical individual representatives are listed as indicative parameters (in brackets and without number). The establishment of controls will be targeted to these individual substances, without prejudicing the inclusion of other individual representatives, where appropriate.

**These groups of substances normally include a considerable number of individual compounds. At present, appropriate indicative parameters cannot be given.

***This priority substance is subject to a review for identification as a possible 'priority hazardous substance'. The Commission will make a proposal to the European Parliament and Council for its final classification not later than 12 months after adoption of this list. The timetable laid down in Article 16 of Directive 2000/60/EC for the Commission's proposals of controls is not affected by this review.

****Only pentabromobiphenylether (CAS number 32534-81-9).

*****Fluoranthene is on the list as an indicator of other, more dangerous polyaromatic hydrocarbons.

[†] Chemical Abstract Services.

[‡] European Inventory of Existing Commercial Chemical Substances (EINECS) or European List of Notified Chemical Substances (ELINCS).

the Protection of the Marine Environment of the North-East Atlantic, signed in Paris on 22 September 1992 and approved by Council Decision 98/249/EC (the OSPAR convention) and the Convention for the Protection of the Mediterranean Sea Against Pollution, signed in Barcelona on 16 February 1976 and approved by Council Decision 77/585/EEC (the Barcelona Convention). In each region, and possibly in the subregions to which they belong, the Member States concerned must coordinate their actions with each other and with the third countries involved.

The OSPAR Commission acts as the decision-making body for the OSPAR Convention. Each year, it discusses, decisions and recommendations and adopts them, either unanimously or by a three-quarters majority of the Contracting Parties. The Hazardous Substances Strategy sets the objective of preventing pollution of the maritime area by continuously reducing discharges, emissions and losses of hazardous substances, with the ultimate aim of achieving concentrations in the marine environment near background values for naturally occurring substances and close to zero for man-made synthetic substances. As its timeframe, the Hazardous Substances Strategy further declares that the Commission will implement this Strategy progressively by making every endeavour to move towards the target of the cessation of discharges, emissions and losses of hazardous substances by the year 2020.

PARCOM has also issued, in 1997, one Recommendation concerning reference values for effluent discharges from wet processes in the textile processing industry (Recommendation 97/1) and one Recommendation BAT and best environmental practice (BEP) for this industry 94/5. The PARCOM Recommendation 97/1 contains limit values for additional metals compared to the HELCOM Recommendation (e.g. Cd, As, Pb). The limit values for Cr (both total and Cr VI) are stricter in the PARCOM Recommendation. The PARCOM Recommendation also contains requirements expressed as mg kg^{-1} of textiles processed for different cases/processes.

1.5.3 Urban Waste Water Directive

Directive 91/271/EEC of 21 May 1991 concerning urban waste water treatment aims to protect surface inland waters and coastal waters by regulating collection and treatment of urban waste water and discharge of certain biodegradable industrial waste water (basically from the agro-food industry). In addition, industrial waste water entering collecting systems should be subject to general rules or regulations and/or specific authorisations (Article 11). Industrial waste water entering collecting systems and urban waste water treatment plants shall be subject to such pre-treatment as is required in order to: (a) protect the health of staff working in collecting systems and treatment plants, (b) ensure that collecting systems, waste water treatment plants and associated equipment are not damaged, (c) ensure that the operation of the waste water treatment plant and the treatment of sludge are not impeded, (d) ensure that discharges from the treatment plants do not adversely affect the environment, or prevent receiving water from complying with other Community Directives, (e) ensure that sludge can be disposed of safely in an environmentally acceptable manner.

1.6 EU legislation on air pollution

With regard to emissions to air, the BREF on Textile Processing reports two sources: (1) emissions of textile processes setting volatile organic compounds (VOC) free and (2) emissions of combustion processes to produce thermal energy. The first type of emissions is covered by the VOC Directive, the second by several directives depending on the pollutant and the thermal input of the installation.

Air quality is one of the areas in which Europe has been most active in recent years. The aim has been to develop an overall strategy through the setting of long-term air quality objectives. A series of directives has been introduced to control levels of certain pollutants and to monitor their concentrations in the air. In 1996, the Environment Council adopted Framework Directive 96/62/EC on ambient air quality assessment and management. This Directive covers the revision of previously existing legislation and the introduction of new air quality standards for previously unregulated air pollutants, setting the timetable for the development of daughter directives on a range of pollutants. The list of atmospheric pollutants to be considered includes sulphur dioxide, nitrogen dioxide, particulate matter, lead and ozone – pollutants governed by already existing ambient air quality objectives – and benzene, carbon monoxide, polyaromatic hydrocarbons, cadmium, arsenic, nickel and mercury.

Emissions associated with the on-site burning of fossil fuels to produce thermal energy for textile processes are CO_2, SO_x, NO_x, and particulates. Directive 2001/80/EC of 23 October 2001 on the limitation of emissions of certain pollutants into the air from large combustion plants applies to combustion plants (technical apparatus in which fuels are oxidised in order to use the heat thus generated) with a rated thermal input equal to or greater than 50 MW, irrespective of the type of fuel used. The aim of the LCP Directive is gradually to reduce the annual emissions of sulphur dioxide and oxides of nitrogen from existing plants and to lay down emission limit values for sulphur dioxide, nitrogen oxides and dust in the case of new plants.

The EU has set national emission ceilings for acidifying and eutrophying pollutants and for ozone precursors in order to provide fuller protection for the environment and human health against their adverse effects. Directive 2001/81/EC of 23 October 2001 on National Emission Ceilings (NECs) for certain pollutants sets upper limits for each Member State for the total emissions in 2010 of the four pollutants responsible for acidification, eutrophication and ground-level ozone pollution (SO_2, NO_x, VOCs and ammonia), but leaves it largely to the Member States to decide which measures to take in order to comply.

According to Directive 2003/87 of 13 October 2003, establishing a scheme for greenhouse gas emission allowance trading within the Community and amending Council Directive 96/61/EC Member States shall ensure that, from 1 January 2005, no installation undertakes any activity listed in Annex I resulting in emissions specified in relation to that activity unless its operator holds a permit issued by a competent authority. For the textiles industry, the activity 'combustion installations with a rated thermal input exceeding 20 MW (except hazardous or municipal waste installations) with carbon dioxide emissions' is of interest. This Directive establishes a scheme for greenhouse gas emission allowance trading within the Community in order to promote reductions of greenhouse gas emissions in a cost-effective and economically efficient manner. Member States shall develop a national plan stating the total quantity of allowances that it intends to allocate for that period and how it proposes to allocate them. Therefore, the influence of these directives on textile companies depends on the specific situation within a country, but emissions from the textile industry are generally low.

Volatile organic compounds (VOCs) are released from particular textile activities such as: (a) cleaning with organic solvents; (b) printing processes in cases when organic solvents are used (e.g. they are contained in pigment printing pastes); (c) vulcanisation of backing layers (carpet sector); (d) heat treatments (e.g. thermofixation, drying, curing) when the textile materials contain substances that evaporate or degrade thermally (for example oils, plasticisers, finishing agents and residues from upstream processes). Emissions of formaldehyde and uncombusted methane can be particularly significant in poorly maintained, directly heated stenters.

Council Directive 1999/13/EC of 11 March 1999 on the limitation of emissions of volatile organic compounds due to the use of organic solvents in certain activities and installations, the so-called VOC Directive, sets the framework of the global strategy to reduce pollution due to tropospheric ozone. The purpose of this Directive is to prevent or reduce the direct and indirect effects of emissions of volatile organic compounds (VOCs) on the environment and human health, by setting emission limits for such compounds and laying down operating conditions for industrial installations using organic solvents.

Industries which use volatile organic solvents and are covered by the Directive are listed in the Annex I to the Directive. For most of the activities concerned, the Directive specifies a consumption threshold (Annex II) above which its provisions apply. For rotary screen printing on textiles with a solvent consumption threshold of 30 tonnes year^{-1}, the emission limit values in waste gases is 100 mg Nm^{-3} of carbon. Fugitive emission values are set at 20% of solvent input.

Member States must take the necessary measures to ensure that all new installations comply with the provisions of the Directive. The industrial operators concerned can conform with the specified emission limits in either of the following ways: (a) by installing equipment to reduce emissions to comply with the emission limit values and the fugitive emission values, or total emission limit values; (b) by introducing a reduction scheme to arrive at an equivalent emission level, in particular by replacing conventional products which are high in solvents with low-solvent or solvent-free products. Solvents containing substances likely to have a serious effect on human health (carcinogens, mutagens or toxic to reproduction), must be replaced, as far as possible, by less harmful substances within the shortest possible time. Stricter emission values are specified for harmful substances.

1.7 Future trends

One of the European Union's fundamental objectives is sustainable development. During the last few years, the Commission has begun to rethink policies relating to the environmental impacts of products. All products and services have an environmental impact, whether during their production, use or disposal. Up to now, product-related environmental policies have tended to focus on large point sources of pollution, such as industrial emissions or waste management issues. Now, however, it is becoming clear that they need to be complemented by a policy that looks at the whole of a product's life-cycle, including the use phase. This should ensure that environmental impacts throughout the life-cycle are addressed in an integrated way – and so are not just shifted from one part of the life-cycle to another. It should also mean that environmental impacts are addressed at the point in the life-cycle where they will best and most cost-effectively reduce the overall environmental impacts and resource use. To this aim, the integrated product policy (IPP) was presented in 2001. The European Union wishes also to modernise European chemicals legislation and to establish REACH, a single integrated system for the registration, evaluation and authorisation of chemicals, which also covers the life-cycle of the chemical substance.

Registration, evaluation, authorisation and restrictions of chemicals (REACH)

The Commission proposed a new EU regulatory framework for the Registration, Evaluation and Authorisation of Chemicals (REACH) on 29 October 2003. The proposed regulation could replace more than 40 directives and regulations currently in force. The aim is to improve the protection of human health and the environment through the better and earlier identification of the properties of chemical substances. REACH would commit firms which manufacture and import chemicals to evaluate the risks resulting from the use of those chemicals and to take the necessary steps to manage any identified risk. The burden of proof that the safety of chemicals placed on the market is ensured would be reversed and passed from public authorities to industry.

The REACH proposal gives greater responsibility to the industry chain to manage the risks from chemicals and to provide safety information on the substances. Manufacturers and importers will be required to gather information on the properties and exposure of their substances (during the production process and in finished articles), which will help them manage chemicals safely, and to register the information in a central database. A Chemicals Agency will act as the central point in the REACH system: it will run the databases necessary to operate the system, co-ordinate the in-depth evaluation of suspicious chemicals and run a public database in which consumers and professionals can find hazard information.

At the moment, final adoption of the proposal is expected by the end of 2006 which could lead to entry into force around April 2007. The new European Chemicals Agency, to be established in Helsinki, Finland, will be fully operational 12 months later.

1.7.1 Globally Harmonised System (GHS)

The Globally Harmonised System of Classifying and Labelling Chemicals (GHS), is voluntary, but it was agreed at the 2002 UN World Summit on Sustainable Development in Johannesburg that the GHS should be implemented worldwide, with a target date of 2008.

The GHS will provide harmonised health and safety information for chemical substances and mixtures. As the GHS has been formally adopted only very recently and because the Commission wishes to examine in more detail the implications of its adoption for stakeholders and downstream legislation, it has not been considered appropriate to put forward a proposal to incorporate GHS into Community law at the same time as the proposal for REACH. Accordingly, the Commission will present the necessary proposals for adopting the GHS once the REACH legislation has been finally adopted.

The new legislation will replace, after a transitional period, the currently existing provisions on classification and labelling of chemicals, as set out in Council Directive 67/548/EEC and Directive 1999/45/EC as amended.

1.7.2 Integrated Product Policy (IPP)

The Commission presented in 2001 a strategy for strengthening and refocusing product-related environmental policies with a view to promoting the development of a market for greener products. This Green Paper of 7 February 2001 on integrated product policy [COM(2001) 68 final] resulted in a communication from the Commission to the Council and the European Parliament of 18 June 2003 Integrated Product Policy – Building on Environmental Life-Cycle Thinking [COM(2003) 302 final]. The backbone of IPP is the 'Product Life Cycle' which covers all phases in the existence of the product: starting from the extraction of natural resources, via the production of raw material, through their design, assembly, marketing, distribution, sale and use to their eventual treatment as waste. This so-called 'integrated chain management' uses techniques of LCA (Life Cycle Analysis, which is an inventory of the environmental impact of a product) in order to assess the environmental impact due to all causes in all phases of the product life-cycle. These product-orientated policies provide the instruments to the EU policy, in order to initiate very concrete and directive-based interventions, to improve products from the point of view of their impact on the environment, for example, water quality. While the Water Framework Directive advocates the 'best environmental practices' to control all discharges to water, IPP gives the means to prevent such discharges through a systematic approach to improve environmental performance of a product across its life-cycle.

1.8 Sources of further information and advice

The European IPPC Bureau exists to catalyse an exchange of technical information on best available techniques under the IPPC Directive 96/61/EC and to create reference documents (BREFs), which must be taken into account when the competent authorities of Member States determine conditions for IPPC permits. The Textile BREF document can be downloaded from the EIPPCB website http://eippcb.jrc.es/.

1.8.1 EPER, the European Pollutant Emission Register

http://www.eper.cec.eu.int/ provides access to information on the annual emissions of approximately 10 000 industrial facilities in the 15 Member States of the EU as well as Norway and Hungary – mostly from the year 2001. It allows information to be grouped easily, by pollutant, activity (sector), air and water (direct or via a sewerage system) or by country. It is also possible to see detailed data on individual facilities by searching by name or by clicking on a map. Alternatively, it is possible to look for the sources of a particular pollutant.

1.8.2 European Union – summary of legislation

The http://europa.eu.int/scadplus/scad_en.htm, site provides user-friendly fact sheets, which summarise EU legislation. The fact sheets are divided into

32 subject areas which are the Activities of the European Union. These provide not only summaries of existing measures, but also a follow-up of legislative proposals in policies. The aim of this site is to provide a complete summary of the latest legislative developments. The dates that appear at the bottom of each summary corresponds to the date of the last substantial modification, for example, the introduction of an amending or a related act.

EUR-Lex http://europa.eu.int/eur-lex/lex/en/index.htm, provides direct free access to European Union law. The system makes it possible to consult the *Official Journal* of the European Union and it includes *inter alia* the treaties, legislation, case-law and legislative proposals. It offers extensive search facilities. With a simple search on document number, the legislative acts and the bibliographic notice can be found.

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http://ecb.jrc.it/biocides/
http://www.unece.org/trans/danger/publi/ghs/ghs_welcome_e.html
http://www.oeko-tex.com/en/main.html
http://ec.europa.eu/environment/ecolabel/index_en.htm
http://www.ospar.org/eng/html/welcome.html
http://www.pops.int/

2

Environmental legislation USA

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2.1 Introduction

Textile dyeing and all the related processes have a long history in the timeline of civilization. During this history, the chemicals used have been researched, synthesized, developed, and chosen to provide the consumer long life and continued fashion appeal of the garments, furnishings, or materials. To provide these qualities, the chemicals used had to resist the effects of the environment. Materials were required that were durable, fast (light and water), and not chemically degradable. However, these same properties that protect the properties of the consumer material create problems for the textile dyeing industry when the chemicals are released into the environment. In 1986, Horning, speaking of dyes, stated that 'The regulatory climate of today is one of increasing complexity.'[1] Today, we might think of those as the simpler days of regulation.

As regulatory agencies in the United States have addressed the chemicals associated with textile dyeing, there have been two approaches. The bulk of the regulations have been those of general environment legislation, while few have addressed specific chemicals, although this trend is changing. Although, environmental legislation related to textile processes was in place before, the passage of the USEPA 1986 Emergency Planning and Community Right-To-Know Act (Title III of SARA of 1986) began the increase in number and stringency of regulations that apply to textile dyeing and related processes. This was reaffirmed with the passage of the 1990 Pollution Prevention Act. Since then, legislation has increased at the Federal, state, and even the local level.

In the United States, the approach on the Federal and state levels, has been to create legislation that deals with the flow of materials in manufacturing and not with the different manufacturing sectors. This has led to regulations on air, water, wastewater, solid wastes, and consumer exposure. Then, industry sectors are examined within the framework of these regulations and, if needed, specific chemicals are limited or banned.

In addition to Federal and State legislation, other requirements that impact textile dyeing operations in the United States have increased. These include non-US regulations for those operating in the global economy, requirements of sustainability and ecological interest groups and, more frequently, the result of the increase in information through the media and, more recently, the internet.

This chapter is intended to provide an introduction to the Federal and state legislation in the United States that has an impact on textile dyeing. Because the US Textile Industry has become more specialized, not all cases where environmental regulations apply can be covered. In addition, legislation not directly related to dyeing, such as pesticide regulations under FIFRA and consumer regulations (flammability) have been excluded. Lastly, information on state legislation and requirements of non-government groups are given in the form of examples. General sourcing for information is given at the end of the chapter including information on the legislation and regulations sited.

2.2 Current regulations

A keyword search of the USEPA (United States Environmental Protection Agency) website (www.epa.gov, September 25, 2006) for the term ‘textile’ returns 11 348 hits while a search of the terms ‘dye’ or ‘dyeing’ returns 2181. A review of the entries doesn’t reveal a good place to start a review without some previous knowledge. This is because the laws and regulations of the United States are not written from an industry viewpoint, but from the regulatory standpoint. Thus, it is important to understand how the processes of the textile dyeing industry are viewed by regulatory agencies. A search of the USEPA publications website NEPIS (National Environmental Publications Information System) by keywords returns 1758 (textile) and 1685 (dye) publication hits. Two publications that are essential in beginning a review of the processes of the textile dyeing industry, laws, and regulations are produced by the USEPA. These are ‘Profile of the Textile Industry – EPA Office of Compliance Sector Notebook Project’, USEPA 310-R-97-009, September 1997, and ‘Best Management Practices for Pollution Prevention in the Textile Industry’, USEPA 625-R-96-004, September 1996. The first publication gives a review of the processes involved, applicable regulations, and some history, while the second gives the details of textile dyeing processes and pollution prevention opportunities. The following summary of current regulations reflects those for which the majority of textile dyeing operations will be responsible for compliance.

2.3 Toxic Release Inventory and Right-To-Know

The requirements of what are commonly called the ‘Toxic Release Inventory’ (TRI) and ‘Community Right-To-Know’ are two parts of the Emergency

Planning and Community Right-to-Know Act (EPCRA) enacted in 1986 and expanded by the Pollution Prevention Act of 1990. This legislation, which is also called SARA Title III, requires manufacturers and related companies to report on their activities based on the usage of hazardous chemicals. The four main activities are Emergency Planning (Section 301-303), Emergency Release Notification (304), Community Right-To-Know (RTK) Reporting (311-312), and Toxic Chemical Release (TRI) Reporting (313). In addition to USEPA regulations, some states have additional requirements that may have to be met. This legislation and associated regulations are in the forefront of the public debate in the United States. The government and private groups publish documents each year and maintain websites that allow the public to review all of the data from the TRI 313 reporting for industries that must report and publicize the results. For example, the reader should review the websites, http://www.rtknet.org/ and http://www.scorecard.org/.

Right-To-Know reporting is required for chemicals present at a facility above listed threshold values. TRI reporting is required for listed chemicals that are used in total at a facility above threshold values during the reporting year. For textile dyeing, reporting under the RTK regulations is commonly required for textile auxiliaries and processing aids such as acids, caustic, and salt since no specific dyes or pigments are covered and the general threshold of 10000 pounds is usually not met for most dyes and pigments. For TRI reporting, several specific dyes are listed, but again the threshold levels (25000 pounds) are usually not met except for high volume dyes. Few of the TRI listed dyes are still in use in the United States.

However, unlike the RTK requirements, TRI reporting is also required for chemical categories. Dyes containing metals such as copper, chromium, cobalt, zinc, and nickel must be considered together as 'metal compounds' and, thus, thresholds can be exceeded. Thresholds for additional categories such as glycol ethers and polybrominated biphenyls may be exceeded by textile dyeing operations. The major impact of the RTK and TRI regulations are found in the reporting from processes related to textile dyeing including boiler operations (emissions and fuels), process water preparation, wastewater treatment, and cleaning operations.

The chemicals and chemical categories covered by the RTK and TRI regulations can change yearly and the trend is for an increasing number of listings and lowering of the threshold amounts. More recent additions include the Polycyclic Aromatic Compounds category (PACS) with a threshold of 100 pounds and the Dioxins category with a threshold of 0.1 grams. The standard summary of the chemicals and chemical categories can be found in the USEPA document called 'The List of Lists'.[2] In addition, two guidance documents have been developed that apply to textile dyeing operations.[3,4]

2.4 Waste

Waste from textile-dyeing operations can be of two types, hazardous and non-hazardous under Federal regulations. The Federal program that regulates hazardous waste is the Resource and Conservation and Recovery Act (RCRA). A summary of textile manufacturing and RCRA has been created.[5] RCRA Regulations establish a 'cradle-to-grave' system governing hazardous waste from the point of generation to disposal. RCRA hazardous wastes include the specific materials listed in the regulations (designated with the code 'P'– acutely toxic chemicals, 'U'– other listed chemicals, 'K'– specific industry wastes, or 'F'– specific industrial process wastes) or materials which exhibit a hazardous waste characteristic (ignitability, corrosivity, reactivity, or toxicity and designated with the code 'D').

The types of materials that can be regulated as hazardous waste in textile-dyeing operations included acids and caustic (corrosives), hydrogen peroxide (oxidizers), solvents used as carriers or cleaning agents, and chromium dyes. These will only be considered hazardous waste if collected and discarded as waste. Under many normal operations, these materials would be passed through a local or facility wastewater system and be exempt from the RCRA requirements. In addition, packaging (drums, totes, boxes) containing any of these materials may be subject to regulation if not cleaned and handled properly. Materials used for maintenance of machinery such as oil, lubricants, and paint are also subject to RCRA requirements. Currently, dyed fabric and apparel are not subject to RCRA regulations. Non-hazardous waste normally associated with textile dyeing operations is not subject to Federal regulations, but may be subject to state and local regulations including those governing recycling requirements.

2.5 Wastewater and water

Wastewater discharge is governed by the Federal Clean Water Act (CWA). States and localities may also have regulations that impose additional requirements. The CWA regulates both direct (point source, onsite) and indirect (public works, offsite) dischargers. In addition, the CWA regulates stormwater from sites that may have been contaminated due to industrial activity.

The regulations that govern the textile point source category are extensive and are divided into each type of textile operation (knits, wovens, carpet as examples) and the complexity of the operation.[6,7,8] These regulations are not specific to textile dyeing, but cover the entire operation of the facility. Typically for textile operations, the parameters covered include BOD (biochemical oxygen demand), COD (chemical oxygen demand), TSS (total suspended solids), sulfide, total chromium, pH, and phenol (wovens category) and require discharges to meet Best Available Technology (BAT) levels. Other requirements of the CWA may include testing for specific contaminants known to be present, which may impact a receiving body of water and for general aquatic toxicity of the discharge towards a sensitive stream species. Many of these requirements may be based on USEPA Water Quality Standards.[9,10] Water Quality Standards define the goals for a waterbody by designating its uses, setting criteria to protect those uses, and establishing provisions to protect water quality from pollutants. The standards cover textile dyeing by regulating discharges of organic species and metals such as copper, chromium, antimony, silver, and zinc.

The sources of organic species in textile dyeing operations include dye carriers, machine cleaners, emulsifiers, and dyestuffs. Metals are most commonly associated with dyes, but can also be found in other chemical products where they are used in the manufacturing process of the chemical products. An exception to this is antimony. The major source in polyester textile dyeing operations is the polyester itself. Polyester is typically manufactured by a process that employs an antimony catalyst. While most dyeing processes will extract small amounts, any form of pressure dyeing will extract antimony at levels that may impact a facility's compliance with CWA requirements. Silver is being used in textiles today as an antimicrobial agent. Normally these agents are applied after dyeing, but in some cases, the silver is present as a fiber or fiber component in the fabric itself. There is the potential for silver to be released from such products during dyeing operations.

Indirect dischargers are governed by the rules of the public utility, which are governed by other USEPA rules.[11] With USEPA approval, all of these systems are governed under state regulations, which are at least as strict as USEPA guidelines with oversight from the USEPA.

2.6 Air

The Clean Air Act (CAA) and its amendments, including the Clean Air Act Amendments (CAAA) of 1990, are designed to protect and enhance the air resources of the United States. The CAA consists of six sections which direct EPA to establish national standards for ambient air quality and for EPA and the States to implement, maintain, and enforce these standards.

CAA regulations appear in 40 CFR Parts 50-99. Pursuant to Title I of the CAA, EPA has established national ambient air quality standards (NAAQSs) to limit levels of 'criteria pollutants,' including carbon monoxide, lead, nitrogen dioxide, particulate matter, volatile organic compounds (VOCs), ozone, and sulfur dioxide. Geographic areas that meet NAAQSs for a given pollutant are classified as attainment areas; those that do not meet NAAQSs are classified as non-attainment areas. Under section 110 of the CAA, each State must develop a State Implementation Plan (SIP) to identify sources of air pollution and to determine what reductions are required to meet Federal air quality standards. Revised NAAQSs for particulates and ozone were proposed in 1996 and may go into effect as early as late 1997. Title I also authorizes EPA to establish New Source Performance Standards (NSPSs), which are nationally uniform emission standards for new stationary sources falling within particular industrial categories. NSPSs are based on the pollution control technology available to that category of industrial source. Under Title I; EPA establishes and enforces National Emission Standards for Hazardous Air Pollutants (NESHAPs), nationally uniform standards oriented towards controlling particular hazardous air pollutants (HAPs). Title I, section 112(c) of the CAA further directed EPA to develop a list of sources that emit any of 189 HAPs, and to develop regulations for these categories of sources. To date EPA has listed 174 categories and developed a schedule for the establishment of emission standards. The emission standards will be developed for both new and existing sources based on 'maximum achievable control technology' (MACT). The MACT is defined as the control technology achieving the maximum degree of reduction in the emission of the HAPs, taking into account cost and other factors.

Title IV of the CAA establishes a sulfur dioxide and nitrous oxide emissions program designed to reduce the formation of acid rain. Reduction of sulfur dioxide releases will be obtained by granting to certain sources limited emissions allowances, which, beginning in 1995, will be set below previous levels of sulfur dioxide releases. Title V of the CAA of 1990 created a permit program for all 'major sources' (and certain other sources) regulated under the CAA. One purpose of the operating permit is to include in a single document all air emissions requirements that apply to a given facility. States are developing the permit programs in accordance with guidance and regulations from EPA. Once a state program is approved by EPA, permits will be issued and monitored by that state. Title VI of the CAA is intended to protect stratospheric ozone by phasing out the manufacture of ozone-depleting chemicals and restrict their use and distribution. Production of Class I substances, including 15 kinds of chlorofluorocarbons (CFCs) and chloroform, were phased out (except for essential uses) in 1996.

The Clean Air Act governs the protection of the US air resources and impact textile dyeing operations in two main ways. First, the release of metals, organics, and particulates can be regulated. These 'Air Toxics' comprise a list of 189 Hazardous Air Pollutants (HAPs). In addition, general Volatile Organic Compounds (VOCs) are regulated. Legislation, referred to as the 'Textile MACT' specifies Maximum Achievable Control Technologies (MACT) under the umbrella of 'Fabric Printing, Coating, and Dyeing of Fabrics'. These rules required a final compliance date of May 29, 2006.[12] The principal HAPs targeted were toluene, methyl ethyl ketone (MEK), methanol, xylenes, methyl isobutyl ketone (MIBK), methylene chloride, trichloroethylene, n-hexane, glycol ethers (ethylene glycol), and formaldehyde.

The second is that all combustion sources are regulated; thus any boiler or other device providing hot water for textile dyeing is covered. A separate MACT Standard has been developed for 'Industrial, Commercial and Institutional Boilers and Process Heaters,' but referred to as the 'Boiler MACT' has a compliance date of September 13, 2007.

2.7 The Toxic Substances Control Act

The Toxic Substances Control Act (TSCA) granted USEPA authority to create a regulatory framework to collect data on chemicals in order to evaluate, assess, mitigate, and control risks, which may be posed by their manufacture, processing, and use. The TSCA framework provides a number of methods to prevent undue risk from exposure to chemicals in the United States. TSCA standards apply to a chemical any time in its 'cradle to grave' lifetime. Under TSCA, USEPA has established an inventory of chemical substances. If a chemical is not on the inventory and has not been specifically excluded by TSCA, a premanufacture notice (PMN) must be submitted to USEPA before manufacture or import. The PMN must give the identity of the chemical and provide available information on health and environmental effects. If enough information is not available to determine the chemical's effects, restrictions can be imposed until the development of information on its health and environmental effects. USEPA can also restrict significant new uses of chemicals based upon factors such as the projected volume and use of the chemical. In addition, USEPA can ban the manufacture or distribution in commerce, limit the use, require labeling, or place other restrictions on chemicals that pose risks beyond acceptable. The most familiar chemicals USEPA regulates under TSCA include chlorofluorocarbons (CFCs), asbestos, and polychlorinated biphenyls (PCBs).

For textile dyeing operations, the major impact of TSCA will be the notification to USEPA of chemicals that are imported from outside the US that are intended to be used in commerce. A textile dyeing operation cannot assume that imported products have met all the requirements, no matter how much testing has been completed or no matter how long the chemical has been used in other countries. Even research chemicals must be evaluated in relation to TSCA Standards. It is the responsibility of the importing company to make sure that any imported chemicals meet all the TSCA requirements.

2.8 California

In 1986, California voters approved an initiative to address their growing concerns about exposure to toxic chemicals. That initiative became the Safe Drinking Water and Toxic Enforcement Act of 1986, better known by its original name of Proposition 65. Proposition 65 requires the State to publish a list of chemicals known to cause cancer or birth defects or other reproductive harm. The current list includes around 750 chemicals.[13] Proposition 65 requires businesses to notify Californians about significant amounts of chemicals in the products they purchase, in their homes or workplaces, or that are released into the environment. By providing this information, Proposition 65 enables Californians to make informed decisions about protecting themselves from exposure to these chemicals. The Office of Environmental Health Hazard Assessment (OEHHA) administers the Proposition 65 program. OEHHA, which is part of the California Environmental Protection Agency (Cal/EPA), also evaluates all currently available scientific information on substances considered for placement on the Proposition 65 list. Chemicals can be added to or removed from the Proposition 65 list under the program.

The list contains a wide range of naturally occurring and synthetic chemicals that are known to cause cancer or birth defects or other reproductive harm. The chemicals include a wide range of uses including ingredients in pesticides, household products, foods, drugs, dyes, or solvents. Listed chemicals may also be used in manufacturing and construction, or they may be byproducts of chemical processes, such as car exhaust.

Businesses are required to provide an obvious warning before exposing anyone to a listed chemical. This warning can be given by a number of means, but for textile dyeing operations, the main way will be by labeling a consumer product or by providing information to the business providing the end product to the public.

There are several listed chemicals that may impact a textile dyeing operation. These include dyes such as Acid Red 114 and Direct Blue 218, both considered cancer risks under Proposition 65. The list also contains several chemicals that may be used in textile dyeing products including formaldehyde, certain glycols, and nickel compounds. Because trace levels of some compounds may be present in products used or because limited exposures are not considered harmful, OEHHA has developed safe harbor numbers. A business can declare ‘safe harbor’ from Proposition 65 warning requirements if exposure to a chemical occurs at or below these levels. These safe harbor numbers consist of no significant risk levels for chemicals listed as causing cancer and maximum allowable dose levels for chemicals listed as causing birth defects or other reproductive harm. OEHHA has established safe harbor numbers for nearly 250 chemicals and continues to study current levels and new possible listings.

2.9 Future trends

The future trends in US textile dyeing regulations will be governed by several forces. These will include US government research, academic research, customer requirements, public opinion, and what can be called the EU influence. Many current avenues of investigation into environmental impacts can be traced to research done in Europe and legislation first implemented in Europe. Examples include Consumer Protection Regulations on dyes from Germany and flame retardant legislation from Sweden.

The future trends in environmental legislation can be summarized by two words, 'specific and lower.' More specific chemical species will be evaluated for their impact on the environment, in addition to looking at general parameters. The trend is to look at individual chemicals or closely related families of chemicals. For 'lower,' analytical methods improve yearly and regulators are taking advantage of these advancements to explore just what is in the air and water. Also, Best Available Technologies (BAT) will allow for lower levels of pollutants to be released into the environment.

2.9.1 Regulatory

For a number of years, agreement has been that the method of regulating metals in wastewater does not take all factors into account, especially the speciation and bioavailability of the metals. The current USEPA effort is to conduct risk assessments of metals that take into account these factors, before imposing regulatory limits. Currently, USEPA has two methods they do allow to show that metals do not impact receiving streams. The older method that has been revised is the Water-Effects-Ratio (WER). This method can reduce the regulatory burden 10–50 times on metals such as copper and 5–10 times for metals such as zinc. This method relies on the use of laboratory Whole Effluent Toxicity Testing and is not accepted uniformly throughout the different states. The newer Biotic Ligand Model (BLM) method relies on data from the site itself and models the risk involved. It is intended to better simulate what is actually occurring in the stream. The method is new and studies continue as to its applicability for different types of metals and regulatory levels.[14]

Tributyl tin complexes have been used in textiles for many years as antimicrobial agents, although the use is not widespread. No Water Quality Criteria existed for these compounds until 2004 when USEPA introduced a part per trillion Water Quality Criteria.[15] The impact of this in textiles is not known since very little data has been collected from textile operations. Most operations do not use these complexes. The concern is the anecdotal evidence of unusual sources of these compounds. These complexes have been used in manufacturing as antitacking agents. It is also believed that some types of piping may have tributyl tin impurities. Could there be impurities from other sources that may impact textile dyeing directly? It is just not known.

Mercury has been regulated in wastewater for many years. What has changed recently is the implementation of a new method, USEPA 1669/1631E which has lowered the mercury quantification limit down to 0.50 ng l^{-1} (parts per trillion). This level is up to 100 times lower than facilities have experienced using previous testing methods. In addition, facilities face another problem with mercury. The National Atmospheric Mercury Deposition Network is collecting data that shows mercury levels in rainfall are up to 15 ng l^{-1}.[16] A concern is that USEPA will attempt to regulate mercury at levels lower than the rainfall in some areas, requiring facilities to treat rainwater or surface water. This would impact textile dyeing in that the water would need to be treated either before use in processing or after processing, for a contaminant not arising from the textile process.

Color continues to be a parameter of concern to USEPA. Although no studies have shown color is a pollutant in the normal sense, it is believed that from a public perception point of view it should be regulated. There are some facilities that have been given color limits in the US, but the practice is not widespread because a consensus has not been formed on when color becomes a problem and how it should be regulated. The State of South Carolina has begun gathering data on the levels of color found in the wastewater effluent of facilities and in the receiving streams. Currently, there are no restrictions on the color levels and the data is being gathered for future evaluation.

Surfactants continue to be a concern worldwide. In many areas of the world, alkyl phenol ethoxylates are banned or restricted. In the United States, the only restrictions are related to their impact on aquatic toxicity of effluents from operations. Suggestions have been made for the replacement of these products including alcohol ethoxylates and quaternary ammonium compounds. However, the impact of these is still under investigation and standard testing procedures for these chemicals have not been developed.[17] Further research will provide guidance on the impact, measurement, and, therefore, requirements for the use of surfactants in textile dyeing operations in the future.

One critical need in determining the impact of textile dyeing on the environment is information. Through the adoption of Globally Harmonized Standards, Material Safety Data Sheets, required by OSHA in the United States, will be more standard in the information on chemical ingredients and hazards.[18] Still in use in the United States is the ATMI Voluntary Product Safety & Environmental Profile, which is a voluntary document completed by vendors, suppliers, and manufacturers to provide textile operations with more detailed information on the products they provide.[19] A new version of the form is currently under development by the Institute of Textile Technology, which will encompass new regulations and information sources that have arisen since the 1997 version.

2.9.2 Sustainability and environmental management

Another source of interest in the environment for textile-dyeing operations is the effort to make operations more sustainable within the regulatory, customer, and public sectors. There are no current regulatory requirements that directly require any textile dyeing operation in the United States to practice sustainability. However, USEPA is beginning to view its programs within the larger frame of the idea of sustainability.[20] Of course, the major problem is that 'sustainability' cannot be defined. The Georgia Tech Research Institute states:

> Sustainability is a relationship, or balancing act, between factors which are constantly changing. Like 'family values,' everyone agrees that sustainability is a good thing, but no one agrees on what exactly it is or, even more significantly, how to achieve it and how to know when we have achieved it.

Various groups are evaluating how textile operations can approach a defined level of sustainability. Groups such as GreenBlue,[21] Business for Social Responsibility,[22] The Institute for Market Transformation to Sustainability,[23] Association for Contract Textiles,[24] Bromine Science and Environmental Forum,[25] and Wal-Mart[26] are all developing either guidelines, standards, or labeling policies for textiles that would impact dyeing operations. Many companies are reviewing systems such as Oeko-Tex for measuring chemical exposures of the consumer from the products they sell.[27] Another approach is the use of Environmental Management Systems (EMS) such as the ISO 14000 Series of Standards.[28] With ISO, the management of the environmental program within a company provides a basis for environmental stewardship.

Whichever systems are actually put into place, textile dyeing operations will be exposed to requirements that may be just as important as those that carry a regulatory burden due to the potential of loss of business. These requirements may also have the potential of being in conflict with each other and may not properly consider the economic impact on textile dyeing operations.

2.9.3 Interest groups

Although not impacted to the extent of larger chemical users, textile dyeing operations are being reviewed. Greenpeace Research Laboratories has published 'An Overview of Textile Processing and Related Environmental Concerns' which highlights '…major sources of environmental contamination'.[29] As stated previously, groups such at the Environmental Defense Fund publish a 'Scorecard' for industrial chemical users, which includes textile dyeing operations.[30] It is not clear how new legislation, such as California's carbon dioxide emission limits, will affect textile dyeing operations.[31] In the future, USA interest groups can impact textile dyeing operations through requests for legislation and new standards.

2.10 Sources of further information and advice

There are many sources of information on textile dyeing operations. These include industry groups, universities, government agencies, and interest groups. In today's electronic world, the internet has become the fastest way to obtain sources, replacing paper sources. The following lists give different types of internet sources where information can be obtained.

Disclaimer: The information provided in this chapter is not intended to relieve the reader of the responsibility of 'due diligence' to comply with all rules, regulations, and statutes. It is believed that the information is accurate at the time of preparation, but no warranty is provided to the reader and no liability will be assumed from the use of this document, regardless of claims.

2.10.1 General sources

Environmental, regulatory, and scientific links of author, www.itt.edu/documents/WebDocs/drhenry.html
Federal Register and CFR portal, www.gpoaccess.gov/index.html
Institute of Textile Technology Textile Links, www.itt.edu/links/liblinks.cfm
NC State University College of Textiles http://www.tx.ncsu.edu/centers_programs_initiatives.html
Textile compliance assistance clearinghouse, cfpub.epa.gov/clearinghouse/
United States Environmental Protection Agency, www.epa.gov
USEPA air portal, www.epa.gov/ttn/atw/
USEPA hotlines and clearinghouses, www.epa.gov/epahome/hotline.htm
USEPA regional offices, www.epa.gov/epahome/whereyoulive.htm
USEPA sustainability portal, www.epa.gov/sustainability/
USEPA TRI compliance portal, www.epa.gov/tri/
USEPA waste portal, www.epa.gov/osw/
USEPA wastewater portal, www.epa.gov/owm/

2.10.2 Textiles groups

American Association of Textile Chemists and Colorists, www.aatcc.org
American Fiber Manufacturers Association, www.afma.org/fiber.html
APE Research Council, www.aperc.org
CCACTI, www.gatip.org/tcwhatisccacti.html
Cotton Incorporated, www.cottoninc.com
Industrial Fabrics Association International, www.ifai.com
National Council of Textile Organizations, www.ncto.org
National Textile Association, www.nationaltextile.org
Oeko-Tex, www.oeko-tex.com

Society of Dyers and Colourists, www.sdc.org.uk
The Textile Institute of Great Britain, www.texi.org

2.10.3 Textiles schools

Auburn University, www.eng.auburn.edu/txen/
Clemson University, mse.clemson.edu
University of Georgia, www.fcs.uga.edu/tmi/index.html
Georgia Tech, www.tfe.gatech.edu
Institute of Textile Technology, www.itt.edu
North Carolina State University, www.tx.ncsu.edu
Philadelphia University, www.philau.edu/schools/tmt/index.htm

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4. US EPA 560-4-88-004h, 'Estimating Chemical Releases From Textile Dyeing', February 1988.
5. US EPA 530-K-02-028, 'RCRA in Focus – Textile Manufacturing'.
6. CFR Title 40, Part 410, 'Textile Mills Point Source Category'.
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8. US EPA 600-2-78-098, 'Textile Dyeing Wastewaters: Characterization and Treatment', 1978.
9. US EPA 823-B-94-005a, 'Water Quality Standards Handbook: Second Addition', August 1994.
10. http://www.epa.gov/wqsdatabase/, accessed September 1, 2006.
11. CFR Title 40, Part 403,437, 'Centralized Waste Treatment Point Source Category'.
12. http://www.epa.gov/ttn/atw/mactfnlalph.html, accessed September 1, 2006.
13. http://www.oehha.org/prop65.html, accessed September 1, 2006.
14. Hogue, C., 'Metallic refinement', *Chemical and Engineering News*, **2004**, **82**(32), 23–24.
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3

Toxicology of textile dyes

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3.1 Introduction

This chapter addresses the toxicology of textile dyes. Section 3.2 takes a brief look at the historical aspects, particularly around the mid-twentieth century when a link between dyes (and their intermediates) and bladder cancer in textile workers became apparent.

In Section 3.3, the acute (short-term) toxicological effects of textile dyes are discussed. The short-term problems are skin irritation and skin sensitisation, caused primarily by reactive dyes for cotton and viscose, and disperse dyes for polyester, polyamide and acetate rayon.

The main part of the chapter, Section 3.4, is concerned with the chronic (long-term) effects of textile dyes. Carcinogenicity (cancer-causing) is the main chronic effect and this is covered in detail. The known data is reviewed and structure–carcinogenicity relationships for textile dyes, particularly the most important class, azo dyes, are discussed. Other dye classes, such as anthraquinone dyes and cationic (basic) dyes, as well as the building blocks of dyes, the chemical intermediates, are also covered. The mode of action of carcinogenic dyes and their metabolites are elucidated and ways to avoid and eliminate carcinogenicity in textile dyes are presented. The section ends with a look at metal complex dyes and the toxicological implications of metals.

Section 3.5 considers future trends for textile dyes in relation to toxicology. This includes the design of safer dyes by utilising the extensive and ever-increasing knowledge of the relationships between the structure of dyes and toxicity, cleaner dyes, and by having more consideration regarding the formation of toxic products during the degradation of waste dyes in effluent treatment plants. The role of natural dyes is also discussed.

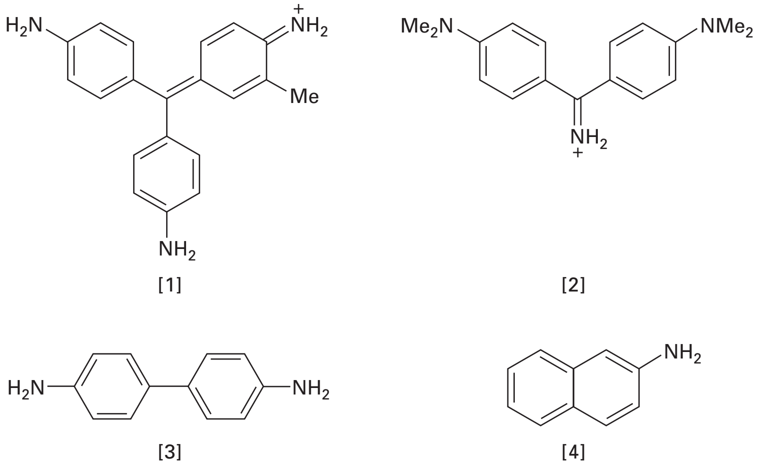
Finally, Section 3.6 concludes the chapter by presenting sources of further information and advice regarding the toxicology of textile dyes.

3.2 Historical aspects

Colorants have been used by mankind for many thousands of years. The earliest known use of a colorant was by Neanderthal man about 180 000 years ago. They used red ochre (essentially iron oxide), an inorganic pigment obtained from riverbeds, to daub the bodies of the dead before burial. The first known use of an organic colorant was much later, *c.* 4000 years ago, when the blue dye indigo was found in the wrappings of mummies in Egyptian tombs (Gordon, 1983). It is highly unlikely that either Neanderthal man or the ancient Egyptians considered the toxicological aspects of the colorants they used.

Until the late nineteenth century, all the colorants were obtained from nature. The main sources of natural dyes were plants, but insects and molluscs were also used. Vast amounts of raw materials were required to produce a tiny amount of impure dye and the process was land and labour intensive (Gordon, 1983). This meant that the workers involved in obtaining natural dyes were generally only exposed to dilute amounts of the dye. Furthermore, they never had to handle any chemical intermediates to synthesise the dyes, unlike their modern counterparts.

It was not until after Perkin's historic discovery of the first synthetic dye, mauveine, in 1856, that dyes (and later pigments) were manufactured on a large scale. The workers involved in the manufacture of dyes became exposed not only to the dyes themselves but also to the chemical intermediates used in their manufacture. Many years later, it became apparent that workers involved in the manufacture of certain dyes, such as fuchsine (see Fig. 3.1, C.I. Basic Violet 14 [1]) and auramine (C.I. Basic Yellow 2 [2]), and particularly



3.1 Structures of fuchsine (C.I. Basic Violet 14 [1]), auramine (C.I. Basic Yellow 2 [2]), benzidine [3] and 2-naphthylamine [4].

dyes based on benzidine [3] and 2-naphthylamine [4], developed a high incidence of bladder cancer (Hunger, 2003). It was established later that both benzidine and 2-naphthylamine are indeed human bladder carcinogens. Once this information was known, all responsible dye manufacturers took action to cease production of these proven human carcinogens and any dyes using them. It is to its eternal credit that the colorant manufacturing industry of Western Europe began to investigate the toxicological and ecotoxicological properties of dyes (and pigments) long before chemical and environmental regulations existed. Thus, in 1974, the member companies of ETAD (Ecological and Toxicological Association of Dyes and Organic Pigment Manufacturers) voluntarily developed Safety Data Sheets with appropriate information on the hazardous potential of colorants. Nowadays, the concept of Safety Data Sheets has spread worldwide (Hunger, 2003).

The world production of colorants is *c*. 1 million tonnes per year, of which *c*. 50% are textile dyes (Nousiainen, 1997). Textile dyes are therefore very important. They are also ubiquitous, being encountered in almost every aspect of our daily lives. For example, we are constantly in direct contact with textile dyes because of the clothes we wear, and in indirect contact with them because of furnishings, such as bedding, carpets, curtains, lounge suites and car seats. Therefore, it is imperative that textile dyes are non-toxic and safe. To ensure this is the case, very strict test protocols exist which every textile dye must pass before it is allowed on to the marketplace. Currently, the three main regulatory bodies worldwide are the European Inventory of Existing Commercial Substances (EINECS), the Toxic Substances Control Act (TSCA) in the USA, and the Ministry of Technology and Industry (MITI) in Japan (Hunger, 1991).

For registration of a textile dye in the European Union, a registration package is required which includes:

1. Identity of the substance
2. Information on the substance
3. Physico-chemical properties of the substance
4. Toxicological studies
5. Eco-toxicological studies.

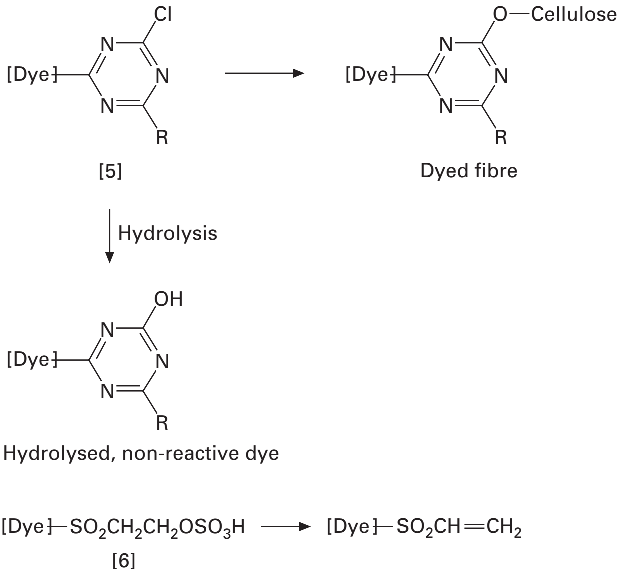
It is the toxicological aspects of textile dyes that are discussed in this chapter. These may be divided into acute, or short-term effects and chronic, or long-term effects.

3.3 Acute toxicity of textile dyes

Acute toxicity involves oral ingestion and inhalation, skin and eye irritation, and skin sensitisation. The main problems of acute toxicity with textile dyes are skin irritation and skin sensitisation, caused mainly by reactive dyes for cotton and viscose, and disperse dyes for polyester, polyamide and acetate rayon. A comprehensive review of acute toxicity data, including skin and eye irritation of numerous commercial dyes, obtained from Safety Data Sheets, revealed that the potential for these acute toxic effects was very low (Anliker, 1979). However, dermatologists have reported skin reactions thought to be caused by reactive dyes and disperse dyes (Hatch, 1984, 1986, 1998, 1999; Pratt, 2000; Tronnier, 2002).

Reactive dyes for cotton are water-soluble dyes, which contain a group capable of forming a covalent bond with the hydroxyl groups in the cellulose polymer during the dyeing process. The two main reactive groups, as shown in Fig. 3.2, are the monochlorotriazinyl (MCT) group [5] and the *beta*-sulphatoethylsulphone [masked vinyl sulphone (VS)] group [6], either alone or in combination (Gordon, 1983). Once the reactive dye has been used to colour the cellulosic fabric, no reactive dye should remain. The reactive dye is bound to the fibre with a covalent ether bond and any reactive dye that did not become attached to the fibre will have been hydrolysed in the dyeing process and removed in the dyebath effluent. Therefore, fabrics dyed with reactive dyes should pose no problems for the end-user of the product, the general public.

Reactive dyes can, however, cause problems in plant workers who manufacture the dyes and textile workers who handle the dyes in the dyeing process. There is evidence that some reactive dyes cause contact dermatitis, allergic conjunctivitis, rhinitis, occupational asthma or other allergic reactions



$[\mathrm{Dye}]\text{–}SO_2CH_2CH_2OSO_3H \longrightarrow [\mathrm{Dye}]\text{–}SO_2CH{=}CH_2$

3.2 The fate of reactive dyes in the dyeing process.

in such workers. The problem is caused by the ability of reactive dyes to combine with human serum albumin (HSA) to give a dye-HSA conjugate, which acts as an antigen. The antigen produces specific immunoglobulin E (IgE) and, through the release of chemicals such as histamine, causes allergic reactions (Hunger, 2003; Luczynska, 1986). A study done in 1985 of 414 workers, such as dye-house operators, dye-store workers, mixers, weighers and laboratory staff, who were exposed to reactive dye powders, found that 21 of them were identified as having allergic reactions, including occupational asthma, due to one or more reactive dyes (Hunger, 2003; Platzek, 1997).

A list of reactive dyes that have caused respiratory or skin sensitisation in workers on occupational exposure has been compiled by ETAD (Table 3.1) (Hunger, 2003; Motschi, 2000). In order to minimise the risk from reactive dyes, exposure to dye dust should be avoided. This may be achieved by using liquid dyes, low dusting formulations and by using the appropriate personal protective equipment. As mentioned earlier, after dyeing and fixation,

Table 3.1 Reactive dyes classified as respiratory/skin sensitisers

C.I.[*] name	C.I. no.	CAS[†] no.
Reactive Yellow 25		[72139-14-1](3Na)
Reactive Yellow 39	18971	[70247-70-0](2Na)
Reactive Yellow 175		[111850-27-2](2Na)
Reactive Orange 4	18260	[70616-90-9](3Na)
Reactive Orange 12	13248	[70161-14-7](3Na) [93658-87-8](xNa)
Reactive Orange 14		[12225-86-4](acid)
Reactive Orange 16		[20262-58-2](2Na) [106027-83-2](2Li)
Reactive Orange 64		[83763-57-9](xNa)
Reactive Orange 67		[83763-54-6](xNa)
Reactive Orange 86		[57359-00-9](3Na)
Reactive Orange 91		[63817-39-0](3Na)
Reactive Red 29		[94006-25-4](5Na) [70865-39-3](4Na)
Reactive Red 65		[70210-40-1](2Na)
Reactive Red 66	17555	[70210-39-8[(2Na)
Reactive Red 123		[85391-83-9](xNa) [68959-17-1](2Na)
Reactive Red 219		[149057-72-7](4Na)
Reactive Red 225		[83399-95-5](xNa)
Reactive Violet 33		[69121-25-1](3Na)
Reactive Blue 114		[72139-17-4](2Na)
Reactive Blue 204		[85153-92-0](6Na)
Reactive Black 5	20505	[17095-24-8](4Na)

[*] Colour Index, a comprehensive listing of the tradenames, properties and structures, if known, of all commercial dyes and pigments.
[†] Chemical Abstract Services.

reactive dyes have completely different toxicological properties because the reactive group is no longer present and the high water-fastness of the dyed fabric ensures that no dye is exposed to the skin of the wearer. Consequently, no cases of allergic reactions have been reported by consumers wearing textiles dyed with reactive dyes (Hunger, 2003).

Certain disperse dyes have been implicated in causing allergic reactions, particularly when they are used for skin-tight, close-fitting clothes made from synthetic fibres. The sweat-fastness properties of the dyes are important as to whether an allergic response is caused or not. Polyester dyed with disperse dyes does not in general pose a problem since the sweat-fastness is high. However, problems can arise with polyamide or acetate rayon dyed with disperse dyes, which have a sensitising potential since the low sweat-fastness allows the dyes to migrate to the skin (Wattie, 1987). Indeed, in the 1980s, some severe cases of allergic reactions were reported (Hausen, 1984) relating to stockings made of polyamide and, in the 1990s, to leggings made of acetate rayon (Hausen, 1993). Because of these allergic reactions, the German Federal Institute for Consumer Protection and Veterinary Medicine evaluated the available literature and concluded that the disperse dyes listed in Table 3.2 represent a health risk to consumers and should cease to be used for clothes (Hunger, 2003).

Currently, there is no legal prohibition on these dyes in any country but some organisations, such as the International Association for Research and Testing in the Field of Textile Ecology, which bestows eco-labels on environmentally and toxicologically proven textiles, refuses eco-labels for some dyes (Oko-Tex, 2000).

3.4 Chronic toxicity of textile dyes

Genotoxicity is the major long-term potential health hazard of certain textile dyes. As mentioned in Section 3.2 this became apparent when a high incidence of bladder cancer was observed in plant workers involved in the manufacture

Table 3.2 Disperse dyes considered a health risk to consumers

C.I. name	C.I. no.	CAS no.
Disperse Yellow 3	11855	[2832-40-8]
Disperse Orange 3	11005	[730-40-5]
Disperse Orange 37/76		[12223-33-5]
Disperse Red 1	1110	[2872-52-8]
Disperse Blue 1	64500	[2475-45-8]
Disperse Blue 35		[12222-75-2]
Disperse Blue 106	11935	[68516-81-4]
Disperse Blue 124	111938	[15141-18-1]

of particular dyes during the period 1930–1960. The specific compounds involved (shown in Fig. 3.1) were fuchsine [1], auramine [2], benzidine [3] and 2-naphthylamine [4]. Strict regulations concerning the handling of all known carcinogens have been imposed in most industrial countries, which has caused virtually all dye companies to cease production of these compounds (Hunger, 2003).

Genotoxic chemicals include mutagens, carcinogens and teratogens. Mutagens produce mutations in living organisms. Indeed, one of the first tests involved in screening a new molecule for genotoxicity, the Ames test, assesses whether the chemical causes mutations in the bacterium *Salmonella typhimurium* (Hunger, 2003). Mutagenic chemicals may or may not be carcinogens (cause cancer) in animals and humans. However, since the Ames test is a highly sensitive assay for the induction of point mutations in bacteria, rather than a test for the complex multiple-step process of carcinogenesis in mammals, a close correlation between the Ames test results and rodent cancer assays cannot be expected (ETAD, 1998). Validation studies (Ashby, 1989) show a fairly low degree of correlation between mutagenicity in bacteria and carcinogenicity in rodents. In practice, further tests are carried out in addition to the Ames test. These include further *in vitro* tests, such as the mouse lymphoma test (a gene mutation test) and the cytogenetic test (a chromosome aberration assay). If these tests prove positive, then *in vivo* tests, such as the mouse micronucleus test and the rats' liver unscheduled DNA synthesis (UDS) are done in order to ascertain if the genotoxic potential demonstrated *in vitro* is expressed as cancer in a living rodent.

Teratogens are responsible for birth defects in the offspring of organisms. Thalidomide was a teratogen, causing deformities in babies born in the 1950s. Teratogenicity is very uncommon in textile dyes and is not discussed further.

3.4.1 Effect of physical properties on genotoxicity

Genotoxic chemicals such as mutagens and carcinogens damage DNA (deoxyribonucleic acid), the genetic blueprint material, usually by chemical reaction. Therefore, it follows that any genotoxic chemical must satisfy two criteria:

1. It must reach the DNA (which resides in the nucleus of the cell) in order for the chemical to interact with the DNA.
2. It must possess the ability to interact with the DNA, usually by a chemical reaction.

In order to express a genotoxic effect, a chemical must first come into contact with the DNA present in a cell nucleus. To do this it must be able to transport across the protective cell membranes. Physical factors such as solubility and molecular size are of paramount importance in determining whether this transport occurs.

In general, smaller molecules are transported across cell membranes more readily than larger molecules. Above a certain molecular size (*c.* MW > 800), molecules become too large to transport across cell membranes. Thus, molecular size offers one way of obtaining non-genotoxic chemicals. Indeed, this approach was adopted by Dynapol to produce non-toxic food dyes (Gordon, 1984). (It is noteworthy that, although the project was technically successful and a small range of prototype polymeric food dyes produced, they never reached the marketplace. Initial tests horrified the volunteers taking part since the dyes were excreted from the body totally unchanged from their original bright colours!). In the textile dye area, phthalocyanine dyes are probably too large to pass through the cell membranes and should be non-genotoxic (Gregory, 1991).

The two extreme cases of high water solubility on the one hand and total insolubility on the other hand generally result in non-genotoxic chemicals (Gregory, 1986; Longstaff, 1983). Pigments, by definition, are insoluble in both water and organic solvents. This insolubility, combined with the relatively large size (*c.* 0.1 to 3 μm) of pigment particles, which are aggregates of millions of individual molecules, ensures that most pigments are not transported across cell membranes. Consequently, the majority of pigments are non-carcinogenic (El Dareer, 1984).

Molecules with high water solubility are also non-genotoxic. There are two major reasons for this. First, the hydrophobic (fatty) nature of the cell membrane is impervious to the hydrophilic water-soluble molecules. Secondly, water-soluble molecules are generally excreted rapidly by a living organism. The best chemical grouping for imparting water solubility is the sulphonic acid ($-SO_3H$) group. Carboxylic acid ($-CO_2H$) groups and hydroxyl ($-OH$) groups are also useful water-solubilising groups, especially when ionised (Freeman, 2005). These three types of groups are employed extensively in textile dyes. A quaternary nitrogen atom ($-N^+R_4$) also imparts water solubility. This group is found in cationic (basic) dyes.

3.4.2 Classes of carcinogens based on chemical structure

DNA is nucleophilic. Therefore, the active species of most carcinogens, known as the ultimate carcinogen, is an electrophile, E. In most cases, the electrophile is either a nitrenium ion R_2N^+ or a carbonium ion R_3C^+. These ultimate carcinogens attack a nucleophilic site in DNA, which may be a carbon, nitrogen or oxygen atom, to form a covalent chemical bond (equation 3.1).

$$E + [DNA] \rightarrow E\text{–}[DNA] \qquad [3.1]$$

As well as chemical reaction, intercalation is another way for molecules to interact with DNA. In this interaction, a flat portion of the molecule inserts itself into the DNA helix (Gregory, 1991).

3.4.3 Carcinogens based on nitrogen electrophiles

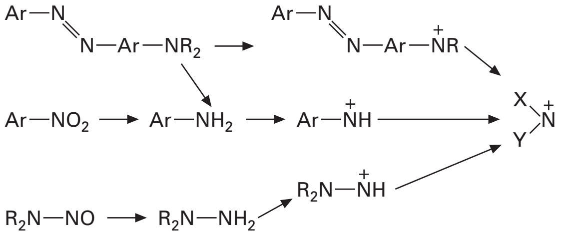
Since an electron-deficient nitrogen atom is a key feature of this class, then obviously all the carcinogens in this class must contain at least one nitrogen atom. The types of chemicals involved vary considerably but include amines, amine derivatives, such as nitrosamines, hydroxylamines and hydrazines, and amine precursors such as nitro compounds. However, the most important type is the amino-containing dye. Figure 3.3 shows how all these compounds produce a common ultimate carcinogen, a nitrenium ion.

Azo dyes are by far the most important class of dye, accounting for over 50% of the world annual production of *c.* 1 million tonnes of dyes (and pigments). Not surprisingly, azo dyes have been studied more than any other class. Therefore, azo dyes will be discussed first.

Azo dyes

The carcinogen may be the dye itself, or it may be a metabolite of the dye. For water-insoluble, but solvent-soluble dyes, such as solvent dyes and disperse dyes, the dye is normally the carcinogen. These dyes usually exist in the azo tautomeric form (Gordon, 1983). For water-soluble dyes, it is a metabolite of the dye which is the carcinogen. These dyes normally exist in the hydrazone tautomeric form. Generally, the azo form has greater stability than the hydrazone form, being more resistant to photo-oxidation (displaying higher light fastness) and to chemical oxidation (displaying better bleach fastness). Indeed, it has been postulated that dyes in the hydrazone form are more easily reduced to their metabolites than dyes in the azo form (Gregory, 1986).

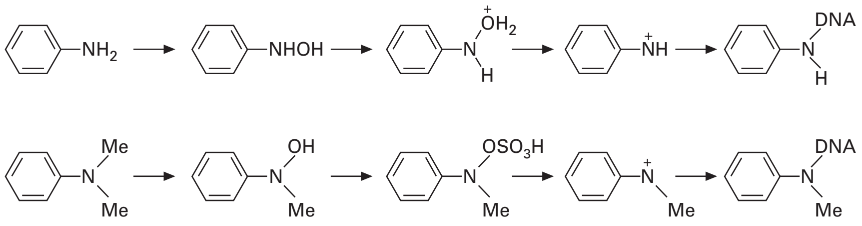
The most prevalent pathway for amine activation for solvent and disperse azo dyes is *N*-hydroxylation. This occurs at a primary or secondary amino



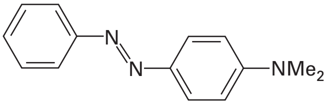
3.3 Carcinogens from nitrogen electrophiles.

group. In dyes containing methylamino- or dimethylamino-groups, the *N*-hydroxylation step is generally preceded by oxidative demethylation. *N*-Hydroxylation appears to be the rate-determining step since it correlates well with the observed carcinogenic activity (Kimura, 1982). Carbon (C– or ring–) hydroxylation can also occur. However, all three oxidative pathways leave the azo group intact (Hunger, 2003), (Hunger, 1994), (Brown, 1993).

The generally accepted mechanism of *N*-hydroxylation is depicted in Fig. 3.4. It applies both to aminoazo dyes, such as Butter Yellow (see Fig. 3.5 [7]), and aromatic amines. Two pathways are shown, one involving a



3.4 Mechanisms for amine activation.



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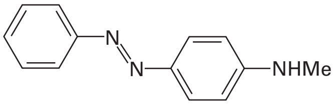

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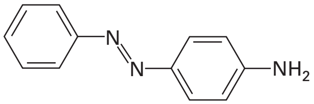

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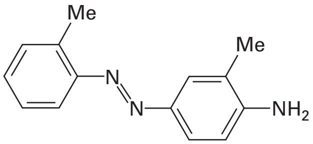

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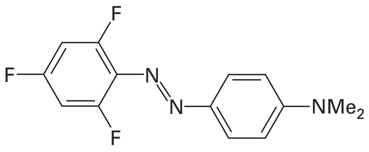

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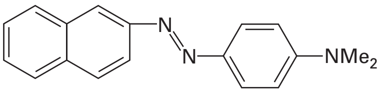

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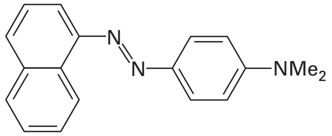
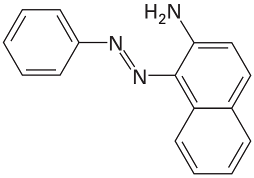


[13]

3.5 Carcinogenic 4-aminoazo dyes including Butter Yellow [7].

dimethylamino-group and one a primary amino-group. In both cases, the *N*-hydroxylated intermediate is formed. The electrophilic species is formed either by acylation of the hydroxyl group (formation of the sulphate ester in the example shown) or by protonation of the hydroxyl group. Both of these are good leaving groups and allow facile reaction with DNA, ostensibly via the nitrenium ion.

The carcinogenicity of aminoazo disperse and solvent dyes has been studied extensively (Beland, 1980; Tarpley, 1980; Kadlubar, 1976; Jen-Kun Lin, 1975a; Jen-Kun Lin, 1975b). Dyes such as Butter Yellow [7] and its analogues may be divided into two groups: 4-aminoazo dyes and 2-aminoazo dyes (Gregory, 1986). A comprehensive study (Longstaff, 1983) showed that all the 4-aminoazo dyes [7–13] in Fig. 3.5 were animal carcinogens. In contrast, the 2-aminoazo dyes [14–16] in Fig. 3.6 were not animal carcinogens. This rather surprising but potentially useful observation may be due to several factors, such as intramolecular hydrogen-bonding, steric hindrance or the facile oxidation to benzotriazole. A plausible mechanism for the reported non-carcinogenicity of 2-aminoarylazo dyes is shown in Fig. 3.7. The nitrenium ion from the 2-aminoarylazo dye is ideally set up for benzotriazole formation. However, not all 2-aminoarylazo dyes are non-carcinogenic (see later).



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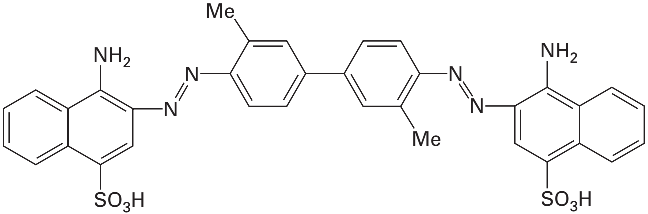

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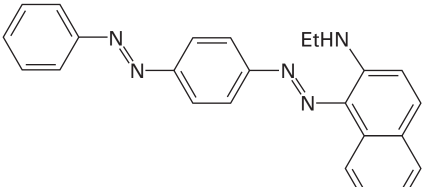
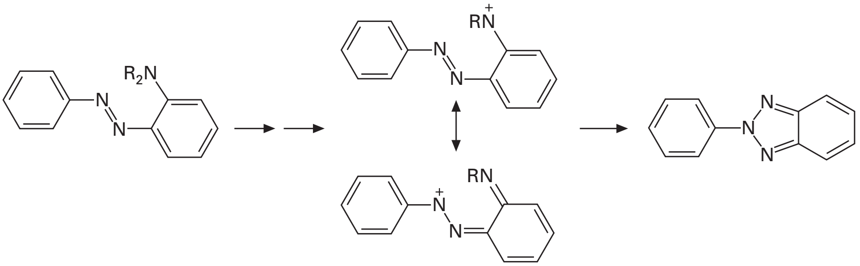


[16]

3.6 Non-carcinogenic 2-aminoazo dyes.



3.7 Benzotriazole formation from 2-aminoarylazo dyes.

Dimethylamino-groups and primary amino-groups are implicated in causing mutagenic and carcinogenic effects in aminoazo dyes (Kitao, 1982). However, one way to render such dyes non-mutagenic is to incorporate a cycloalkyl group, such as a piperidino-group, into the dye. Thus, the piperidino-analogue [17], Fig. 3.8, of Butter Yellow [7] is non-mutagenic (Ashby, 1983).

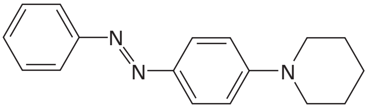
Azophenols also exist in the azo tautomeric form. These dyes are relatively unimportant commercially and have therefore received little attention in terms of toxicology studies. One dye [18], Fig. 3.9, that has been studied was found not to be an animal carcinogen (Gregory, 1986).

Water-soluble azo dyes based on the letter acids such as H-acid, J-acid and Gamma-acid represent a very important class of dyes for dyeing hydrophilic textiles such as cotton and viscose rayon. Cotton is the world's most widely used textile fabric so the tonnages of these water-soluble dyes are extremely large. The dyes are conveniently divided into two types:

1. Those which are capable of generating a carcinogenic metabolite, and
2. Those that are not.

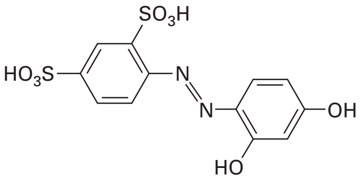
The workers who developed bladder cancer from handling dyes based on benzidine or 2-naphthylamine got the disease not from the dyes themselves, but from the benzidine and 2-naphthylamine metabolites. Indeed, it has been demonstrated that workers exposed to the dust of benzidine-based dyes excreted benzidine and the related metabolites *N*-acetyl and *N*,*N*-diacetylbenzidine (Anliker, 1988). Benzidine has also been detected in the blood serum of female textile workers in dye printing, warehouse and colour room shops (Korosteleva, 1974). The dyes [19–21], shown in Fig. 3.10, are typical of water-soluble azo dyes that generate a carcinogenic metabolite upon reduction in the animal body (Longstaff, 1983), (Gregory, 1986). For example, the dye [21] generates benzidine [3].

There are two main ways to circumvent the carcinogenicity of such dyes. The first way is to use non-carcinogenic analogues of the amines in question, such as benzidine or its derivatives. For example, in Fig. 3.11, C.I. Direct Black 171 [22] uses a non-carcinogenic aromatic benzimidazole diamine [23] (Gregory, 1991) instead of the benzidine [3] used in the similar dye C.I.



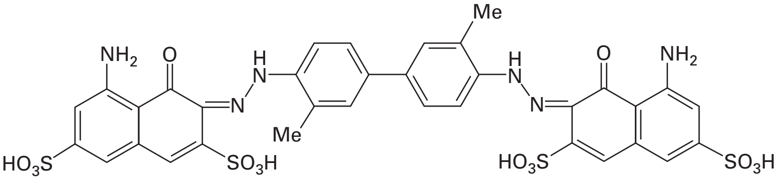
[17]

3.8 The piperidino analogue of Butter Yellow [7].



[18]

3.9 A non-carcinogenic azophenol in the azo tautomeric form.



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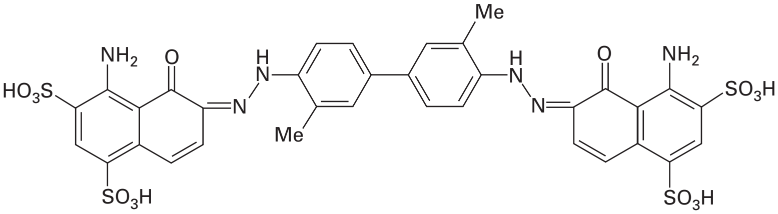

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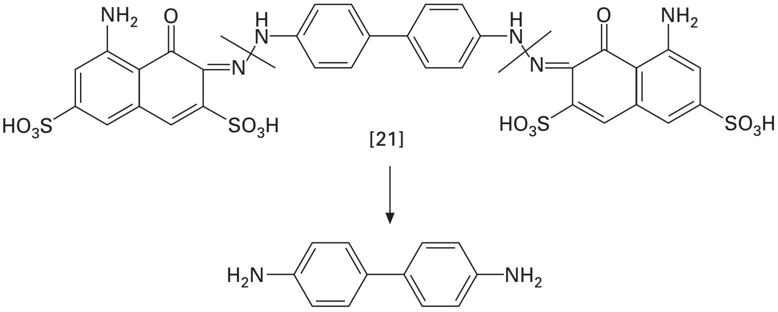
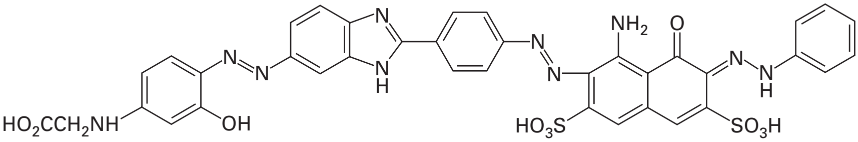


[21]

[3]

3.10 Typical water-soluble azo dyes that generate carcinogenic metabolites.



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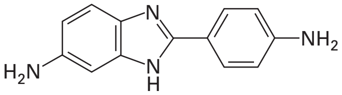
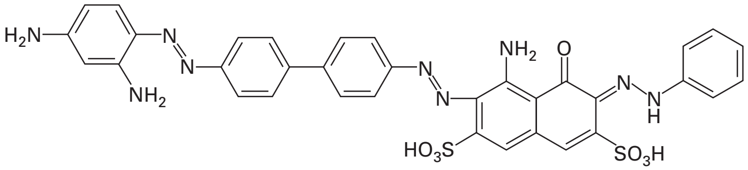


[23]



[24]

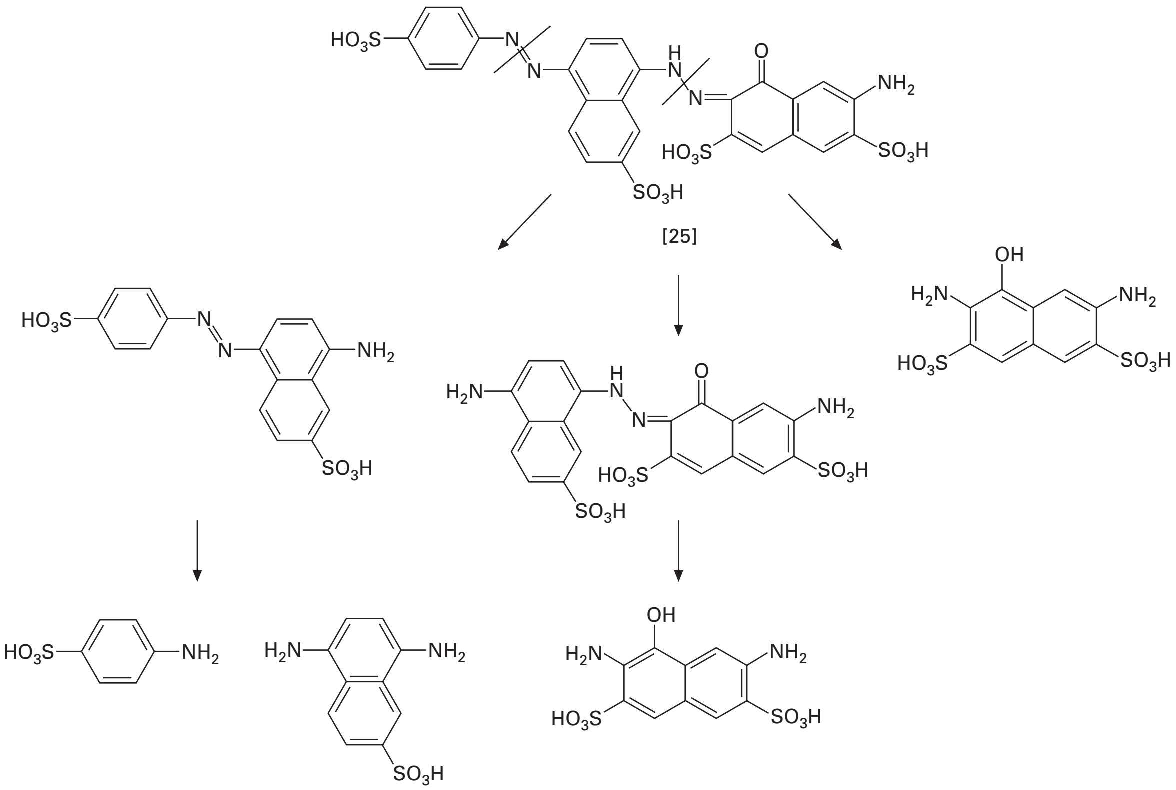
3.11 Use of non-carcinogenic aromatic benzimidazole diamine [23] and benzidine [3] in C.I. Direct Black 171 [22] and C.I. Direct Black 38 [24].

Direct Black 38 [24] (Freeman, 2005). When the latter dye was fed to Rhesus monkeys, benzidine was detected in their urine (Rinde,1975).

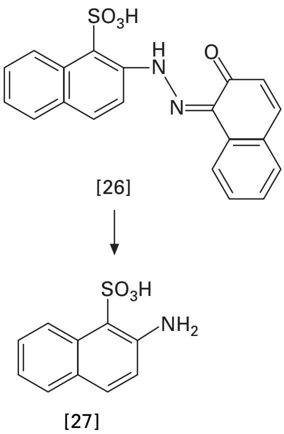
The second way to avoid carcinogenicity is to ensure that all possible metabolites of the dye are water-soluble. An excellent example of this principle is shown in Fig. 3.12, where the degradation of C.I. Food Black 2 [25], a dye used in black inks for ink jet printers (Gregory, 1991), gives metabolites of the dye which contain at least one water-solubilising sulphonic group. This ensures that the dye itself, plus any of its metabolites, are water-soluble.

Further water-soluble dyes that generate water-soluble metabolites and are non-carcinogenic, are given in Gregory (1986). The power of the water-solubilising sulphonic acid group to detoxify dyes and intermediates is beautifully demonstrated by the dye [26] in Fig. 3.13. This dye is non-carcinogenic. Upon reductive cleavage, it would produce, as one metabolite, 2-naphthylamine-1-sulphonic acid (Tobias acid) [27]. As seen earlier, 2-naphthylamine is a potent human bladder carcinogen. However, the presence of just one sulphonic acid group renders it harmless! Indeed, the sulphonic acid group is an excellent detoxifying group both for dyes and their intermediates.

The position of a genotoxic group within a dye also determines whether or not the dye expresses genotoxicity. C.I. Direct Black 17 [28] provides such an example as shown in Fig. 3.14. In this dye, the carcinogen cresidine [29] is present as a middle component (M-component). The dye is a mutagen,

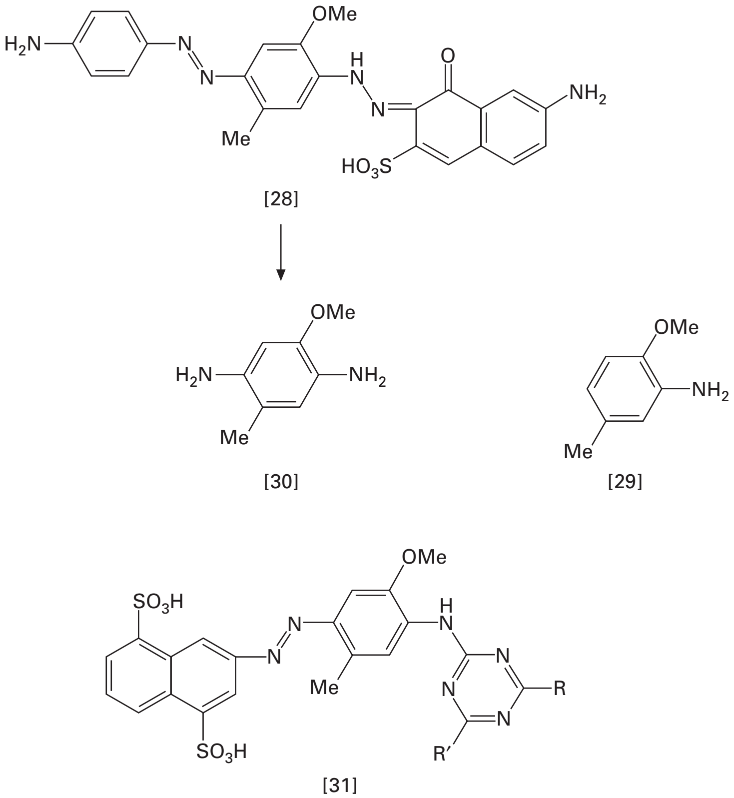


3.12 Probable degradation products of C.I. Food Black 2 [25].


[26]

[27]

3.13 Use of a water-solubilising sulphonic acid group in reductive cleavage of dyes to give a non-carcinogenic metabolite.


[28]

[30]

[29]

[31]

3.14 Effect of position of genotoxic group (cresidine [29]) in a dye; [28] is mutagenic but [31] is not.

presumably because of the aminocresidine metabolite [30]. However, the yellow dye [31], in which the cresidine is present as an acylated (triazinylated) end component (E-component), is non-mutagenic. Acylation of the amino-group in cresidine obviously eliminates the mutagenic activity.

Care has to be exercised when using isomers of carcinogens. Thus, 1-naphthylamine is non-carcinogenic. However, during its synthesis, some of the isomeric 2-naphthylamine, a known carcinogen, is produced. This carcinogenic impurity must be removed to a level below which it is not a problem. For dyes that use 1-naphthylamine, every batch must be checked to ensure that the level of 2-naphthylamine is below the recommended level.

In Germany, bladder cancer is recognised as an occupational disease for textile workers (Myslak, 1988). Some dyes have the potential to release an aromatic amine that is known to be a rodent carcinogen upon metabolism in an organism and this has prompted some authorities to conclude that such dyes should be considered to be carcinogenic. This knowledge is the reason for the recommendation of the German MAK Kommission to handle the dyes in the same way as the amines which can be released under reducing conditions. Subsequently, the German, Dutch and Austrian authorities prohibited the use of such dyes in some consumer articles (ETAD 1998). Thus, the dyes may not be used for textile, leather or other articles which have the potential for coming into direct and prolonged contact with human skin, e.g. clothing, bedding, bracelets, baby napkins, towels, wigs (Moll, 1994). The ban, which is across the EU, also covers the import and marketing of the above-mentioned articles dyed with these dyes. Table 3.3 lists the amines that are classified as carcinogenic according to TRGS 614 (Limitation of use of azo dyes which are likely to cleave into carcinogenic aromatic amines (TRGS 614, 2001)) (Hunger, 2003). A list of azo dyes which, upon reduction of the azo group would form the aromatic amines shown in Table 3.3, has been compiled by ETAD. The list includes more than 500 azo dyes, of which at least 142 are still available on the world market (IFOP, 2001).

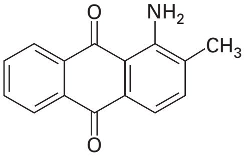
Anthraquinone dyes

From being the second most important class of dye after azo dyes, anthraquinone dyes have declined in importance. Primarily, this is because they have low cost effectiveness due to a combination of low colour strength and relatively expensive manufacture. Consequently, they have been studied less extensively than azo dyes. However, structure–activity relationships in anthraquinone dyes appear to follow a similar trend to those in azo dyes (Brown, 1976). Thus, anthraquinone dyes of the solvent or disperse class containing one or more primary amino- or methylamino-groups tend to be mutagenic or carcinogenic. For example, in Fig. 3.15, C.I. Disperse Orange

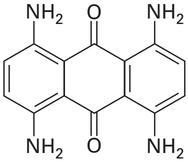
Table 3.3 Carcinogenic aromatic amines defined by the German MAK Kommission

C.I. name	CAS no.	Category of carcinogen*
4-Aminobiphenyl	[92-67-1]	1
Benzidine	[92-87-5]	1
4-Chloro-*o*-toluidine	[95-69-2]	1
2-Naphthylamine	[91-59-8]	1
4-Aminoazobenzene	[60-09-3]	2
o-Aminoazotoluene	[97-56-3]	2
4-Amino-3-fluorophenol	[399-95-1]	2
o-Anisidine	[90-04-0]	2
p-Chloroaniline	[106-47-8]	2
4,4′-Diaminodiphenylmethane	[101-77-9]	2
3,3′-Dichlorobenzidine	[91-94-1]	2
3,3′-Dimethoxybenzidine	[119-90-4]	2
3,3′ Dimethylbenzidine	[119-93-7]	2
4,4′-Methylenedi-*o*-toluidine	[838-88-0]	2
4-Methoxy-*m*-phenylenediamine	[615-05-4]	2
6-Methoxy-*m*-toluidine	[120-71-8]	–
4,4′-Methylenebis-(2-chloroaniline)	[101-14-4]	2
4-Methyl-*m*-phenylenediamine	[95-80-7]	2
4,4′-Oxydianiline	[101-80-4]	2
4,4′-Thiodianiline	[139-65-1]	2
o-Toluidine	[95-53-4]	2
2,4,5-Trimethylaniline	[137-17-7]	2
5-Nitro-*o*-toluidine	[99-55-8]	3

*Category 1 denotes a proven human carcinogen, category 2 a proven animal carcinogen and category 3 a suspected animal carcinogen.



[32]



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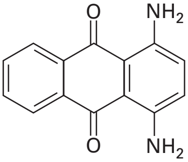


[34]

3.15 Carcinogenic C.I. Disperse Orange 11 [32] and C.I. Disperse Blue 1 [33] and mutagenic C.I. Disperse Violet 1 [34].

11 [32] and C.I. Disperse Blue 1 [33] are carcinogens (Hunger, 2003), whilst C.I. Disperse Violet 1 [34] is a mutagen (Gregory, 1991).

Some anthraquinone dyes express genotoxicity by intercalation. In this case, they act via insertion of the planar anthraquinone portion of the dye between adjacent base pairs of the DNA helix as shown in Fig. 3.16 (Gregory, 1991).

Cationic dyes

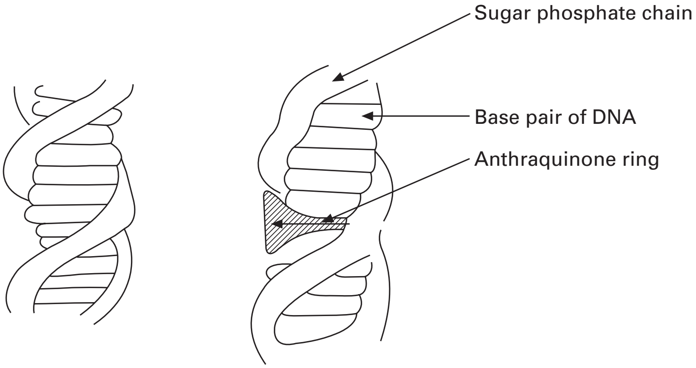
Cationic dyes, along with benzidine and 2-naphthylamine, were implicated in the high incidence of bladder cancer in the textile industry between 1930 and 1960. As seen earlier, the cationic (basic) dyes involved were fuchsine [1] and auramine [2] (Hunger, 2003). Further cationic dyes have been found to be carcinogenic, such as the triphenylmethane dyes C.I. Acid Violet 49 [35] and C.I. Basic Red 9 [36] (Hunger, 2003), and several fluorescent red dyes, such as Pyronine B [37], are mutagenic (Combes, 1982), Fig. 3.17.

Carcinogenic dyes

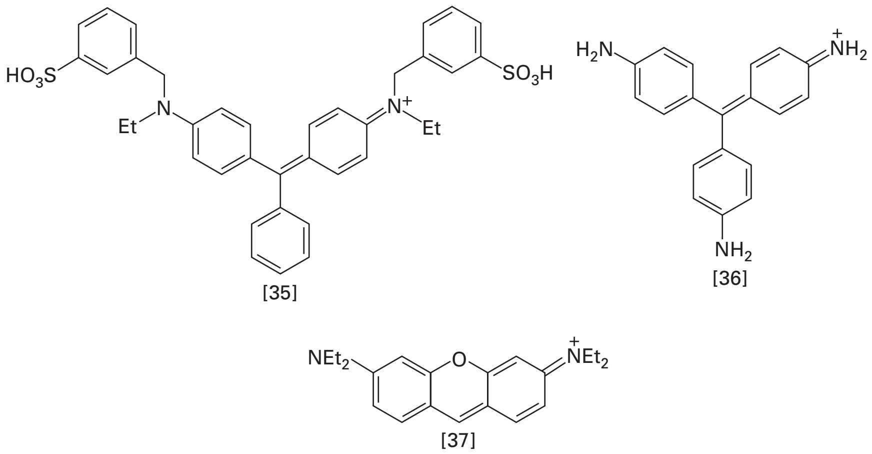
A list of dyes has been compiled that are proven animal carcinogens and which are probably carcinogenic to humans. Table 3.4 lists the dyes that are known to cause cancer in animals and are therefore classified as potential human carcinogens (Hunger, 2003).

Pigments

As mentioned earlier, insolubility is an effective way to reduce toxicology. Pigments, by definition, are particulate, insoluble colorants. Therefore, they will be difficult to reduce to the active amine metabolites and extremely



3.16 Intercalation of anthraquinone dyes in DNA.



[35] [36] [37]

3.17 Carcinogenic C.I. Acid Violet 49 [35] and C.I. Basic Red 9 [36] and mutagenic Pyronine B [37].

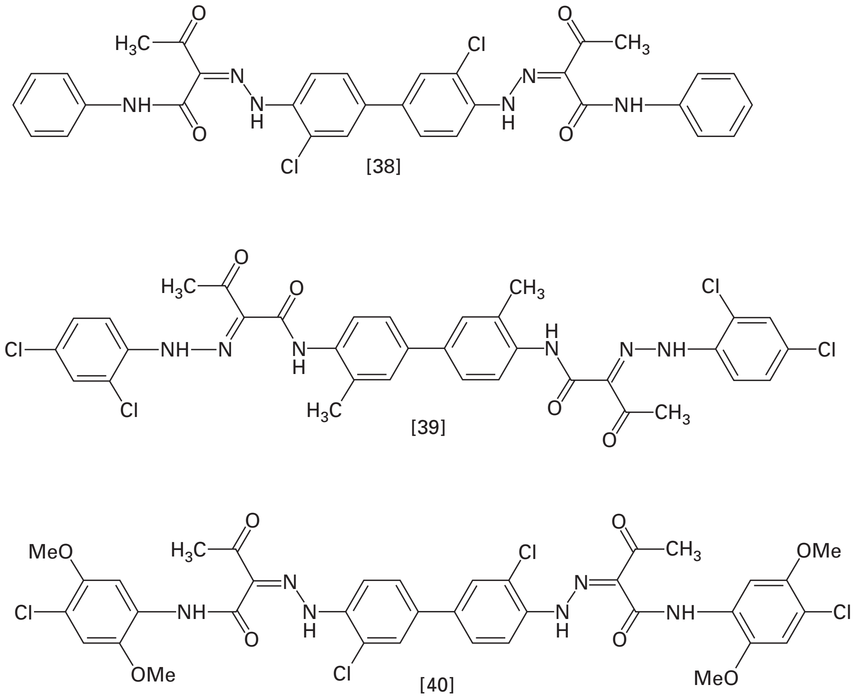
Table 3.4 Dyes classified as potential human carcinogens

C.I. name	C.I. no	Chemical class
Acid dye	16155	azo
Acid Red 26	16150	azo
Acid Violet 49	42640	triphenylmethane
Basic Yellow 2	42100	ketonimine
Basic Red 9	42500	triphenylmethane
Basic Violet 14	42510	triphenylamine
Disperse Orange 11	60700	anthraquinone
Disperse Blue 1	64500	anthraquinone
Solvent Yellow 1	11000	azo
Solvent Yellow 2	11020	azo
Solvent Yellow 34	41001:1	diphenylmethane

difficult to transport across the cell membranes. Consequently, they should be non-carcinogenic. All three azo pigments, C.I. Pigment Yellow 12 [38], C.I. Pigment Yellow 16 [39] and C.I. Pigment Yellow 83 [40], in the study by Longstaff (1983) were found to be non-carcinogenic (Gregory, 1986), Fig. 3.18.

Aromatic amino- and nitro-compounds

Aromatic amines and aromatic nitro-compounds are particularly important as far as organic colorants are concerned since they are the precursors to many textile dyes (and pigments), especially azo dyes. The most potent carcinogens within this class contain two or more aromatic rings and either primary amino- (–NH_2), methylamino- (–NHMe) or dimethylamino- (–NMe_2)



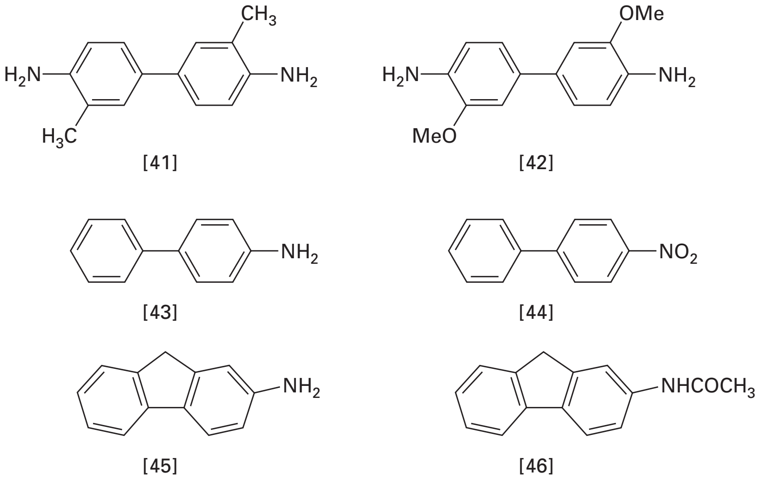
3.18 Non-carcinogenic azo pigments: C.I. Pigment Yellow 12 [38], C.I. Pigment Yellow 16 [39] and C.I. Pigment Yellow 83 [40].

groups. For nitroaromatic compounds, it is believed that a reduced species, such as amino or hydroxylamino, is the carcinogen. Typical compounds include those already discussed, such as benzidine [3] and 2-naphthylamine [4], and the compounds related to benzidine (Fig. 3.19) such as *ortho*-tolidine (3,3′-dimethylbenzidine) [41], *ortho*-dianisidine (3,3′-dimethoxybenzidine) [42], 4-aminobiphenyl [43], 4-nitrobiphenyl [44], 2-aminofluorene [45] and 2-acetylaminofluorene [46] (Gregory, 1991).

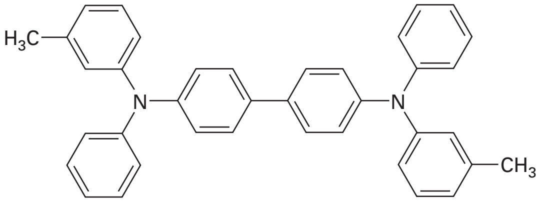
One way to eliminate the carcinogenicity of aromatic amino compounds is to arylate the amine. An excellent example of this principle is provided by dimethyltetraphenylbenzidine [47] Fig. 3.20. In complete contrast to the potent carcinogen benzidine, this compound is non-carcinogenic. It is used widely as a charge transport material in photocopiers and laser printers (Gregory, 1991).

Nitrosamines, hydrazines and hydroxylamines

Nitrosamines are of interest because they are formed in every diazotisation reaction of a primary aromatic amine and every commercial azo dye is made by a diazotisation and coupling reaction. However, such nitrosamines pose


[41] [42] [43] [44] [45] [46]

3.19 Carcinogenic *o*-toluidine (3,3′-dimethylbenzidine) [41], *o*-dianisidine (3,3′-dimethoxybenzidine) [42], 4-aminobiphenyl [43], 4-nitrobiphenyl [44], 2-aminofluorene [45] and 2-acetylaminofluorene [46].


[47]

3.20 Non-carcinogenic dimethyltetraphenylbenzidine [47].

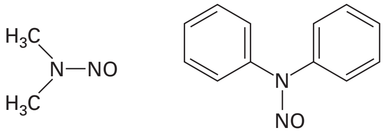
little threat since they are transient species and are contained in reaction vessels. Almost all nitrosamines are carcinogenic, e.g. [48]; the few known exceptions being when the substituents are non-alkyl, such as [49], Fig. 3.21, (Gregory, 1991).

Hydrazine, and many of its derivatives such as dimethylhydrazine [50] and phenylhydrazine [51], Fig. 3.22, are carcinogens; phenylhydrazines are used in the dyestuffs industry to produce heterocyclic coupling components such as pyrazolones.

3.4.4 Carcinogens from carbon electrophiles

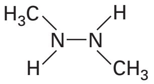
Unlike the carcinogens from nitrogen electrophiles, carcinogens from carbon electrophiles are rarely encountered in dyes. However, they are encountered in the synthesis or chemical modification of dyes.

Carcinogens based on carbon electrophiles may be divided into three types: directly acting alkylating agents, Michael acceptors and polycyclic

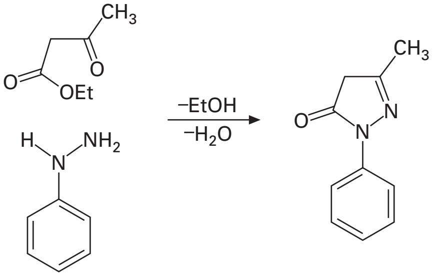


[48] [49]

3.21 Carcinogenic nitrosamine [48] and non-carcinogenic non-alkyl nitrosamine [47].



[50]



[51]

3.22 Dimethylhydrazine [50] and formation of a pyrazolone from phenylhydrazine [51].

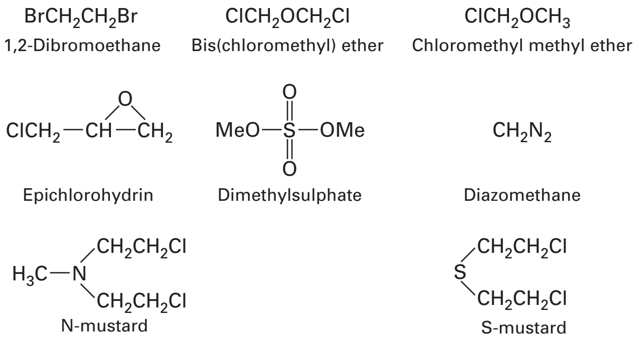
aromatic hydrocarbons. For all three types, the ultimate carcinogen is a carbonium ion.

Direct-acting alkylating agents

Direct-acting alkylating agents contain either alkyl substituents bearing a leaving group, such as chlorine, bromine and methosulphate, or a strained small ring system, usually three or four-membered rings, which ring open to generate the electrophilic centre. Directly acting alkylating agents are employed in the synthesis of the dye (and its intermediates), although chloroalkyl groups have been present in some dyes. Some common examples are shown in Fig. 3.23.

Michael acceptors

Michael acceptors have an ethylene group directly attached to an electron-withdrawing group. Vinyl chloride, acrylamide and acrylonitrile are typical examples.



3.23 Direct-acting alkylating agents: common named examples.

The electrophilic carbon atom is produced by the polarisation induced by the electron-withdrawing group. Like the directly acting alkylating agents, Michael acceptors are used in the synthesis of dyes. For example, acrylonitrile is used to introduce cyanoalkyl groups into disperse dyes as shown in Fig. 3.24. An important exception is the (masked) vinyl sulphone group present in reactive dyes, such as C.I. Reactive Black 5 [52], Fig. 3.25. This important reactive dye was comprehensively studied for its toxicological and ecological profile. It proved to be of low acute toxicity and is non-irritant, a weak sensitiser, and has no genotoxic potential. Also, the hydrolysed dye is not hazardous to effluent water (Hunger, 1991).

Polycyclic aromatic hydrocarbons

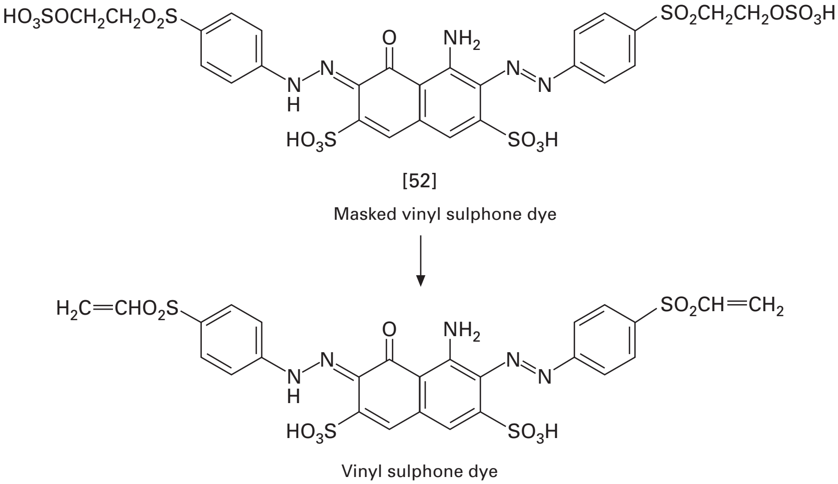
The one-ring, two-ring and three-ring aromatic hydrocarbons benzene, naphthalene and anthracene, respectively, are the basic building blocks for the majority of textile dyes. These lower homologues are usually non-carcinogenic. In contrast, many compounds containing four or more fused benzene rings are carcinogenic. Such compounds are believed to express their activity via epoxide formation, as shown for 1,2-benzanthrene in Fig. 3.26 (Gregory, 1991).

3.4.5 Metals

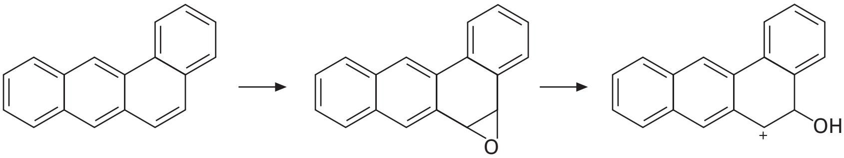
In water-soluble dyes, the sulphonic acid group is invariably present as a metallic salt, usually sodium, although lithium and potassium are also used. In these dyes, sodium, lithium and potassium pose no problems regarding toxicity. However, heavy metals are also used in dyes and these can present toxicity problems (Stefanovic, 1999).

The main source of heavy metals is that from metal–complex dyes. Metal–complex dyes are used for a number of reasons but primarily to improve the

3.24 Cyanoalkylation of an aromatic amine.



3.25 The masked vinylsulphone dye C.I. Reactive Black 5 [52] undergoing hydrolysis.



3.26 Metabolic pathway for polycyclic aromatic hydrocarbons.

light fastness of the dyes. The metals used most frequently in metal–complex dyes are copper (Cu^{2+}), chromium (Cr^{3+}), and cobalt (Co^{3+}), although nickel (Ni^{2+}), is also used to some extent. These metals are chosen since they not only impart the desired properties to the dye, but also they form the most stable complexes. Therefore, under normal use, no free metal should be encountered.

Chromium causes most concern. However, the concern is caused by perception rather than reality. Chromium (VI) (Cr^{6+}), found in chromates, is carcinogenic. Chromium (III), as used in metal–complex dyes, is non-carcinogenic and would not be converted into chromium (VI) under normal conditions. However, they are both chromium.

3.5 Future trends

The production and use of textile dyes is now a very mature industry where the majority of commercial products have been used for many years. As the structure–toxicology relationships of dyes and their intermediates have become better understood, those dyes with known toxicity problems have either been withdrawn or their use strictly regulated. Because of the extensive battery of toxicological (and ecological) testing that a new dye has to pass before it is allowed on to the market, it is extremely unlikely that new dyes will have toxicity problems.

The design of new textile dyes will take advantage of the ever-increasing knowledge of the relationships between the structure of dyes and toxicity (Freeman, 2004, 2005). New dyes will tend to avoid heavy metals, with the important exception of copper phthalocyanine dyes. These dyes produce technically excellent blues and cyans and are the most stable of all the metal–complex dyes.

Efforts will, and indeed are, already being made to reduce toxic components in dyes and produce cleaner, and more environmentally friendly products. For example, Clariant AG has developed a range of sulphur dyes with a much lower sulphide content of 0.3%. This greatly minimises the quantity of the toxic and smelly hydrogen sulphide gas emitted during the dyeing process (Kreutzer, 2004).

The relentless search over the past few decades for better, stronger, more colourful and extremely stable textile dyes, has, inadvertently, caused problems with the disposal of the dyes. The dyes are difficult to degrade in the wastewater treatment plant and some degradation products are toxic (Rossbach, 2000). Indeed, there have been a number of publications recently addressing the treatment of dye effluent and its impact on toxicology (Kandelbauer, 2005; Guivarch, 2004; Upadhyay, 2002; van Lier, 2001; Bahorsky, 1998). In the future, more consideration will have to be given to addressing the balance between the dye properties for its end use and the degradation profile.

Some people have called for a return to natural dyes at the expense of synthetic dyes (Jeet Singh, 2003). Such an approach is seriously flawed. It has been shown (Glover, 1995) that there is not enough arable land in the whole of the world to grow the plants required to generate enough raw material to produce the natural dyes! Nousiainen also asserts there is no way that the annual consumption of 0.5 million tonnes of textile dyes can be met by natural dyes (Nousiainen, 1997). The colours of acceptable natural dyes would be very restrictive, the fastness properties poor, and the costs prohibitive. Also, it is unsound to believe that natural dyes are safe. Of those that have been tested, some have been found to be toxic (Glover, 1995). Indeed, just because something is natural does not automatically mean that it is safe. For instance, some of the most toxic substances known are natural products, such as aflatoxin B_1, found in peanuts. In the case of peanuts intended for human consumption, the potent animal carcinogen aflatoxin B_1 has to be regulated to parts per billion! (Gregory, 1991). Finally, whilst there is a role for natural dyes to play, it is not a major role.

3.6 Sources of further information and advice

For a general and comprehensive coverage of the toxicology of chemicals, including dyes, the compendium of Sax (Lewis, 1992) is a good starting point. The recent account on the health and safety aspects of industrial dyes (Hunger, 2003), which is referred to several times in the main text, is also highly recommended. The chapter on the toxicology of organic colorants is also useful (Gregory, 1991).

There are several noteworthy reviews worth consulting. These include a survey of azo colorants in Denmark (Ollgard, 1998), Freeman's approach to eliminating toxicity in dyes (Freeman, 2004, 2005), Steingruber's review of the product health impact and toxicology of organic dyes and pigments (Steingruber, 2004), and Desai's and Starodumov's reviews of the toxicology of dyes (Desai, 1992; Starodumov, 1991).

Important specific references are those on the safe handling of dyes (USOC, 1995) and a product stewardship programme for dyes (Helmes, 1994).

ETAD has published numerous Position Papers, Guidelines, lectures and studies on specific problems of colorants concerning toxicology, ecology and legislation. The address is: ETAD General Secretariat, Clarastr.4, CH-4005 Basel, Switzerland, Tel. (+41) 61-690-996, Website www.etad.com. ETAD has also developed an online database containing sources of toxicological, environmental and legal publications on colorants with almost 12 900 documents concerning more than 2000 different dyes (and pigments). It is only available to ETAD member companies.

Material Safety Data Sheets (MSDS) are another useful source of information. They provide the necessary information for safe handling of the dye by the user. Although in Europe they must only be legally provided for hazardous substances according to EU Directive 91/155/EEC, the majority of dye manufacturers provide MSDS for all products, including those that are not hazardous. The Safety Data Sheet contains information such as the identity of the dye, possible hazardous components, and physicochemical, toxicological and ecological data, first aid and emergency measures, occupational exposure limits, and information on personal protective equipment (Sewekov, 1994).

Finally, the research group that is currently most active in studying and designing non-toxic dyes is Freeman's group. The address is: Harold S Freeman, North Carolina State University, Raleigh, USA.

3.7 References

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4

Environmentally responsible dye application

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4.1 Introduction

Dyes have been applied to textile and other substrates for thousands of years, and dyers and their suppliers have continually sought to develop new processes and products that lead to better results or lower costs, in turn translating into commercial gain. Over the last few decades, the environmental impact of those products and processes has become an increasingly large part of the dyer's task. Given the growing emphasis on the environment, it is common to have almost any technical advance in the application of dyes, be it dye, auxiliary, or machine, claimed as environmentally beneficial, however spurious such a claim might be. Distinguishing real environmental advantage from apparent is not easy.

In seeking to achieve environmental responsibility in dye application there is no single solution since there is no single definition of what is green, or environmentally responsible. Even in a rare case where a dyeing operation is planned from first principles with environmental responsibility as a main goal, the best approach might be widely debated. More realistically, existing operations can be made 'greener' in many ways, with the different approaches each tending to answer a particular perceived impact. Local circumstances will often dictate which path is the preferred one. A recurring theme in the efforts to become more environmentally responsible is one of swings and roundabouts; a change made in one aspect of a dye application process for environmental reasons can often (negatively) impact another part of the process.

Environmentally responsible dye application involves the principles of pollution prevention that were developed and promulgated in the early 1990s with the hierarchy of 'reduce, reuse, recycle'.[1] This replaced the earlier 'end-of-pipe' response to growing environmental legislation.

A common mantra of the environmentally concerned is 'think globally, act locally', and this readily applies to dyeing and associated operations. A dyehouse may have limited impact on the immediate locality if its air emissions and wastewater are uncontaminated (or minimally so). For the former, volatile organic compounds (VOCs) and odour are the usual concerns. The main problems centre on water, where biological and chemical oxygen demand (BOD, COD), pH, total dissolved solids (TDS), temperature, oil/grease, heavy metals and colour are typically regulated. Since local government and nearby neighbours are the immediate constituencies to which a dyer has to answer, modifying processes to meet the legal limits for these pollutants is the starting point, and essential to staying in business. Unfortunately for the bigger picture, most limits are expressed as concentrations in waste water rather than as total mass or mass per unit of production, which encourages wasteful use of water and 'dilution as the solution to pollution.' Simple local environmental responsibility may come, therefore, at the cost of inefficiencies of water or energy, machinery, or the use of dyes and chemicals whose use is benign but whose synthesis creates pollution elsewhere. Thus, simply meeting regulations ('being as bad as the law allows') cannot be considered as environmentally responsible, and dyers must be creative and ingenious in modifying processes to go beyond what the law requires, and to minimise the effect of their work on a much larger scale.

To be effective and justifiable, broad and general changes, such as in the reduction of water and energy consumption or the reduction in mass of chemicals used or discharged, should be based on solid data, and ongoing environmental audits should be a routine. They will provide a baseline against which to measure progress, and may reveal financial as well as environmental advantages.[2]

The global impact of a locally 'clean' operation may be considerable, and it is ultimately worth considering to whom or what group environmental responsibility is answering. It may simply be a case of conscience, of 'doing the right thing.' It may also be in response to the demands of the customer who wishes to proclaim a product 'green'.

Environmental acceptability in textile products generally falls into one of two categories. The first and simplest to demonstrate is that the product will not harm the user, or harm the environment in use. A primary example is the Oeko-tex 100 scheme that certifies items being sold as environmentally sound, based on what is present or might be released from them.[3,4] The second category of greenness is based on the environmental impact of the production of the item: from cotton field or fibre factory to end use, and beyond to ultimate disposal. For some products, such a 'life-cycle analysis' is feasible, and produces clear results. The textile chain is long and complex, and weighing the balance of all the alternatives makes life cycle analysis for textiles difficult if not impossible. Which is worse: an antimony catalyst used in the production of polyester, or the herbicide applied to cotton? Obviously, the application of dyes is a key component in any such analysis, considering the effect of the application itself, and the fate of the dye when the item is composted or recycled. Efforts to judge textile materials' environmental impact in the architectural field have led the way and have begun to spill over into the apparel market.[5]

4.2 Background and scope

The general theory and practice of the application of dyes to fibres has been extensively covered in many standard sources.[6–8] These cover the different types of dye available, the various fibres to which they can be applied, and the types of machine used for the application at various stages of fabrication from fibre through to garment. The following discussion largely assumes the reader's familiarity with this background.

Since it is often the task of the dyer to prepare materials before dye application to ensure satisfactory results, and decisions about preparation can be taken in conjunction with dye application to minimise environmental impact, preparation is included in this discussion. Similarly, although textile printing is distinct from dyeing, as it involves the application of colour to textiles and shares the same preparation processes, it is given brief consideration here.

4.3 The influence of environment on the dyer's task

The aims of a dyer are to achieve the correct shade and fastness properties on a substrate in a level manner as efficiently and profitably as possible. Process changes to improve environmental responsibility can affect each of these aspects.

4.3.1 The correct shade

A dyer is usually trying to match the colour of some 'standard'. This may be electronic, in the form of reflectance data, or a real physical sample of coloured material. As the textile supply chain has become global, the move to numerically based standards has accelerated. In either case, the dyer should know under which light source the match is to be judged. It is helpful if the standard is as colour-constant as possible under different lighting conditions.[9]

Achieving a specific colour typically involves a mixture of three dyes. The usual dyeing primaries comprise a 'trichromie' of yellow, red and blue. A dyer will often have a preferred set of 'workhorse' primaries that have good dyeing behaviour and from which the widest range of shades can be economically obtained, along with additional dyes for specific requirements of shade, fastness or metamerism. Metamerism can be reduced by the choice of dyes used to create the colour, but not completely eliminated if different colorants are used to make the match than are present in the original standard. The mixture used should be formed of dyes that have compatible dyeing behaviour so that level dyeings are easier to obtain. If environmental factors limit the choice of dyes to be used, it can become more difficult to produce a non-metameric match and a compatible trichomie can also be more elusive.

The choice of dyes and the amount of each to be used (the 'recipe') can be based on trial and error laboratory scale dyeings, and/or an instrumental (spectrophotometer + computer) match prediction system (IMP). Recently, systems of standard colour swatches with associated recipes have been introduced. In addition to the quantities of dye required, a commercial dyeing recipe includes all the other variables that are under the dyer's control. These include the additives to the dyeing (auxiliary chemicals such as electrolyte, pH adjustment, levelling agents etc.), the time/temperature profile and the liquor ratio. Some of these may be dictated by the machinery available, for example, the liquor ratio and the degree of agitation. These in turn might control the rate at which the temperature can be increased. It is sometimes thought surprising that dyeings are rarely completely reproducible, but a well-known 'fishbone' diagram of the variables that can contribute to shade variation and that should be controlled makes it clear that dyeing consistent shades is not easy.[10] Dyers routinely add less dye than is required by the recipe, and make an 'add' to correct the shade. 'No-add' dyeings are sought after: a loftier ideal to which well-controlled dyehouses aspire is 'blind dyeing' where the goods are removed without being checked for shade. No-add and blind dyeing represent a level of environmental responsibility by minimising energy consumption.[11–13]

Given that dyeings are rarely completely reproducible, the question arises 'how close is close enough?' Instrumental colour measurement is now capable of making this judgement objectively, and more reliably, than the human eye, although getting to this point has taken much effort.[14] The CMC (2:1) colour difference equation developed in the 1980s has become the most widely used in the textile world. Objective passing of shades requires that the customer accept the method, and that dyer and customer agree on the pass–fail tolerance. As the textile supply chain has become global, the use of objective shade acceptance has necessarily increased, but instances remain when a subjective customer intervenes and tolerances shift with the demand for product. Dyers making repeated adds to get perfect matches waste valuable resources and risk damaging the substrate. Customers who accept objective shade passing, or who do not insist on unrealistically tight colour tolerances contribute to environmental responsibility by providing the dyer with known and achievable end points, thus limiting the time (and energy consumption) of the process.

4.3.2 Level dyeing

A level dyeing refers to one in which dye is distributed evenly throughout the substrate. Strictly speaking, each fibre should be fully and evenly penetrated, but this is rarely achieved in practice. Fibres in the middle of a yarn are often dyed lighter than those on the outside, and yarns within a fabric may have pale areas where they cross each other. As long as the overall appearance is level, such micro-unlevelness is acceptable. Unlevelness on a larger scale, unless it is a deliberate decorative effect, is not acceptable. Dyeings may have streaks, spots, crease-marks, as well as more gradual and subtle variations from side-to-side, side-to-middle, back-to-front, or end-to-end of a fabric. Unlevelness may render a material unsaleable, or require reworking which once again consumes additional energy, water and chemicals. Unlevelness can often be traced to poor fabric preparation (‘well prepared is half dyed’). In manufactured fibre fabrics, unsuspected dyeability variations, from ‘mixed merges’, may be present. Beyond that, levelness relies on the use of the correct procedure based on the substrate, and the agitation provided by machinery being used. The use of compatible dye mixtures is desirable, especially in pale shades. Any limitation of dye choice for environmental reasons can make this more difficult.

Levelness derives from level initial padding of dye for a continuous dyeing, or an even initial ‘strike’ in batch (exhaust) dyeing. Conditions (temperature rise, pH, auxiliaries) can be adjusted in batch dyeing to achieve this. Levelness can also come from migration (‘levelling’) of low affinity dyes during batch processes extending the time of dyeing to ‘even out’ an initial rapid (unlevel) application.

Attempts to improve environmental responsibility and make processes more efficient by using higher rates of heating and cooling, by using low liquor ratios, or by adjusting conditions to achieve maximum exhaustion, all increase the risk of unlevelness. Unlevel dyeings may need to be stripped and redyed, wasting resources and risking damage to the substrate.

4.3.3 Fastness

Fastness is the resistance of a dye to removal or destruction. In both industrial processing (finishing, for example) and in ultimate use, a textile might meet a range of challenges. Standard laboratory tests put forth by, e.g. ISO or AATCC correspond to these agencies and predict their effects.

Fastness is achieved mainly by the selection of dyes. As with the issues of shade and levelness, restriction of dye choice for environmental reasons can limit the fastness achievable. Fastness also depends on the removal of hydrolysed reactive dye or any dye that remains loosely bound to the fibre surface at the end of the dyeing process. The use of rinsing processes that are efficient in water and energy use can reduce the impact of these rinses. Subsequent finishing processes should also be carefully controlled, since under the conditions of finishing, dye desorption can take place, and recontaminate the fibre surface. Customers can contribute to a reduced environmental impact by not requiring excessive or unnecessary levels of fastness.

4.3.4 Efficiency and environmental responsibility

Dyeing is a commercial process, and a notably competitive one, and success depends on achieving all the above factors (shade, levelness, fastness, no damage) while being as efficient as possible. Efficiency can involve machine time, energy, labour, water, dyes and chemicals, but must also consider environmental impacts of the process. Finding the best process that allows the most efficient and reliable dyeing is another reason why commercial dyeing is a skilled process.

Issues of environmental responsibility are thus encountered in trying to achieve each of the basic requirements of shade, fastness, levelness and efficiency. Holding fewer dyes in stock may be more efficient, and selecting dyes that are considered more environmentally benign might be environmentally responsible, but reduced dye choice may make a level, fast or non-metameric match harder to achieve. If dyes are not standardised accurately, or do not form a compatible combination, they may involve the dyer in additional machine time to make adds and/or reprocess the material. The efficient use of water, dye, energy and chemicals is promoted by using low liquor ratios, but as these decrease the likelihood of unlevel dyeing increases. Chemical auxiliaries might reduce dyeing time, promote levelness or increase exhaustion, but ultimately represent a burden in the waste stream.

Nor does the dyer exist in isolation. The customer's requirements may force a dyer to carry out a process that is not environmentally responsible by insisting on tighter than necessary colour tolerances or fastness.

4.4 General comments

4.4.1 Machinery

While dyers may specialise in the substrates they dye, or the volume at which they work, some level of flexibility is built into the way they do business. A dyeing operation may be equipped with different styles of machine, of different sizes, from different manufacturers.[15] At a certain scale, continuous processing becomes more efficient. Continuous working is quite common in fabric preparation, since fabrics are prepared on a larger scale than they are dyed, and is normal in textile printing, but it is relatively unusual in dyeing, where limited runs of single shades are the norm. Continuous processing also involves the application of relatively concentrated solutions to fabrics, and an opportunity to recycle leftover pad baths. Low-volume pads mean less to recycle, and reduce 'ending'.[16] In any continuous process, multiple low volume rinses and counter-current working should be the norm.

Whether batch or continuous, machinery can become contaminated with colour and at times, machines have to be taken off-line to be cleaned. The need for such cleaning can be minimised by sequencing the colours or patterns being produced from light to dark. Incidentally, that also tends to be the case as dyers have, given a range of shades to dye in a given lot, traditionally made black the final shade as an opportunity to overdye any uncorrectable shade/levelness problems from prior colours.

In batch processing, machines that agitate well, while not damaging delicate substrates, and that work at low liquor ratios (especially when run at less than full capacity) are inherently more environmentally responsible.

4.4.2 Utilities, plant organisation

The majority of preparation and dyeing processes require heat, and water is by far the most common medium from which dyeing is carried out. Water has a high specific heat that makes heating and boiling it energy intensive, and the recovery of heat from waste streams a realistic and sensible thing to do. Heat exchangers can be installed on individual machines, or in a common collection point for hot waste streams. It is now surprising to think that in the late 1970s the use of organic solvents (with low specific heats) was widely researched for both dyeing and preparation as a means of reducing energy consumption.[17,18] The search for alternatives continues and the use of supercritical carbon dioxide as a medium for dyeing has been the subject of considerable research and semi-commercial application.[19] The technique has been suggested for virtually all dye–fibre combinations. While it is environmentally attractive, and eliminates drying, the method requires highly specialised equipment and dyeing auxiliaries and seems a long way from wide-scale implementation.

Most dyehouses have a constant stream of incoming water to be used in all processes. In some, the water has to be pre-treated to bring it to a level of quality that will not cause problems in processing. However, many processes do not require clean water, and it is feasible to collect grey water (e.g. from final rinses) to be used as is, especially when it is hot.

It is generally most efficient to maximise the amounts of material that undergo common processing. Thus, for example, in most cotton dyehouses, there will be a common preparation sequence (usually desize/scour/bleach) for all fabric. However, while an evenly absorbent fabric is essential, a perfect white is necessary only for pastel shades, and to bleach goods when they are to be dyed dark, dull shades is wasteful and unnecessary.

4.4.3 Dyes and auxiliaries

Surfactants are used in preparation of fabrics before dyeing. Depending on the dye–fibre system, a range of chemical auxiliaries may be present in the dyebath. They fall into various categories: electrolyte, pH, oxidising/reducing and surfactants. Some are chemically consumed in the process, but most survive unchanged and are present in the final bath. Inorganic materials are usually bought and used as generic products, but organic surfactant-type auxiliaries are often supplied as proprietary materials. These can be detergents, or added to slow strike, promote levelling, allow for the use of a preferred pH, improve fibre lubrication and reduce crack marks, improve penetration, and so on. Their use is well established, but many are based on alkylphenol ethoxylates, which are suspected endocrine disruptors, and substitution may be appropriate.[20,21] More generally, a dyebath additive is often the first answer in solving a problem. However, the more that is added, the more complex the system becomes, interactions increase, and new problems can occur. Simpler is better, and for environmental responsibility, 'less is more' and beyond choosing environmentally appropriate products, dyers should work to minimise the use of auxiliaries: it reduces cost, and reduces the environmental load.

In many dyeing processes, a proportion of the dye remains in the bath at the end of the process, along with the non-exhausting auxiliary chemicals. It is environmentally responsible to reuse the dyebath, and not waste either resource. The use of 'standing baths' is an old idea, but in a modern dyehouse, bath reuse requires careful monitoring to achieve correct shades, and avoid the build-up of non-dyeing impurities. It also requires that some system of holding tanks be installed to hold the bath while rinsing etc. is carried out. Dyebath reuse has been conducted on at least a semi-commercial scale for several dye–fibre systems, and suitable analytical hardware has been developed.[22–24] In the case of reactive dyes, where the dye present at the end of the process is hydrolysed and not available for recycling (except, perhaps, as an acid dye[25,26]) the bath typically contains large amounts of electrolyte that is worth recycling. Considerable work has examined the oxidative decoloration of such baths to allow the reuse of the electrolyte.[27–30]

Many of these environmentally responsible process modifications require a level of planning and organisation that is not the norm in a working dyehouse. They are difficult to retrofit to an existing operation. As discussed earlier, changes should be quantified and referenced to a pre-change audit of the operation. The benefits, however, are often substantial. Ultimately (depending on the processes carried out and the level of waste treatment available to the facility), a plant may be able to operate as a closed loop system for water, representing an ideal of environmental responsibility.

4.5 Preparation

The goal of fabric preparation is a substrate that is free of impurities and colour that might interfere with subsequent dyeing processes. Preparation is typically carried out in the same plant as dyeing. The subject is generally covered well in texts related to the dyeing of the various fibres.[31–33]

Cotton comes to the dyehouse in the least pure state. It originates in agriculture, it requires sizing to be woven successfully, and it usually has had no prior wet treatments. It therefore requires the most extensive preparation treatments. The global nature of textile processing means that the knitter or weaver and dyer are often far apart, and the precise nature of the impurities, especially the knitting oils or size used, may be unknown. Since much of this ends up in the dyer's waste stream, the effluent problems of a dyehouse can often be traced to this source. In an ideal world, a dyer would receive fabric from an environmentally responsible weaver who used a recyclable size and removed it before shipping the fabric. In practice, some of the worst problems of dyehouse effluent often involve the high BOD/COD from the size, made worse with any preservatives or insecticides present. Knitting oils are generally present in lower amounts, but may be water-insoluble.

The basic steps in woven cotton fabric preparation of desize/scour/bleach may be accomplished in a variety of ways and with a range of different chemicals. The choice is often based on the scale of the operation with fully continuous processes the most efficient on the large scale, and pad-batch, or batch processes (the latter often in dyeing machines) preferred on the small scale. While hypochlorite bleach has been essentially replaced by peroxide and other oxygen-based bleaches (making spurious any environmental claim of 'no chlorine bleach used'), the use of alkali is an essential part of the traditional process, and waste streams are overwhelmingly alkaline, requiring neutralisation. Carbon dioxide from boiler exhaust can be used: an interesting example of combining two waste streams to generate a benign effluent. The concentrations of alkali are generally too low to be successfully recycled; in contrast, the higher concentrations of caustic soda from mercerising are routinely recycled.

These basic preparation steps can be made more environmentally responsible by all the usual efficiencies: reducing water, chemical and energy use, etc. Combining the basic steps, all of which can be accomplished by alkali and oxidising agents, is an additional opportunity for efficiency, and oxidative desizing has been re-examined.[34] More interesting is the trend to develop enzyme-based processes that operate at lower temperatures and near-neutral pHs. While amylase has been used for many years to desize starch-sized fabrics, the broader use of enzymes in fabric preparation has been widely researched, and offers many potential environmental advantages. Much work has been reported on the use of pectinases and other enzymes to scour cotton.[35–38] The product is absorbent, but not white, and still contains seed fragments. This may be sufficient for dyeing dark colours, but the broader goals of totally enzyme-based preparation are yet to be realised. 'Bio-polishing' with cellulases has become well established and is, incidentally, part of the preparation of lyocell fabrics in a defibrillation step.[39,40]

Catalase enzymes are suggested for use in destroying excess peroxide in bleaching that might otherwise damage dye in later dyeing. In contrast, with the use of peroxide-resistant dyes, combined dyeing and bleaching becomes possible and represents an opportunity to reduce processing by one step.[41,42]

The other common natural fibre is wool. The environmental impact of raw wool scouring, which occurs before yarn spinning, is beyond the scope of this chapter. Wool processing is generally on a smaller scale and mostly batch-wise processes are employed. Grey fabrics that come to the dyehouse will undergo many possible processes and combinations thereof and wool dyers are adept at making these efficient. Scouring and milling are commonly combined. Sulphuric acid is used to carbonise wool: the acid left in the fabric may be used as an auxiliary in acid milling, and/or acid dyeing.

Silk is usually degummed, and this process has been the subject of research to make it more environmentally responsible.[43]

Synthetic fibre fabrics are generally cleaner and require less preparation. In many cases, the surfactant-based dyeing auxiliaries (levelling agents, for example) are sufficiently detergent to allow scouring to be combined with dyeing.

4.6 Dyeing, fibre by fibre

4.6.1 Cellulose

Cotton is by far the largest volume of the cellulosics, but most of what applies to cotton applies to other natural and regenerated cellulose fibres. The dye types for cellulose reflect a range of strategies depending on fastness and shade requirements. In general, dye exhaustion is lower on cellulose fibres and, thus, waste streams are more highly coloured. The greater exhaustion of dye on protein fibres was noted centuries ago and, in the nineteenth century, processes for 'animalising' cotton were researched. The most recent incarnation of such efforts has been the treatment of cotton to incorporate cationic moieties to which anionic direct and reactive (and acid) dyes are attracted with high exhaustion and minimal use of electrolyte.[44–47] Despite the extensive work, the added complication and perhaps the later 'scavenging' of colour in laundering has hindered commercial development.

Reactive dyes

In recent years, the 'default' choice has come to be reactive dyes for their generally good fastness to wet treatments, and good range/brightness of shades. The dyes range in substantivity and reactivity, rendering them more or less suitable for long liquor exhaust applications, blends with polyester, continuous application etc. Some are metal complexes, most often with copper. In exhaust application, electrolyte is required, often in amounts large enough to be considered a pollutant and, as discussed earlier, a candidate for recycling. Unique to this class of dye is the distinct separation at the end of the process between fixed and unfixed dye. The latter must be removed in thorough rinsing to achieve optimum fastness properties. Rinsing processes have been most studied for reactive dyes[48] and enzymatic processes for decolorising the rinse water have been developed.[49] The rinsing process is most efficient when the dye has a high fixation and low substantivity. These two seemingly antagonistic requirements (and hence environmental responsibility) are best achieved in cold pad-batch application.[50] Little or no electrolyte is required, energy is minimal, and fixation is high. Unfortunately, this method of application does not allow 'adds' to adjust the shade, and dyers have been reluctant widely to adopt this method of dyeing.

In other application methods, 'low salt' dyes have been developed,[51,52] as have dyes with high fixation, often via the use of two or more reactive groups of the same (homo-) or different (heterobifunctional) types.

Vat dyes

Vat dyes offer the best levels of fastness on cellulose. Their manufacture tends to be polluting, so their use raises some environmental questions on the global scale. The reducing agent used in their application, most commonly sodium dithionite (hydrosulphite), is an environmental burden. Alternatives continue to be sought:[53] most recently electrochemical means of reduction have been explored and offered on a commercial scale.[54,55] Oxidising agents to bring the dye to its final oxidised form can, with care, be replaced by exposure to air.

Direct dyes

Direct dyes still have their place in the market. Environmental responsibility means ensuring that none of those based on potentially carcinogenic amines should be used.[56,57] The use of copper-based after-treatments to boost the limited fastness is now largely outmoded. Direct dye baths can be recycled.[58,59]

Sulphur dyes

Sulphur dyes have long been used for economical dark shades of fairly good fastness. Sulphides, the reducing agent used in their production (and thus inevitably present in the dye as sold) and their use are polluting, and as dyemakers have minimised the free sulphide present in the dye, dyers have sought non-sulphide reducing agents with which to apply them. Glucose-based materials seem to be satisfactory and have been widely adopted.[60,61] As with vat dyes, the use of electrochemical reduction has been explored.[62] In contrast to vat dyes, the oxidation of sulphur dyes is a less straightforward process, with the shade and fastness of the resulting dyeing depending markedly on the oxidising agent used. Chromates were ideal, but are environmentally unacceptable: the current favourite seems to be sodium bromate with sodium metavanadate present as a catalyst.[63]

4.6.2 Dyeing wool

Dye application on wool is generally more straightforward than on cellulose fibres: exhaustion is higher, auxiliary levels are lower and pH values nearer neutral are often preferred. Waste dyebaths are thus more readily disposed of, and less stringent rinsing is required. Since exhaustion is readily accomplished, it is customary to use larger volumes of water to ensure levelness, however. Where specialised auxiliaries are used (for example, to allow the use of pHs that minimise wool damage) dyebath reuse can be advantageous.

The major environmental challenges are based on the choice of dye. Metal (usually chromium) complex dyes, either as 'premetallised' complexes, or those formed *in situ* by the separate application to the fibre of dye and dichromate are widely used to provide dark, fast shades. Where dye and chrome are applied separately, some chrome is inevitably discharged. Modifications to the dyeing method to minimise the amount of chrome used and discharged were widely studied, along with means to ensure that any discharge was as Cr(III) and not as Cr(VI).[64–66] Premetallised dyes (produced in a way that minimises free chromium) are less of an environmental challenge since the bound metal is less, or perhaps not, bioavailable. Nonetheless, alternatives are sought. Despite limited use in routine wool dyeing, where levelness may be challenging, reactive dyes for wool have been suggested and, in some cases, adopted as non-metal alternatives for fast, dark colours.[67] The use of the environmentally benign iron as an alternative to chrome in metal complex dyes continues to attract interest.[68,69]

4.6.3 Dyeing nylon

Like wool, nylon is most often dyed with acid dyes, and the issues involving the chrome content of premetallised dyes are the same. Nylon is subject to more challenges in use, and the fastness of dyeings is of concern. The use of post-dyeing treatments to improve fastness is common. Backtanning processes (involving antimony salts) have largely been replaced by 'syntans'. Modified after-treatments, and non-antimony tanning systems have been examined.[70,71] The use of alternatives to acid dyes, such as sulfur dyes, vat dyes and reactive dyes have been suggested as ways to improve fastness, although the environmental impact of these alternatives is not clear.[72,73]

4.6.4 Dyeing with disperse dyes: polyester and acetate

Disperse dyes were developed first for use on acetate: these dyes were later found to be useful when polyester was introduced. Newer disperse dyes specifically for polyester were eventually developed. Until the introduction of polyester in the 1950s, there had been little need for dyeing machines to be pressurised to achieve temperatures above 100 °C, but diffusion of dye into polyester is slow at the boiling point of water. The satisfactory dyeing of polyester initially involved the use of 'carriers', essentially fibre plasticisers. These materials, typically phenols or chlorinated aromatics, were used at quite high concentrations (2–5 $g.l^{-1}$) and ended up as pollutants in the waste stream. Over the past half-century, as polyester has become the most widely used fibre in the world and its dyeing has become commonplace, pressurised dyeing machines have largely obviated the need for these chemicals. The machines have also allowed faster dye cycles. For some dyes/shades/fibres carriers are still required and more benign 'migration assistants' with carrier-like function have been developed. In general, polyester dyebaths are well exhausted, and a good candidate for the reuse of the levelling and dispersing agents they contain.

When dyeing dark shades, the low aqueous solubility of disperse dyes leads to the presence of surface dye and low rubbing fastness. This is traditionally removed in a 'reduction clearing' process with dithionite and alkali, with the same environmental question marks as for their use in the application of vat dyes. Dyes clearable on alkali treatment have been developed.[74] In most polyester dyeing processes, a pH of 5–6 is maintained for dye stability. Recent interest has focused on the selection and use of dyes stable in alkaline baths. As well as their benefits in the dyeing of polyester cotton blends discussed below, on polyester their use reduces the need for post clearing, and reduces oligomer deposits.[75–77]

4.6.5 Dyeing acrylic fibres

The dyeing of acrylic fibres presents few specific environmental challenges beyond those discussed previously. Dyes exhaust well. Levelness can be challenging, which tends to increase the use of levelling agents. Both factors would make dyebath reuse an attractive proposition.

4.6.6 Dyeing blends

Fibres are blended for both technical and economic reasons, and myriad blends and blend levels are encountered. Dyers may be required to reserve one fibre, cross-dye, union dye, or produce a tone-on-tone effect. The subject has been extensively covered.[78] The same principles of environmental responsibility as for single fibre fabrics apply here, in somewhat more complicated form.

Since cotton and polyester together make up around 70% of all fibre consumption, it is not surprising that their blend is where the majority of attention has been focused. The fibres have very different dyeing behaviour, and extensive published work has described considerable ingenuity in turning a two-bath, two-stage batch process into a more efficient one-bath, two-stage, or even a one-bath one-stage process.[79–82] The rewards in terms of reduced time, and energy and water consumption, are potentially large. The success of such efforts has been mixed. The feasibility is rarely applicable to all cases; a successful short procedure for pale shades of limited fastness may not be applicable to heavy depths where cross-staining may occur and good fastness to laundering or rubbing is required. In continuous dyeing similar efforts have been expended.[83] The opportunity to employ a single class of dye on both fibres has attracted attention, but is of little environmental value.

4.7 Textile printing

Textile printing is usually continuous. The most widely used printing process involves the application of thickened colour pastes through screens. The lack of reliable colour mixing prevents the use of primary ‘process’ colours and each colour in the design must be applied as pre-mixed ‘spot’ colour. Thus, a print may involve the application of up to 20 different print pastes. At the end of a print run, there will be 20 excess pastes to deal with and 20 screens to clean. Environmental responsibility requires waste minimisation meaning that just enough paste is prepared for the job in hand. This is best accomplished by initially preparing a limited amount of each paste, monitoring the use ($kg.m^{-1}$) in the pattern being printed, and then preparing whatever is needed to finish the job exactly. If there is excess paste, it should be reused, or worked off by incorporating it into another colour. Akin to the use of IMP in dyeing, software can predict how to work off excess paste in new colours.[84,85] Even the rinse water from screen washing can be used as make-up water in the production of dark-colour pastes. Most pastes are stable, the exception being those based on reactive dyes mixed with alkali, which have a limited ‘pot-life’, and any reuse must be relatively expedient.

Unlike the level application of colour in dyeing, where the use of pigments is largely confined to the continuous application of pale shades, the coloration of textile prints is evenly divided between dyes and pigments. Each type has environmental considerations.

In printing with pigments, the sequence is simply print-dry-cure and so the use of water and energy is low. The use of a low-solids thickener is required, since it remains with the fabric after printing. The former use of essentially zero-solids emulsion thickeners (mineral spirit and water) that generated large amounts of VOCs has largely ceased. The low solids acrylic thickeners that replaced them do contain some solvent, however, and air emissions are the usual environmental concern.[86]

When dyes are printed, a steaming step is usually employed to provide the energy and moisture that will allow the dye to penetrate the fibres. A thorough washing is required to remove unfixed dye, and all the auxiliaries in the print paste (thickeners, pH controllers etc.). These end up in the waste stream, and they should be chosen to minimise their impact. The same comments about washing efficiency that apply in continuous dyeing or preparation apply here.

The use of ink-jet printing is increasing. This technology does use process colours that mix on the substrate, so each pattern and colour is generated from the same inks, and waste is minimal. While the volume of ink-jet printed material remains low due to the limited print speed, it has found wide use in strike-off prints. Sample patterns can be printed, and screens are only manufactured for those that find orders. This represents a measure of environmental responsibility in avoiding the production of large numbers of nickel mesh screens that will not be used in production. The drawbacks of ink jet printing stem largely from the need to pre-prepare the substrates with all the auxiliaries required for fixation.[87]

4.8 Conclusions

A dyer (or printer) wishing to engage in environmentally responsible colour application has many avenues to explore beyond meeting local regulations. Reduced water and energy consumption can bring economic as well as environmental benefits, and can be achieved in many ways: more efficient machinery, heat recovery, elimination of redundant processes. Many options exist for the replacement or reduced use of chemicals, particularly those that are environmentally questionable. More advanced methods for reducing the environmental burden of dyeing such as dyebath reuse, enzymatic preparation or dyeing from supercritical carbon dioxide, have been tested on a commercial scale. Many others have been the subjects of detailed research.

It is understandably challenging to devote time and money to aspects of a competitive business that may not bring immediate reward. Ultimately, the dyer will respond to the needs of the market place. When environmental consciousness is important to the customers, many methods of demonstrated effectiveness may find implementation.

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5

Supercritical fluid textile dyeing technology

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5.1 Introduction

Chemical processes and products that are environmentally and economically sound are key factors in the development of a sustainable society. Process technology that delivers sustainable products is expected to fulfil a number of requirements. For sustainable products, renewable or recyclable raw materials should be used and all materials involved in the production process have to be evaluated as to their risk and toxicity potential. During processing, raw materials and energy have to be used as efficiently as possible and production of emissions and waste has to be kept to a minimum. The quality of sustainable products must also be high. Commercial competitiveness of the products and the process technology to produce them is another important factor which has to be evaluated (Saling *et al.*, 2002; Rebitzer *et al.*, 2004; Pennington *et al.*, 2004; Stewart and Jolliet, 2004; Anon, 2005a).

Although the product (textile) itself cannot be considered as sustainable, the dyeing process of fibres in supercritical carbon dioxide (scCO_2) is an example of a ‘clean’ process suitable for fulfilling many of the requirements of sustainability, as listed above. In this process, a recyclable process medium (CO_2) is used together with an efficient and minimum input of chemicals (only dyes, no auxiliaries) and energy (low dyeing times, fusion of processes, no drying) and with minimal emissions and waste production. The quality of the dyed materials is also very high. Economical feasibility has to be determined in the future after industrial scale up of the plant and the process.

5.1.1 Environmental compatibility of CO_2

There are many beneficial environmental effects when scCO_2 is applied as process medium: CO_2 does not contribute to smog, it has no acute ecotoxicity and the ozone layer is not damaged. It is also non-carcinogenic, non-flammable and non-toxic (Jessop and Leitner, 1999); however, air with a CO_2 content of more than 10% can be life-threatening if breathed. Due to its higher specific gravity of 1.539 (Anon, 2003) compared with air, gaseous CO_2, if released at high concentration in a closed room, at first accumulates on the ground. Therefore, CO_2 defection systems have to be installed. The maximum allowable workplace concentration (MAC) is 5000 ppm (Anon, 1992).

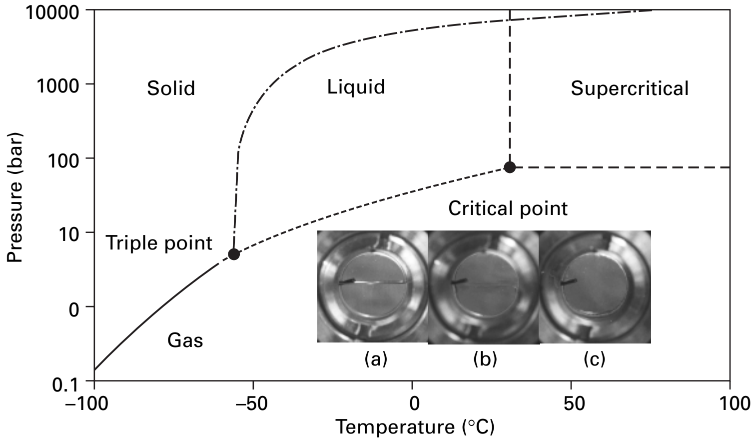
On the other hand, CO_2 is known as a greenhouse gas and there is an international growing concern about global warming and its inter-relationship with levels of CO_2 in the air (Anon, 2003). Around 1800, before the industrial revolution, the CO_2 concentration in the atmosphere was about 280 ppm and, in 1960, it was already 315 ppm. Since the mid-1900s, CO_2 levels have been continually increasing at an average annual rate of slightly more than 1 ppm, due to an increased combustion of fossil fuels and natural processes. At present, the average CO_2 concentration in the atmosphere is about 380 ppm (Anon, 2003).

In this context, processes which do not emit but apply CO_2 as a solvent have also been discussed very critically. Therefore, it is essential to investigate the sources of CO_2 and how it is recovered. Commercial quantities of CO_2 are produced by separating and purifying relatively CO_2-rich gases coming from combustion or biological processes that would otherwise be released directly to the atmosphere. Common sources are hydrogen and ammonia plants, magnesium production from dolomite, limekiln operations and fermentation operations such as the production of beer or the manufacture of ethanol from corn (Anon, 2003). CO_2 may also be recovered from wells (Anon, 2003). That means that processes such as supercritical fluid dyeing do not increase CO_2 emissions, but rather provide an opportunity for recycling of waste CO_2.

5.1.2 Physicochemical properties of CO_2

Generally, a supercritical fluid is defined (Angus *et al.*, 1976; Span and Wagner, 1996; Darr and Poliakoff, 1999) as a 'substance for which the temperature and pressure are above their critical values and which has a density close to or higher than its critical density' (Kemmere, 2005). The supercritical state can also be described (Baldyga *et al.*, 2004) as 'statistical clusters of augmented density with a structure resembling that of a liquid surrounded by less dense and more chaotic regions of compressed gas. The number and dimensions of these clusters vary significantly with pressure and temperature resulting in high compressibility near the critical point' (Kemmere, 2005).

At the critical point, CO_2 has a temperature of 31.1 °C and a pressure of 73.8 bar (Angus *et al.*, 1976; Span and Wagner, 1996). As shown in the photos (from left to right) in the phase diagram in Fig. 5.1, below the critical parameters two distinct phases of liquid and gaseous CO_2 are separated by the phase boundary. As the temperature and pressure rise along the vapour–



5.1 Behaviour of CO_2 along the liquid/gas phase equilibrium line in the phase diagram (Anon, 1992) observing a high pressure view cell (from left to right 20 °C/58 bar, 30 °C/71 bar, 33 °C/75 bar).

liquid coexistence line, liquid CO_2 expands and the two phases become less distinct forming a so-called supercritical phase. Above the critical point, the vapour–liquid line completely disappears.

Supercritical CO_2 can be regarded as a 'hybrid solvent' due to the fact that by simply changing the pressure or the temperature, the properties can be tuned from liquid-like to gas-like without crossing a phase boundary (Kemmere, 2005) as presented in Table 5.1.

Generally, the liquid-like high and variable density of supercritical fluids causes a tunable solvating power. The density of CO_2 at the critical point is 468 kg m^{-3} (Anon, 2003). Pressure increase enhances solvent power and solubility due to a higher density of the fluid. When the temperature is raised, fluid density decreases, but solute vapor pressure is increased, resulting in a specific temperature-dependent behaviour of each solute (Arunajatesan, 2002). Viscosity of supercritical fluids is more gas-like resulting in a reduced pressure loss (ΔP) due to lower friction and transport limitations in technical processes. The negligible surface tension leads to excellent 'wetting' properties. Moreover, higher diffusivity compared with a liquid can affect the selectivity of chemical reactions (Arunajatesan, 2002) but it can also accelerate $scCO_2$ processes such as dyeing.

5.1.3 Current environmentally sound applications of CO_2

CO_2 is applied in many industrial processes: in the food industry, for cleaning of surfaces, for neutralization and large quantities are used as a raw material in the chemical process industry, especially for the production of methanol,

Table 5.1 Range of physical properties of gases and liquids compared with supercritical fluids at T_c and P_c and after fourfold ($4P_c$) increase in pressure

Property	Gas	Supercritical fluid		Liquid
		T_c P_c	T_c $4P_c$	
Density ρ* (kg/m^3)	0.6–2	200–500	400–900	600–1600
Viscosity η† (Pa·s)	10^{-5}	10^{-4}	–	10^{-3}
Diffusivity* (m^2/s)	1×10^{-5}– 4×10^{-5}	0.7×10^{-7}	0.2×10^{-7}	0.2×10^{-9}– 2×10^{-9}

*Weibel, 1999 and Anon, 2005b.
†Lucien and Foster, 1999.

urea and oil (Anon, 2003). CO_2 is a 'green' industrial extraction medium replacing organic solvents for purification of odorants but also for the removal of agrochemicals from ginseng extract, of caffeine from coffee beans, of water from ethanol and of monomers from polymers on an industrial scale (Anon, 2003). CO_2 dry cleaning, as another example of an environmentally sound extraction process, as proved by LCA studies (Flückinger, 1999), has meanwhile become commercialized to replace the carcinogenic perchloroethylene in future (Peterson, 2003). Newer developments are the solvent substitution by CO_2 in lithography (Hoggan *et al.*, 2004) and in polymerization reactions, e.g. in the manufacturing of certain grades of polymers based on tetrafluoroethylene (Teflon™) by DuPont (DeSimone *et al.*, 1992; Romack and DeSimone, 1995; DeSimone, 2002). Moreover, production of fine particles with a narrow spectrum of particle size distribution by rapid expansion of supercritical solutions are of great interest for pharmaceutical applications (Subramaniam *et al.*, 1997). CO_2 can also be used as a coolant in air conditioning of automotives (Brown *et al.*, 2002) to replace chlorofluorocarbons.

5.2 History of supercritical fluid dyeing

To this day, extraction is the main field of industrial application of CO_2. The first patents on impregnation of thermoplastic polymers with fragrance or pest control agents or pharmaceutical compositions appeared in 1986 (Sand, 1986). One year later in 1987, another patent claimed that 'polymers can be infused by additives such as UV-stabilizers and sensitizers, antioxidants and dyes (colorants) in supercritical carbon dioxide'. The main field of interest in this patent was the impregnation of PVC and rubber, but as polymer substrates poly(ethylene terephthalate) (PET), polyamide, polyacrylic and polyurethane polymers, and polyolefins are also mentioned (Beres *et al.*, 1987).

In 1988, the first patent focused on dyeing of textile substrates in pure $scCO_2$ and the application of polar co-solvents such as water, alcohol, and/or salts in order to change the polarity of the supercritical fluid was described (Schollmeyer *et al.*, 1990). It was later on supplemented by other more far-reaching patents on dyeing by DTNW (Schollmeyer and Knittel, 1993; Knittel *et al.*, 1993a; Knittel and Schollmeyer, 1995b) and on dyes suitable for $scCO_2$ by Ciba Specialty Chemicals Inc. (former Ciba Geigy AG) (Schlenker *et al.*, 1992a, 1992b, 1992c; Schlenker *et al.*, 1993).

5.2.1 Milestones of process and plant development

First experiences of dyeing of PET in $scCO_2$ were made by DTNW in 1989 on a laboratory scale in close co-operation with Professor G. M. Schneider at the Ruhr University of Bochum, Germany, in a high pressure phase equilibrium plant of 6 ml volume (Poulakis *et al.*, 1991). After the first tests had been successful, in 1990, a static dyeing apparatus consisting of a 400 ml autoclave with a stirrable, perforated dyeing beam was developed by DTNW (Knittel *et al.*, 1993b; Knittel and Schollmeyer, 1995c). Based on the optimum dyeing conditions obtained on a laboratory scale in this plant (Saus *et al.*, 1992, 1993a, 1993b, 1993c; Knittel *et al.*, 1994a, 1994b; Knittel and Schollmeyer, 1995a) in 1991, the first dyeing machine on a semi-technical scale was constructed and built by Josef Jasper GmbH & Co. Velen, Germany, in close cooperation with DTNW (Knittel *et al.*, 1993b; Knittel and Schollmeyer, 1995c). The autoclave had a volume of 67 l for dyeing a maximum of four bobbins with a yarn weight of 2 kg each. Within this co-operation, several patents concerning the machinery equipment and the dyeing plant technology have been published by Jasper (Jasper, 1993a, 1993b, 1993c, 1993d, 1993e).

In 1994, one of the Jasper $scCO_2$-dyeing machines was installed by Amann & Söhne GmbH & Co. Bönnigheim, Germany, for dyeing of PET sewing threads and for testing whether this technology was transferable to the textile industry (Anon, 1995). On this machine, many technical problems arose in the test phase and Jasper gave this technology up after the last presentation of parts of a $scCO_2$-dyeing machine at the International Textile Machinery Exhibition ITMA 95 in Milan, Italy. In this context, Amann transferred the machine to the faculty of Process Engineering II of the Technical University of Hamburg-Harburg, Germany, for further research and development (von Schnitzler, 2000). Since 2004, JVS Engineering, a start-up of the Technical University of Hamburg-Harburg has been attempting to develop applications in CO_2 with this modified Jasper-plant (von Schnitzler, 2004).

In 1995, a new approach was started by Uhde High Pressure Technologies GmbH Hagen, Germany, and DTNW resulting in a new construction of a $scCO_2$-dyeing pilot plant with a volume of the autoclave of 30 l. Whereas with the Jasper $scCO_2$-dyeing machine only impregnation processes were possible, the new Uhde plant was extended by an extraction cycle for removal and separation of excess dyes and spinning oils during the dyeing process, for cleaning of the plant at colour changes and for recycling of CO_2. Moreover, a separate dye storage vessel and a pump with a much higher flow rate was integrated. The pilot plant was first presented at the ITMA 95 in Milan, Italy, and, in 1996, at the OTEMAS in Osaka, Japan (Bach *et al.*, 2002a).

In 1999, the German producer and finisher of home textiles, Ado Gardinenwerke GmbH & Co. Aschendorf, joined Uhde and DTNW and, after evaluation of the dyeing results within a research project of just under three years (Bach *et al.*, 2002b), it became the objective of the partners in 2003 to push this technology forward together with other textile companies and scale up the $scCO_2$-plant to an industrial scale.

Since 1995, growing interest has been observed worldwide in this technology, starting in the USA and Asia and later on also in Europe. Besides the numerous publications on results of $scCO_2$ dyeing of natural and synthetic fibres on a laboratory scale, as summarized by Bach *et al.* (2002b), up to now, three separate major runs have been taken to scale up the $scCO_2$ dyeing process and the plant to an industrial scale.

Besides the development in Germany, an American consortium of NC State University, North Carolina, Unifi® Inc., Ciba-Geigy Corp. (USA), and Praxair Inc. intended to test the $scCO_2$ technology mainly for dyeing of yarns and fabrics from PET, cotton, polyamide, and PET/cotton blends. According to information from the NC State University website, the project ended in 1999 (Seastrunk, 1999). After that time, no further activities have been published where Unifi® Inc. was involved. Meanwhile, it seems that a 'prototype supercritical fluid dyeing system capable of dyeing multiple, commercial-size PET yarn packages has been built' (Montero *et al.*, 2000), but up to now no dyeing results or experience with this machine have been published and no information is available as to in which textile finishing company this machine is placed.

In 2003, an Asian consortium comprising textile-finishing and fibre-producing companies, and researchers from Fukui University started an approach with a budget of five million euro from the Japanese government to develop within three years a plant and processes on an industrial scale for $scCO_2$ dyeing of fibres that are difficult to dye by conventional water technology. The machine is built by Hisaka Works. Mitsubishi Rayon and Teijin as project partners are working on dyeing of polypropylene and aramide (Stylios, 2004; Aoyma, 2005). Results have not yet been published.

5.3 Current supercritical fluid dyeing technologies

In 2005, world fibre production was 60.8 million tonnes with PET being the leading synthetic fibre. The annual growth of PET production over the last three years was between 7 and 9% with a market share of 40.6% in 2005 (PET filament fibres 23.7%, PET staple fibres 16.9%). For comparison, polyamide had a share of only 6.4% (3.9 million tonnes) (Anon, 2005c).

Since 1999, production of cellulosic fibres has continuously increased with a slight decline for cotton in 2005. The market share of cotton with 41.2% in world fibre production is very similar to the share of PET. Over recent years, only wool and silk have had minor and stagnant shares of 2.0 and 0.2%, respectively (Anon, 2005c).

Because of the significance of PET and cotton, the development of supercritical fluid dyeing technologies worldwide is mainly focused on these fibres and only to a minor extent on wool, silk, polyamide and other technical fibres. While the dyeing of PET works very well in $scCO_2$, dyeing of polar fibres like cotton is still challenging when high fastness properties and colour yields are required. The limitations of dyeing natural fibres in $scCO_2$ arise from the inability of CO_2 to break hydrogen bonds (Kazarian *et al.*, 1996; Saus *et al.*, 1993d), the low degree of fibre swelling and the low reactivity of the OH-bonds in cellulose in the slightly acidic CO_2 medium (Bach *et al.*, 2002a). Furthermore, disperse dyes only show slight interactions with polar fibres, leading to unacceptably low fastness data, while reactive-, direct-, and acid dyes which are used in conventional water dyeing are nearly insoluble in $scCO_2$.

In this way, attempts have been made to increase the dye solubility and the dye uptake of cellulose and protein fibres in $scCO_2$ by using polar co-solvents. The affinity of disperse dyes to the fibre was increased by impregnation with swelling and crosslinking agents, and by modifications of the surface of the fibre with functional groups, as summarized by Bach *et al.* (2002a). In other $scCO_2$ experiments, reactive disperse dyes for dyeing of unmodified natural polar fibres and polyamide were used (Bach *et al.*, 2002a; Liao, 2004; Cid *et al.,* 2004; Maeda *et al.*, 2004).

For ecological reasons most of the dyeing experiments on natural fibres described so far lose the main advantages of being a water-free process. For dyeing of cotton, pre- and after-treatment are frequently more water- and energy-consuming than the conventional water-based dyeing process.

In order to obtain convenient high colour depths, substances are permanently fixed on the fibre surface in high concentrations of the modifying agent. This leads to significant changes in the fibre properties (of e.g. cotton) which are unacceptable for most applications (Bach *et al.*, 2002a).

Recently, there have been new developments based on reverse micellar systems for solubilization of conventional basic, acid, direct or reactive dyes from water dyeing for $scCO_2$-based dyeing of cotton, wool, silk, acrylics and polyamide (Sawada *et al.,* 2002, 2003, 2004a, 2004b; Sawada and Ueda, 2004; Jun *et al.*, 2004; Lewin-Kretzschmar and Harting, 2004; Jun *et al.*, 2005). In the future it has to be evaluated whether this can be an ecologically sound alternative for $scCO_2$ dyeing of cellulose and protein fibres. Currently, many questions concerning dye fixation, suppression of dye fibre repulsion, colour yield and the optimum reverse micellar system remain unanswered.

The most suitable $scCO_2$ dyeing technology under ecological aspects for natural fibres with all the advantages known from PET dyeing is the application of reactive disperse dyes. However, the dyes that have been applied in $scCO_2$ dyeing experiments so far are not commercially available yet and were custom-made in the laboratories of the different research groups.

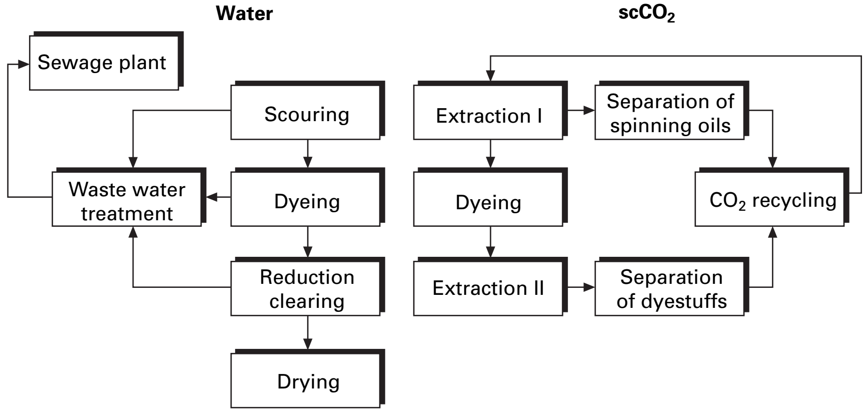
5.3.1 Environmental aspects of PET dyeing in $scCO_2$

Worldwide, the dyeing of PET in $scCO_2$ is the most extensively investigated finishing process and, while a convenient number of data sets are accessible to evaluate this process in particular in terms of many ecological aspects, there is a lack of published data for the equivalent water dyeing process which makes it very difficult to compare both processes in detail and to quantify the differences in their environmental impact.

From Fig. 5.2 it is evident that conventional water dyeing is an *end-of-the-pipe* process, whereas with $scCO_2$ a quasi-*closed loop* process can be accomplished. After precipitation of spinning oils and excess dye in a separator, CO_2 is recycled and can be reused. ‘Quasi’ means that extraction residues of dyestuffs and spinning oils are not recyclable as well as about 10% of CO_2 which is released into the atmosphere (Bach *et al.*, 1998).

5.3.2 Process steps for PET dyeing in $scCO_2$

The definite process steps for dyeing of PET in $scCO_2$ can be seen in Fig. 5.2. In short, the first step (Extraction I) represents the partial extraction

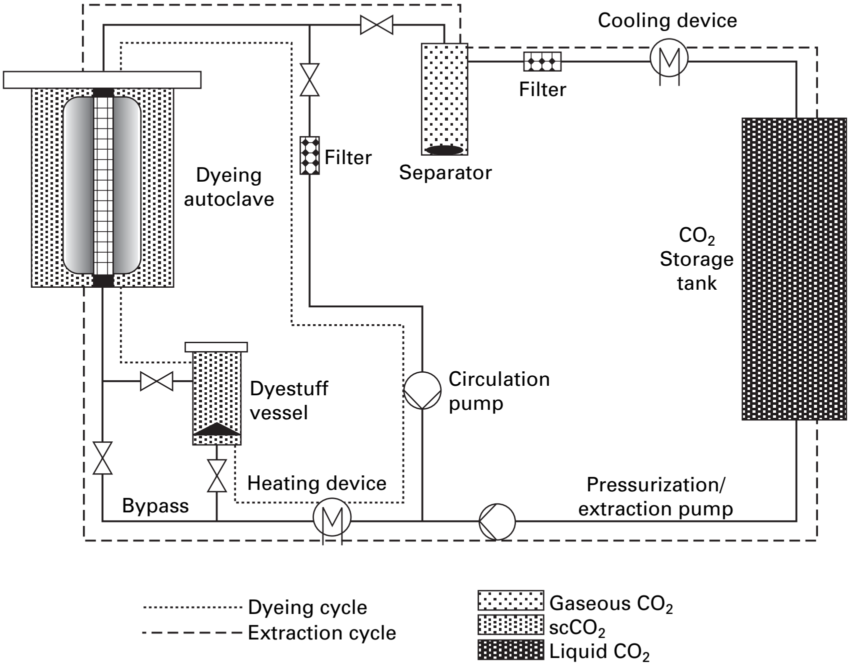


5.2 Comparison of the process steps for dyeing of PET using water and $scCO_2$ (Bach *et al.*, 2002a, modified).

of spinning oils, followed by dyeing. Then extraction step II is started for removal of adhering dye from the fabric surface and the inner of the plant by rinsing with fresh cold $scCO_2$. The temperature in the plant is decreased as fast as possible below the glass transition temperature of the polymer to avoid extraction of dye from the fibre bulk. Extracted dyes and spinning oils are precipitated in a separator. At the end of the dyeing process, CO_2 in the plant is depressurized under liquefaction to the pressure in the CO_2 storage tank of about 50–55 bar. Remaining gaseous CO_2 in the plant is released into the atmosphere. In illustration of the complete process, in Fig. 5.3 extraction and dyeing cycles are drawn in as well as CO_2 phase conditions in the different parts of the Uhde plant (Bach *et al.*, 1998). A flow scheme and a detailed description of the process has been published elsewhere (Bach *et al.*, 1998, 2002a, 2002b).

5.3.3 Scale-up parameters of the $scCO_2$ dyeing process and the plant

Based on the experience with the Uhde plant on a technical scale, data for an up-scaled process and plant have been published for the dyeing of 120 kg PET fabrics relating to a fabric length of 200 m and a width of 3 m (Bach



5.3 Schematic of the Uhde dyeing plant (Bach *et al.*, 1998, modified).

et al., 2004b). The volume of the whole plant is approximately 950 l and that of the dyeing autoclave 600 l. The up-scaled plant fulfils the process conditions as described in Table 5.2. A schematical drawing of parts of the front and side view of the plant is presented in Fig. 5.4.

In Table 5.2 only the most important parameters are presented. Besides temperature and pressure, the flow rate of the circulation pump in the $scCO_2$ dyeing cycle has a significant influence on the levelness of the dyed goods which is essential for a high product quality (Bach *et al.,* 2002a).

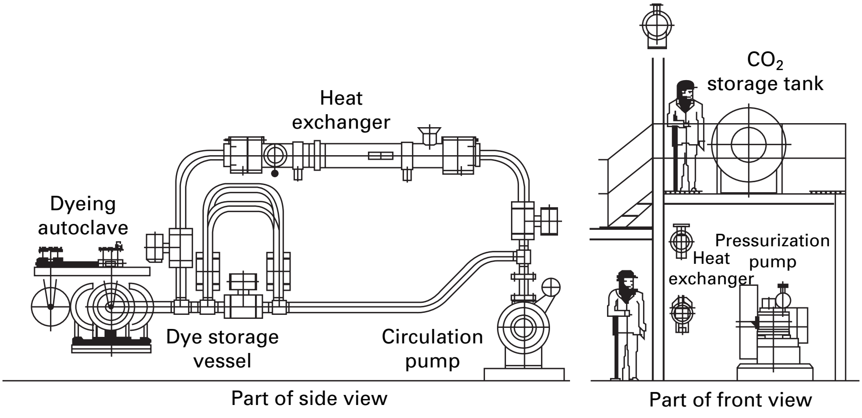
Determination of the process time in $scCO_2$

In environmentally sound processes, raw materials and energy should be used as efficiently as possible. In this context, the process time for a complete $scCO_2$ dyeing cycle is one of the key factors in the calculation of energy consumption of an up-scaled plant and has to be evaluated. For estimation of the dyeing time, knowledge of the solubility of dyes in $scCO_2$ is a very important parameter, but the relationships of solubility and dye distribution between the fibre and CO_2 are highly complex. In the literature, mainly

Table 5.2 Process conditions for dyeing of PET fabrics in $scCO_2$ based on the Uhde plant*

Parameter	Setting
Working temperature	100–140 °C
Working pressure	250–350 bar
Density of $scCO_2$	450–750 kg/m^3
Flow rate of $scCO_2$	1800–4200 kg min^{-1}

*Bach *et al.*, 2004b.



5.4 Schematic of the up-scaled Uhde dyeing plant (Bach *et al.*, 2004b).

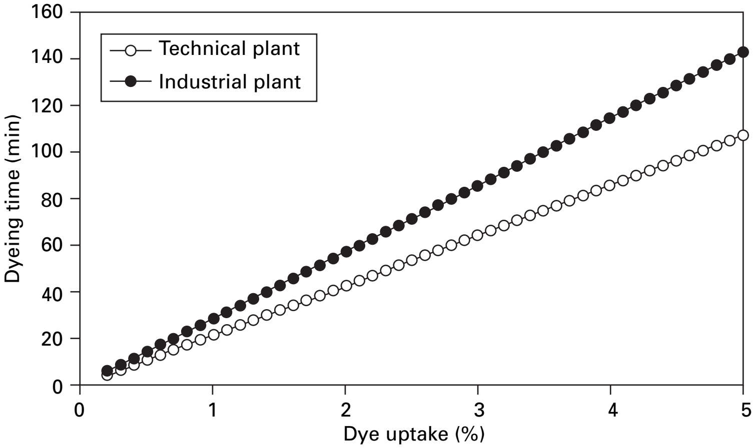
solubility data at equilibrium are available (Özcan *et al.*, 1997; Draper *et al.*, 2000; Lee *et al.*, 2001; Tabata *et al.*, 2001; Bach *et al.*, 2001; Bao and Dai, 2005), but this is scarcely applicable for practical use. Due to the very short contact times between the dyeing medium and the dyes in the dyestuff vessel, saturation of $scCO_2$ with the dyes is nearly impossible. Therefore, a theoretical model was developed for determination of dye solubility as described elsewhere (Bach *et al.*, 2004b).

Based on the model, dye solubility of several disperse dyes was determined at various flow rates of the circulation pump in the Uhde plant. The data show (not presented here) that doubling of the flow rate decreases the solubility of nearly all dyes tested by 30%, proving that non-equilibrium conditions predominate in the dyestuff vessel at optimum process parameters (Bach *et al.*, 2004b).

For a dye uptake of 2% – relating to 20 g of pure dye per kg of PET – calculated from the non-equilibrium solubility data in $scCO_2$, a dyeing time of 40 min in the Uhde plant and 60 min in the up-scaled plant is needed, as presented in Fig. 5.5. The dye uptake of PET in $scCO_2$ is equivalent to a minimum of 4% in water dyeing, when estimating an amount of auxiliaries in the dye formulation of 50%. Dye content of the disperse dyes used for water dyeing normally varies between 30 and 50% (Bach *et al.*, 2004b).

Energy consumption of the industrial $scCO_2$ dyeing plant

After evaluation of the dyeing step, which is the most time-consuming one, the total process time can be extrapolated. As schematically shown in

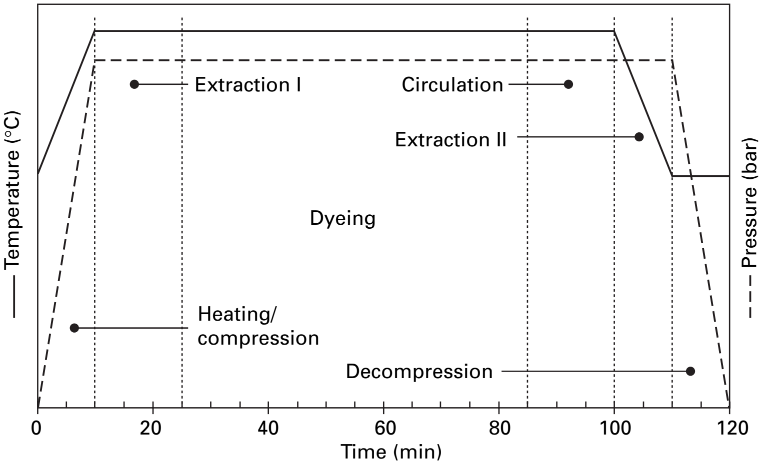


5.5 Theoretically calculated dyeing times for PET in the Uhde plant (technical plant) and in an up-scaled plant (industrial plant) based on the non-equilibrium solubility measurements under optimum dyeing conditions (Bach *et al.*, 2004b).

Fig. 5.6, process time is divided into pressurization/heating and decompression of 10 min each, extraction I and II of 15 and 10 min, respectively, and dyeing within 60 min followed by a level-out phase of 15 min, which can even be left out for many dyes tested (Bach *et al.*, 2004b). All in all, the whole process will take two hours.

Heating and cooling energies of the devices and the energies needed for heating and pressurization of the CO_2 were determined based on the data in Fig. 5.6, as summarized in Table 5.3.

The total specific energy consumption of the $scCO_2$ process is very close to that as published in 1994 by van Asselt and Klein Woltering from Tebodin B.V. for high-temperature beam dyeing of PET in water including rinsing/washing and drying of the dyed fabric. They obtained a value for the energy consumption of 4.53 kWh kg^{-1}, estimating a dyeing process time of 7.5 h (van Asselt and Klein Woltering, 1994). The calculations also



5.6 Flow scheme of the temperature and pressure programmes during the $scCO_2$ dyeing process in the up-scaled industrial plant (Bach *et al.*, 2004b).

Table 5.3 Specific energy consumption per kg of textile estimated for the up-scaled plant*

	Specific energy consumption (kWh kg^{-1})
Heat	1.5
Electrical energy incl. energy for cooling	3.0
Sum	4.5

*Bach *et al.*, 2002b.

agree to a great extent with the data of Ado Gardinenwerke GmbH & Co. (Schüler, 2002).

Although treatment time in $scCO_2$ is significantly lower compared with the water dyeing process including drying, the energy consumption of both processes seems to be similar. Probably, one reason could be that warm up before dyeing and cooling in extraction step II (Fig. 5.2 and 5.6) of the thicker steel walls of the $scCO_2$ plant, which are essential to handle the high pressure of the process, need more energy compared with a water dyeing plant. Another reason is that data of the electrical energy consumption in Table 5.3 also include cooling energy for liquefaction of CO_2 for recycling, which was not considered for the water-based process.

For reduction of energy consumption, it may be possible to keep the $scCO_2$ plant at a mean temperature during the whole dyeing process, thus avoiding unnecessary heating and cooling of plant parts. A cooling down to room temperature would only be necessary for maintenance work, repair or by a fall in production (Bach *et al.*, 2004c).

In particular, it might be possible to keep the temperature of the autoclave and the dyestuff vessel constant during the complete process cycle. In this case, only the temperature of the dyed goods, the interior of the autoclave and the CO_2 is changed in extraction step II. This would help to minimize the energy consumption of the process and the plant but a final quantification will only be possible after an industrial plant is put into operation (Bach *et al.*, 2004b).

CO_2 consumption of the industrial dyeing plant

For minimization of emissions in $scCO_2$ dyeing, most of the CO_2 in the process can be recycled, as presented in Table 5.4. The loss in CO_2 from the industrial dyeing plant was estimated by Uhde under consideration of CO_2-recycling under optimum conditions up to the pressure of the storage tank of about 50–55 bar.

Table 5.4 Specific loss in CO_2 of the up-scaled plant*

	CO_2-loss (kg)
Dyeing and dyestuff cycle	140
Separator	18
Total	158
Specific loss including separator (per kg textile)	1.23
Specific loss without separator (per kg textile)	1.17

*Bach *et al.*, 2002b.

Emptying of the separator is not needed after each dyeing. Therefore, the lower value of the specific loss of CO_2 is much closer to reality than the higher one (Bach *et al.*, 2002b) relating to a total loss in CO_2 of about 18%.

In order to recycle larger quantities, CO_2 can be evacuated by a compressor from the plant into a pressure vessel. There, the gas is cooled, compressed to 55 bar and returned into the storage tank. An increased recycling rate is also possible by cooling the CO_2 in the storage tank down below room temperature. However, this needs additional energy.

For both methods, a cost–benefit analysis has to be carried out for the rate of CO_2 recycling, on the one hand and costs for energy and machinery equipment needed for compression, liquefaction and storage of CO_2, on the other.

Economization in chemicals compared with water dyeing of PET

When considering minimal waste production as demanded for environmentally sound processes, $scCO_2$ dyeing of PET is really a 'clean' finishing process because only dyes are needed. For comparison, the environmental impact of the analogous water-based process is summarized in Table 5.5, according to the chemical composition of the effluents, to the waste air production during passage through the stenter and a listing of all *additional* chemicals which are essential in water dyeing. The data are calculated on the actual construction parameters of an up-scaled $scCO_2$ plant for dyeing and finishing of 120 kg of PET fabrics as described at the start of Section 5.3.3.

The data of the water consumption in Table 5.5 take into consideration the water input, wastewater and water for cooling. The effluent contamination is characterized by the chemical oxygen demand (COD), the nitrogen content and the phosphorus content of the wastewater after scouring, dyeing, reductive

Table 5.5 Ecologically relevant data of industrial finishing of PET fabrics in water*

	per kg PET	per process	per annum
Water consumption (m^3)	0.28	34	7480
Effluent contamination			
COD (kg)	0.26	30.6	6732
Nitrogen (kg)	0.002	0.22	48.62
Phosphorus (kg)	0.002	0.26	56.1
Waste air			
Waste air (m^3)	75	9000	1980000
Total carbon (kg)	0.002	0.21	45.7
Auxiliaries			
Dyeing (l)	0.07	8.6	1892
Reduction clearing (l)	0.06	6.8	1496

*Schüler, 2002.

afterclearing including rinsing after each process, and softening. The waste air results from drying of the PET fabric after the final softening process.

It should be noted that the data on the amount of auxiliaries of dyeing and reduction clearing are not quite exact, because they are all in liquid form and may contain a certain amount of water. The data on the auxiliaries in dyeing represent the input of an antistatic agent, a dispersing agent, a migrating agent and acetic acid. Process chemicals in reduction clearing are an antistatic agent, a reducing agent and sodium hydroxide.

The column '*per annum*' in Table 5.5 shows the data calculated for one dyeing process per day and 220 working days per year.

Generally, a complete finishing operation in water takes about 6 h (Schüler, 2002). Based on the significantly shorter process times, in $scCO_2$ theoretically up to six process cycles could be accomplished per day. That means, when working with one CO_2 dyeing plant, 20.3 m^3 of auxiliaries from dyeing and reductive afterclearing and about 45 000 m^3 of water and wastewater could be avoided per year.

Product quality after $scCO_2$ dyeing

For the transfer of a new process into industry, it is essential, that the field of application is broad and the quality of the products produced with the new technology must be at least equally as good as from the current technology. Based on the experience with the $scCO_2$ dyeing technology on a technical scale, it is obvious meanwhile that, for PET under optimum dyeing conditions, all shades as in water dyeing but also high colour yields are obtained. As proven by colorimetric measurements after multi-chrome dyeing of PET, no differences in the reflectance spectra at the inside, middle, and outside of the fabric pack were found indicating a high levelness of dyeing. All dyes applied in this technology are approved by the Oecotex Standard 100.

The quality of the dyed material concerning washing, rubbing and sublimation is also very good. Generally, fastness notes of five are obtained even when dye concentrations of 4.5% were applied. Compared with the water dyeing process on an industrial scale, wash fastness of PET when dyed in the same shade is sometimes up to one grade higher (Bach *et al.*, 2004a).

Stress–strain and viscosimetric molecular weight measurements of $scCO_2$ dyed PET show that no fibre damage takes place under optimum dyeing conditions. In fact, the breaking force and breaking elongation is sometimes higher compared with the blank and water-dyed fabric as tested by Ado. If heat-set PET is applied, shrinkage during CO_2-dyeing is very low: a maximum of 1.5%. In these special cases, shrinkage in CO_2 was generally lower than in water for all PET fibres tested (Bach *et al.*, 2004a).

Finally, it can be concluded that all of the quality standards of textile-finishing companies can be fully met with the $scCO_2$ dyeing technology (Bach *et al.*, 2004a).

5.3.4 Commercial competitiveness of the $scCO_2$ dyeing process

Another very important parameter for the transfer of this new technology into industry is the estimation of the economic efficiency of the $scCO_2$ dyeing process compared with water dyeing of PET. In Germany in particular, water and wastewater are very expensive. Related to the costs for energy and auxiliaries in water dyeing of PET and subsequent drying, the costs for water are about 60% of the total process costs (Schüler, 2002).

CO_2 is a relatively cheap gas with high purity grades and it is commercially available worldwide. CO_2 is very easily recyclable and can be reused as a process medium (Jessop and Leitner, 1999; Kemmere, 2005). Consequently, compared with a conventional water dyeing process, the operational costs in $scCO_2$ are much lower (Bach *et al.*, 2002a, 2002b; Schüler, 2002).

Moreover, by applying CO_2, industry becomes independent from water sources without generation of liquid wastes. While water quality can differ from city to city within the same country depending on the source of water, CO_2 is subject to international quality standards of worldwide validity. Because of the globalization of textile-finishing companies, dyeing recipes will be applicable worldwide, but compatibility of the dyeing plants has also to be checked in the future.

When considering process costs, there is an obvious economic advantage in the $scCO_2$ process, which is partly compensated by the high investment costs of the plant. It has to be kept in mind that process costs can be further diminished by installing three autoclaves in one plant (van Asselt and Klein Woltering, 1994). For example, in autoclave one, CO_2 is pressurized and the fibre extracted, in the second autoclave impregnation/dyeing takes place and the third one is in the operation mode of decompression, emptying and loading of new textile to be dyed. This parallel processing is possible just by opening and closing certain valves because two different pumps for pressurization/extraction and $scCO_2$ circulation are used (see Fig. 5.3 and 5.4). Some diagrams and flow schemes of plants using this concept have been presented by van Asselt and Klein Woltering (1994).

5.4 Future trends in supercritical fluid dyeing technologies

5.4.1 Fusion of finishing processes and dyeing of fully fashioned textiles

When there is a requirement for fast colour changes in fashion and fixture design, investigating the fusion of finishing processes such as impregnation of dyes, softeners and flame retardant agents in CO_2 will become more and more important. This would significantly decrease the process time for finishing of textiles and increase the flexibility of the process due to a make-to-order finishing within very low delivery times and small contingents of stock-keeping.

Flexibility can be further improved if fully fashioned textiles such as curtains, zippers, underwear, brassieres, and sportswear could be dyed in $scCO_2$ as claimed in a patent by Kerle *et al.* (2004). However, the optimum form of supply of the textiles in the autoclave has to be examined at first.

5.4.2 Dyeing of high-performance fibres in $scCO_2$

For many years $scCO_2$ has been regarded as a solvent that has the potential to overcome all of the problems of water dyeing for difficult-to-dye technical fibres such as meta- and para-aramides, poly(ether ether ketone) (PEEK), polybenzimidazole (PBI), polyimide (PI) and liquid-crystal polyesters (Vectran®). Meanwhile, it has become more and more evident that, if a synthetic fibre can hardly be dyed in water, the same will be valid in $scCO_2$ (Bach *et al.,* 2002a).

In order to improve the dye uptake of many high-performance fibres in $scCO_2$, application of co-solvents known as carriers from water dyeing such as 1-methyl-2-pyrrolidone, acetophenone, benzylalcohol, benzaldehyde and also water, alcohols and acetone in combination with high temperatures were suggested (Knittel and Schollmeyer, 1997; Bach, 1997; Hatano *et al.*, 2001) but dyeing of high-performance fibres in $scCO_2$ is still challenging. For the development of dyeing processes for difficult-to-dye technical fibres which are used in the textile industry, a deeper understanding of the CO_2/co-solvent (carrier) dyeing process is needed, suitable dyes have to be selected and removal of the solvent from the fibre by CO_2 extraction has to be determined to avoid an extra drying step. In addition, cleaning of the plant at color changes has to be optimized due to an increased solubility of many disperse dyes in $scCO_2$ when co-solvents are applied (Bach *et al.,* 2002a).

From the economical point of view, process costs will rise when working with organic co-solvents due to higher investment costs for explosion proof $scCO_2$ dyeing plants. Sealing rings in the plant have to tolerate the co-solvent and temperatures of up to 150 °C, which may also cause extra costs.

From the environmental point of view, dyeing of high performance fibres in $scCO_2$ with co-solvents has the advantage that separation of co-solvent and CO_2 is easily feasible due to the 'volatile' solvent properties of CO_2 (Jessop and Leitner, 1999; Kemmere, 2005); however, for recycling of the process medium, separation of dissolved substances from the spinning process and dyes has to be determined in much more detail.

In this way, as opposed to the conventional water-based process, carrier dyeing in $scCO_2$ has the potential to be a more environmentally sound and suitable dyeing process for difficult-to-dye technical fibres, but there are some challenges which must first be overcome.

5.4.3 Future of $scCO_2$ dyeing technology

Although a considerable amount of experience with the $scCO_2$ dyeing technology worldwide exists on a laboratory or technical scale, it is not possible to speculate about the future of this technology until a plant has been built and validated on industrial scale by a textile-finishing company. Testing and optimization of the process and the plant should be carried out at first with PET as the easiest-to-dye textile material in $scCO_2$ in order to deal with the questions that can only be answered in an up-scaled plant (Bach *et al.,* 2002a, 2002b, 2004b). Additionally, if this technology has been successfully proven on an industrial scale, this may also push forward the development of other water-free processes in textile finishing such as sizing, scouring, bleaching and dyeing of natural fibres, e.g. cotton, wool and silk. This will need co-operation between research organizations and the chemical industry, because examination and approval of new or modified finishing agents and dyes is very expensive.

5.5 Sources of further information and advice

For a deeper insight into the scientific aspects of $scCO_2$ dyeing, the possibilities and limitations of the technology for synthetic and natural fibres, dyeing concepts and mechanisms, the thermo-mechanical behaviour of fibres and solubility of dyes and the worldwide state-of-the-art, the review article of Bach *et al.* (2002a), is recommended.

For information about the phase behaviour and the physico-chemical properties of CO_2 and CO_2/co-solvent mixtures, there are two databases which can be used via the internet: http://webbook.nist.gov/chemistry/and http://www.questconsult.com/~jrm/thermot.html. Comprehensive information about CO_2 can also be obtained from the internet sites of many gas producers.

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6

Pollution abatement and waste minimisation in textile dyeing

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6.1 Introduction

‘Save the Earth to save the future’. Right from the inception of urbanisation and industrialisation with advancement in science of technology, it was gradually realised that growth cannot be considered to be a good thing if we ignore the environment in which we live. The textile chemical processing industry has importance of its own, being one of the basic needs of society and currently it is in the midst of a major restructuring and consolidation phase with the emphasis on product innovation, rebuilding and environmental friendliness. Given the dynamic nature of the textile wet processing industry in India as well as in other countries and its tremendous potential, this chapter aims to focus on the sources of water pollution as well as pollution minimisation and prevention strategies, followed by some suggestions and possible future trends in dyeing operations to protect the environment.

The terms pollution and contamination are sometimes used interchangeably in environmental matters to describe the introduction of a substance at a concentration sufficient to be offensive or harmful to human, animal or plant life. The word pollution is more strictly used to describe contamination caused or induced by human activities and is typically measured by reference to predetermined permissible or recommended tolerance limits.

The textile industry has a major impact not only on the nation’s economy but also on the economic and environmental quality of life in many communities. Textile processing generates various types of waste streams, including water-based effluent as well as air emissions, solid wastes and hazardous wastes. The nature of the waste generated depends on the types of fibres and the chemicals used, the type of textile facility, and the processes and technologies being operated. In quantity, wastewater generation is a major source of pollution from a textile processing factory as the treatments carried out on textile materials are essentially carried out through aqueous medium.

After the pre-treatment processes to remove impurities (either naturally present or added to perform certain temporary functions) from the fibres, the textiles are ready for value addition, which includes colouration. Dyes are applied to textiles for imparting colours fast to various agencies and the majority are synthetic, being derived from coal tar and petroleum-based intermediates. They are sold as powders, granules, pastes, liquid dispersions and solutions with concentrations of the dyestuff ranging between 20 and 80%. Although some naturally occurring dyes derived from animal or plant sources are also used, they are commercially less important. They, however, have their own market due to their biodegradability and hence are said to be environmentally friendly as far as the treatment of unutilised dye is concerned. Different fibre types accept different dye classes, which are applied in a variety of ways and impart the colour via different mechanisms, as indicated in Table 6.1.

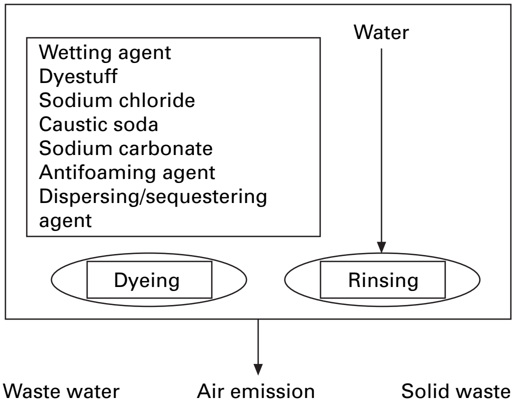
The components generally present in a textile dye bath are the dyestuff (colorant), solubilising chemicals, buffer system/pH controller, electrolyte (common salt or Glauber's salt), specialty dyeing assistants (such as retarder/accelerant, levelling agent, lubricant, defoamer, surfactant/dispersant, sequesterant, etc.) and water (Fig. 6.1).

Because of the variety and massive quantities of fibres used in textile manufacturing, even trace contaminants associated with them can accumulate into amounts, which may cause large scale pollution. At the same time, the usage of water as a vehicle for wet processes and a number of intermittent washing operations have the effect of diluting the pollutant concentrations. This makes the recovery of pollutants or discharged useful chemicals either impossible or uneconomical. The sequences in the manufacture of textile apparel, as far as wet processing is concerned, are slashing and sizing of yarn followed by fabric formation, desizing, preparation, dyeing, printing and finishing. In addition to the air- and water-pollutants released due to the chemical entities used, a considerable amount of packaging waste (like bale

Table 6.1 Use of different dye classes for various fibres

Dye class	Fibres
Acid	Wool and nylon
Azoic	Cotton and other cellulosic
Basic	Acrylic, CDPET*
Direct	Cotton and other cellulosic
Disperse	Polyester, other synthetics
Reactive	Cotton and other cellulosics, wool
Mordant	Natural fibres after pretreating with metals
Sulphur	Cotton and other cellulosic
Vat	Cotton and other cellulosic

*Cation dyeable polyethylene terephthalate.



6.1 Typical dye bath ingredients and the pollutants generated.

wrap materials), yarn waste in spinning, fabric waste from weaving, preparation and dyeing is also generated.

6.2 Reducing pollution in textile dyeing

In earlier days, the dyestuff selection, application and use were not given a major consideration with respect to their environmental impact. Until recently, textile dyers had little access to the information concerning the environmental impact of the dyes they used and, as of 1984, even the chemical composition of at least half of the dyes used in the industry was estimated to be unknown. In the last few years, however, more information on the environmental consequences of dyestuff usage has become available and the dye manufacturers themselves have substantially eliminated toxic or hazardous dyes from their product lines while actively searching for safer substitutes. Presently, the dye manufacturers seek to offer dyes that provide water and energy savings, reduce pollution and increase efficiency in usage of dyes and chemicals and at the same time, raise the productivity consistent with the customer needs and product. Computer colour matching systems are being widely used to control the shade variations from batch to batch. The dyeing process as a whole creates several environmental concerns, which are possible to reduce by knowing their sources and taking appropriate measures. These sources and the measures adoptable may be categorised as follows:

1. Textile raw fibres may be contaminated with polluting chemicals.
2. Dyes contain pollutants and hazardous materials.
3. Auxiliary chemicals used during dyeing may have their own impact.
4. Dyeing operations are water-intensive leading to large volumes of effluent.
5. As far as possible recycling, reuse of the dyestuffs and chemicals should be practised.
6. Implement overall best management practices.

6.2.1 Raw fibres contain pollutants

Both natural and man-made fibres may contain polluting chemicals employed during their growth or manufacturing process to protect them from adversities. As shown in Table 6.2, natural fibres exhibit great variability in their quality and the extent of contamination and thus should receive careful attention in any pollution prevention program. A comprehensive incoming raw material QC program is highly advisable to detect and control these contaminants before they become serious pollution problems. Trace levels of the heavy metals like copper, tin and zinc as well as pesticide residues imparting high BOD and COD are known to be present in the natural fibres.

Wool is a significantly important commercial natural fibre. The main concerns about wool processing are the presence of fats, oil and grease (FOG) and aquatic toxicity arising from pesticide residues present on raw wool. Waxes and oils from such fibres derived from animal sources can contribute to BOD and COD. Both FOG and the pesticide residues can contribute to the aquatic toxicity. Pesticides are applied directly to sheep to reduce parasitic infestation, and these residues are released into wool-processing wastewater during preparation and dyeing.[1] Wimbush[2] reported that a specific agricultural residue, pentachlorophenol (PCP), was found at levels as high as 100 parts per million (ppm) in consumer products such as wool carpets, because of the extremely high variability of pesticide application. For the residues in raw wool, a comprehensive raw material testing protocol is necessary for pollution prevention. Industry standards, such as the Woolmark carpet certification system, have been set up for proper raw material pre-screening. This certification system requires that all the incoming raw materials be tested to ensure that they do not contain PCP above the regulatory level of 5 ppm.

Metals can accumulate in sludge or in the waste treatment system itself, causing potential long-term environmental problems. The spinning mill should perform the incoming quality control check to eliminate as far as possible the heavy metals in their effluent.

In the case of synthetic fibres, the added spin finishes must be removed to ensure uniform penetration of the fabric by dyes and to avoid their reaction

Table 6.2 Natural fibre contaminants and associated pollution problems

Contaminant	Resulting pollution
Natural waxes and oils	BOD, COD, FOG
Metals	Aquatic toxicity, treatment system inhibition, accumulation in sludge
Agricultural residues	Aquatic toxicity
Lubricant residues arising from harvesting and processing	BOD, COD, FOG

or precipitation with the dyes. If left on the fibre, volatile components of the spin finishes can produce toxic air emissions when vaporised by high-temperature processes such as drying, heat setting, thermo-fixation and curing in ovens. To prevent these emissions, spin finishes must be scoured from fibre material before dyeing. Although such scouring eliminates the air pollution problem, it is substituted with the pollution of water. For synthetic fibres also incoming quality control should be performed to identify the spin finishes with their components that could vaporise during heat setting. One method for such pre-screening is to heat the fabric (or yarn) in a laboratory oven and collect a sample of air from the oven vent for evaluation. Sampling can be performed using various methods described in the literature.[3–7]

6.2.2 Dyes contain heavy metals and hazardous pollutants

Commercial dyes constitute active ingredients ranging typically from 20 to 80%. Dyes may themselves contain pollutants and hazardous materials like heavy metals, copper, nickel, chromium, mercury and cobalt. In most dyestuffs, metals are present only as trace impurities. They are, however, highly dangerous due to their absolute resistance to biodegradation and tendency to accumulate into higher concentrations, thereby increasing their toxicity to living beings. Metals such as copper are known to be toxic to aquatic organisms.[8] The extremely low concentrations of these metals make their removal/recovery from wastewater not only difficult but also uneconomical. They, therefore, either become part of the sludge generated from the wastewater through flocculation or are likely to pass through the entire effluent treatment system.

Metals are present in dyestuffs for two different reasons:

- During the manufacture of some dyes, mercury or other metals are used as catalysts and may be present as a by-product.[9] Many anthraquinone dyes are derived by sulphonation in the presence of mercury catalysts.
- Some dyes include metals as an integral part of the dye molecule as the metallic content is essential to the performance of a dye as a textile colorant.

Dye manufacturers are now very conscious about the environmental impact of dyestuffs along with the requirements of better economy of the manufacturing process, and the high tinctorial value and higher wet fastness of dyed textiles. Some dye manufacturers make use of mercury-free manufacturing practices.[10] The metals most commonly found in dyes as part of the dye structure are shown in Table 6.3.[8] In addition, other types of colorants can also contain metals, notably yellow pigments based on lead chromate and orange pigments based on molybdate.[11] Also, some other pigments of various colours are based on cadmium. Some studies present the lists of dyes and printing inks

Table 6.3 Metals in various dye classes

Dye class	Typical metals*
Direct	Copper
Reactive	Copper and nickel
Vat	None
Disperse	None
Acid	Copper, chromium, cobalt
Metal complex	Copper, chromium, cobalt
Mordant	Chromium

*Does not imply that all dyes contain these metals.

that contain metals.[12,13] The metal content of dyes can be found out by consulting the Material Safety Data Sheet (MSDS) for the dye.[14]

This, however, does not imply that all the dyes in a given application class contain these metals. It is always advisable to pre-screen the dyes to be used and their environmental information before procuring them in order to reduce the incoming pollution load.

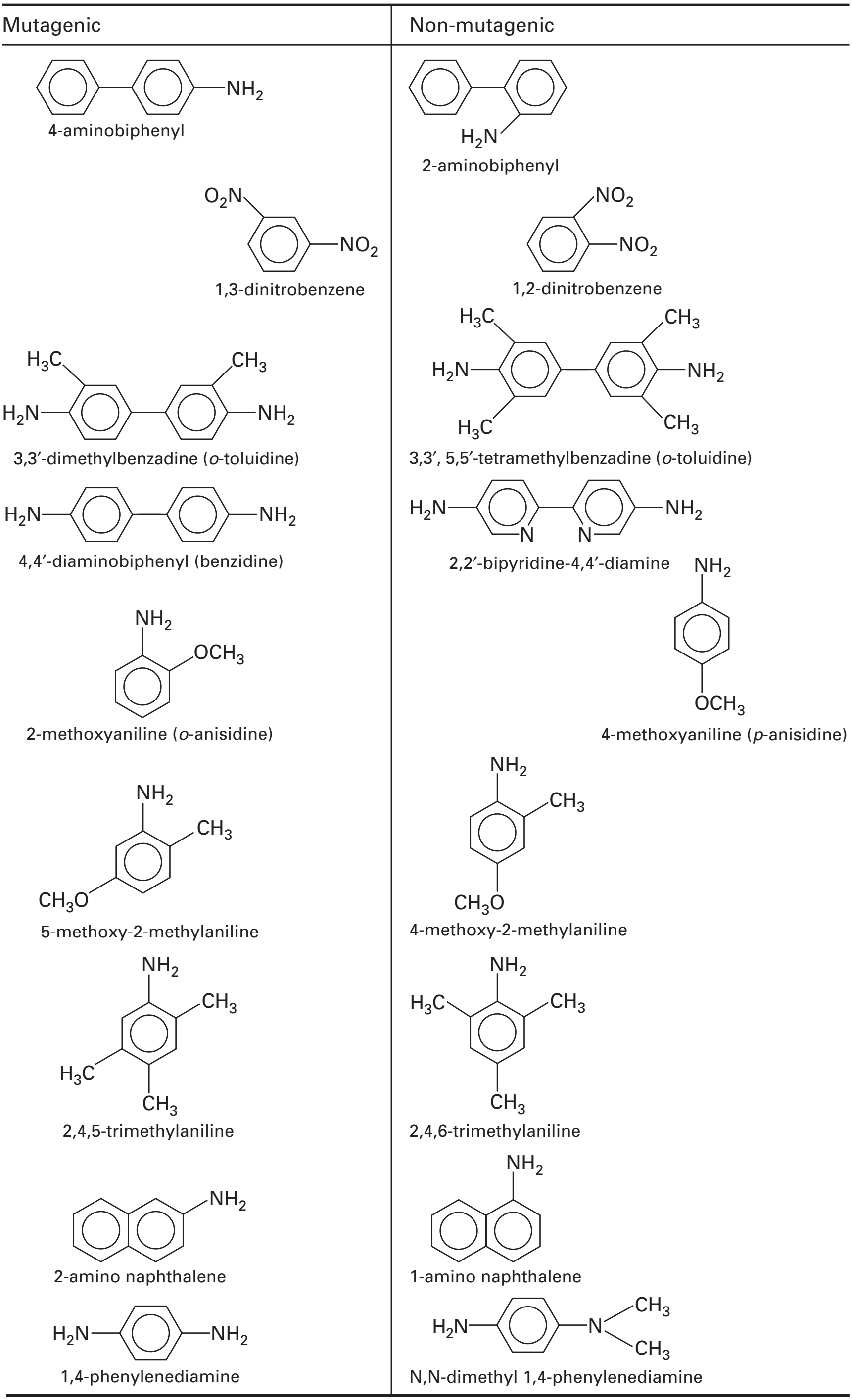
In recent decades, several environmental agencies[15] and activist groups have advocated a ban on chlorine and chlorinated chemicals as essential to protect the environment. The dioxin reassessment began in 1991. Greenpeace activity demands that chlorine should be banned in incinerators, paper and plastic because levels of dioxin currently found in the bodies of the general human population, in the food chain, and in the environment are claimed to be already in the range at which severe effects on reproduction, development and the immune system occur. Greenpeace[16,17] began its US anti-chlorine campaign based on potential birth defects in late 1992.

As more than half of the chemical production in Europe is directly or indirectly dependent on chlorine, the impact of such a ban would be immense, particularly for organic colorants which are predominantly dependent on chlorine chemistry at some stage in their manufacture; about 40% of the organic pigments produced worldwide contain chlorine in the pigment itself, although this corresponds to less than 0.02% of total chlorine production.[18,19]

Some mutagenic dye intermediates and their safer substitutes are shown in Fig. 6.2.

6.2.3 Auxiliary chemicals may increase pollution load

Some auxiliary chemicals used during dyeing may have an adverse environmental impact. Although their function is to assist effectively the adsorption and fixation of the dyes into the fibres, they are unlikely to be consumed completely during the dyeing process and hence, may lead to pollution load on rinsing the dyed material using large amounts of water. The



6.2 Some potentially mutagenic dye intermediates and their proposed safer substitutes.

spent dye bath contains varieties of such auxiliary chemicals including salt with each one having a different environmental impact.

The BOD values for dyestuffs may be up to 100 000 ppm. The BOD load of auxiliary chemicals added to the dye bath varies between moderate and high. There is no effective and economic way to control this pollution load other than either to use less or to opt for ecofriendly substitutes. Care needs to be exercised that, by adopting these measures, the quality of the dyed material is not affected.

Even process modification may help sometimes. As a simple example, the use of pressure dyeing at 120 °C to 130 °C for polyester can eliminate the need for adding carriers to the dye bath. As far as possible, textile processors should seek to reduce the use of dyeing auxiliaries, particularly paying attention to those used for dyeing of synthetics. Table 6.4 suggests some alternative methods.

Formaldehyde, which is widely used in the synthesis of auxiliaries, such as dye-fixing agents in direct and reactive dyeing and printing or dispersing agents for disperse and vat dyeing, is a respiratory sensitiser and skin irritator and should be either totally eliminated or substantially reduced by substitution with non-formaldehyde-based products.[20] Chavan *et al.*[21] have shown some success in the dyeing of cotton with sulphur dyes substituting the toxic sodium sulphide, which is hazardous to health and environment, by reducing sugars obtained from acid hydrolysis of molasses. Mathur and Gupta[22] have reported that the dried aqueous extract of banana flower petaloid can be used as a mordant for dyeing of wool. Shukla[23] suggested some processes for a reduction in the use and reuse and for recycling chemicals as well as a change in the process design for ecofriendly processing of protein fibres. A range of optimised chroming methods is available to minimise the dye house effluent load.

Some important aspects are to be considered carefully. Reduction of dyes by sulphide should be avoided. Dichromate oxidation of vat dyes and sulphur dyes should be substituted by peroxide oxidation. The use of sodium hydrosulphite should be minimised and, if used, it should be stabilised in an environmentally safe manner, say, mechanically or by polymers instead of aldehydes and toxic metal-containing compounds. Halogenated solvents and

Table 6.4 Non-chemical methods to assist in eliminating dyeing auxiliaries

Fibre type	Dyeing assistants to target	Alternative methods of control
Acrylic	Retarder	Rate of temperature rise
Nylon	Retarder	pH, temperature
Nylon	Leveller	pH, temperature
Polyester	Carrier	Temperature, time
Polyester/cotton	Lubricant	Fabric transport mechanism

dispersants for dyes and chemicals should be substituted where possible by water-based systems. For polyester, bio-eliminable dispersants should be used. Urea should be substituted as a dye-solution assistant as much as possible. To reduce the need for auxiliaries (buffers, levelling agents, retarders etc.), dyeing should be carried out as much as possible with decarbonated water controlled by temperature and pH. It is advisable in some cases to substitute EDTA by NTA. Polyester dyeing should be carried out without carriers if possible. Carriers containing chlorine (e.g. trichlorobenzene, chlorinated aromatics) should not be used: high temperature (HT) dyeing is to be preferred. If carriers are necessary (polyester/wool blends), non-hazardous, non-halogenated carriers must be used. Hazardous carriers include di- or trichlorobenzene, butylbenzoate, methylcresolate, *o*-phenylphenol, biphenyl, biphenyloxide, benzylbenzoate and chlorinated aromatics. Stabilised hydrosulphite should be used to prevent oxidative decomposition of sodium hydrosulphite in continuous pad-steam dyeing of cellulosic and cellulosic blend fabrics with vat dyes. In view of the environmental concern about possible harm from the use of aldehyde (formaldehyde or acetaldehyde-forming sulphoxylate), stabilisers and toxic metallic salts (Ni cyanides) or borohydrides for release of the reducing agent, such systems, if used, should be replaced by either mechanical methods or high molecular weight polymeric auxiliaries.

In dyeing vat and sulphur dyes, the reduced solubilised dyes are oxidised after dyeing to the insoluble state. Traditionally the oxidant is dichromate, still used to a large extent. ‘Chrome’ oxidation should be replaced immediately or, if this is not possible, strictly controlled. Two alternatives for chrome replacement are alkaline and acid hydrogen peroxide.

Last but not the least, efficiency should be optimised by initial trial and re-evaluation by improving the selection of dyes and recipes and the processing technique as well.

6.2.4 Dyeing operations are water-intensive

Contents of wastewater

Dyeing operations consume large volumes of good-quality water, which is becoming scarce and, hence, the most essential desire of any processor is to reduce the water consumption. A number of advantages are associated with this. Apart from reduction in the cost of the process, the pollution load also decreases as the addition of chemicals based on liquor volume is reduced and, therefore, the amount of effluent subjected to treatment is reduced. Table 6.5 indicates the water requirements of various machines and processes used in dyeing. Effluent from dyeing and rinsing operations contains unreacted or unfixed dyes and numerous types and quantities of auxiliary chemicals, including salt. The effluent containing these compounds may be highly coloured

Table 6.5 Water consumption in typical machines and processes

Dyeing machine/process	Water consumption (l kg^{-1})
Beam	167
Beck	234
Jet	200
Jig	100
Paddle	292
Skein	250
Stock	167
Pad-batch	17
Package	184
Continuous	167
Indigo range	8 to 50

and interferes with the transmission of light in receiving waters; high doses of colour in the wastewater can interrupt photosynthesis and affect aquatic life. Aesthetic concerns about textile-mill effluent have led to increased regulatory attention even at the local level.[24]

Colour can also interfere with ultraviolet (UV) disinfection of the treated wastewater.[25] Some commercially important dyes have acute fish toxicity: 48 h acute toxicity to *Daphnia magna* and a 72 h algal growth inhibition (*Scenedesmus subspicatus*) in accordance with ECO Guidelines. The toxicity to aquatic organisms was assessed based on the results from toxicity tests covering three trophic levels; fish (test 203), Daphnia (test 202) and algae (OECDs test guidelines, test 203, 202 and 201, or equivalent). Data for the most sensitive organism were used in the assessment according to: LC/EC/IC50 < 1 mg l^{-1} (very high toxicity), 1–10 mg l^{-1} (high toxicity), 10–100 mg l^{-1} (moderate toxicity) and >100 mg l^{-1} (low toxicity) where LC is lethal concentration, EC is effective concentration and IC is inhibition concentration.

A significant number of the dyes could be classified in the EU as 'dangerous' for the environment solely due to their much lower algal LC_{50} values (the concentration of a substance required to inhibit the growth rate or other function of organisms exposed to it). However, it has been demonstrated that, in most cases, this algal growth inhibition is caused by the light absorption of the coloured test solutions rather than by actual toxicity.[26] This result exempts these compounds from classification under the EU criteria.[27–29]

Water conservation

Wastewater from processing is the most common source of environmental concerns for textile operations.[29,30] The main unit processes that produce waste are the large number of rinsing and washing operations that are interspersed between almost all main process categories, i.e. preparation, dyeing/printing and finishing.[31] These stages consume large volumes of water. This is very obvious, since the wet processing by itself is a heterogeneous operation thereby restricting the exhaustion on fibres of the dyes and chemicals from the bath and delivering them as a waste leading to pollution of the wash liquor. Thus, washing and rinsing operations are the major operations in textile processing that have significant potential for pollution prevention/ reduction. Optimisation of these operations conserves significant amounts of water and, in turn, reduces the ultimate pollution load to be treated. In some cases, careful auditing and implementation of controls can achieve wastewater reduction of even up to 70%.[32]

Several typical washing and rinsing processes include:

- Drop and fill batch washing
- Overflow batch washing
- Continuous washing (counter current, horizontal or inclined washers).

In the drop-fill method of batch washing, spent wash water is drained and the machine is refilled with fresh water. The fabric in the machine retains much of the previous bath, sometimes as high as three to four times of weight of material, if it is a natural fibre material such as cotton. This amount of liquor held by fabric can be reduced mechanically by using techniques such as extraction or blow down. Brenner *et al.*[32] present a computer program that calculates the amount of contaminant remaining in the fabric at any given time. The overflow method of washing consumes large amounts of water since, instead of removing the unfixed dye and auxiliary chemicals in a successive batch-wise manner, the removal is by continuous dilution of the pollutants till their concentration drops nearly to zero. In both these methods, there are fewer chances for reuse of water, which has been heavily contaminated with pollutants.

The counter current washing method is the right approach towards efficient reuse of water for washing. It is relatively straightforward and inexpensive to implement in multi-stage washing processes. The principle used is very simple. The very first wash contains the maximum amount of pollutants, which goes on decreasing with successive washings and the final wash liquor contains such low quantities of pollutants that it is virtually as pure as the fresh water used for washing. Thus, the wash water contaminated with the least amount of pollutants from the final wash is reused for the next to last wash and so on until the water reaches the first wash stage, after which it is so highly contaminated that it is uneconomical to attempt any kind of its reuse, unless compelled to do so. It is then simply discharged into the effluent stream. This continuous technique of washing is useful for the washing of textiles after they have been subjected to continuous dyeing. A comparison of several methods of washing shows the benefits of the counter current washing technique, which can produce significant savings as against the standard drop-fill method. The counter current washing process requires the addition of holding tanks and pumps.

Counter current washing may be conducted by employing horizontal or inclined washers as shown in Fig. 6.3. The mechanical construction of an inclined or horizontal counter current washer has to be better than a traditional vertical washer since the weight of water pressing down on the fabric can cause it to sag, balloon or stretch. If properly constructed and maintained, horizontal or inclined washers can produce high-quality fabrics with much better washing efficiency and reduced water use.

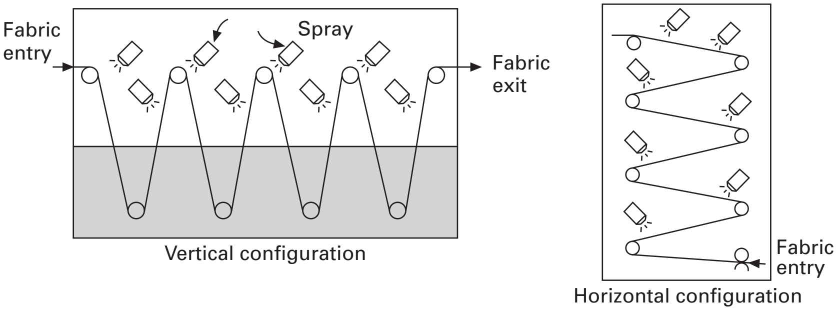
A report on water consumption for a typical continuous bleach range found that consumption at washing stages accounted for 90% of the total. The application of properly regulated counter current flows reduces the water use. A process modification such as a combined one-stage bleach and scour also would save an additional 55% of water, along with energy savings.[33]

6.2.5 Recycling and reuse of dyestuffs and chemicals

Dye bath replenishment technique

To save on the consumption of dyes and chemicals, the dye bath constituents should be analysed after exhaustion onto the textile and then replenished for subsequent use for dyeing another batch. In this manner, a single processing bath can be reused for a number of times before being discharged as effluent.[34,35] The capital cost of setting up such a reuse system is not very high.[36] This practice has the potential to reduce significantly the concentration of pollutants in the effluent of a textile-processing plant. It has been reported that the COD as well as the volume of effluent was reduced by about two-thirds due to dye bath reuse through a replenishment programme.

The dye bath replenishment also offers the potential not only for savings in water and dyestuffs, but also in auxiliary chemicals. It is an economically attractive alternative to conventional batch dyeing wherein after a single dyeing operation the dye bath is drained irrespective of the dye concentration



6.3 Washing configuration.

left back in the dye bath. Recent research and applications have shown that the technique is applicable to many types of batch dyeing programmes. Dye baths having few types and minimum quantities of auxiliary chemicals are comparatively easier to manage for dye bath reuse through the replenishment technique as, other than dye exhaustion, there are few chemical changes during the dyeing processes. Thus, the dye bath of direct dyes for cotton contains only dye and salt and hence is very easy to manage for the so-called 'standing bath' technique of dye bath replenishment. Similarly, for dyeing of acid dyes, the dye bath consists of the dye, the salt as retarder and the acid as pH controller/exhausting agent. Such a dye bath is possible to replenish. The dye baths of disperse dyes for polyester are also manageable since they comprise the dye, acetic acid and a dispersing agent. In all these cases, difficulty will arise in reuse of the dye bath only because of the high temperature that the bath has attained during earlier dyeing. This causes the starting temperature of reuse bath to be higher than that of fresh water. Cooling is necessary before reuse of the replenished dye bath for achieving uniform dyeing results. Generally, the loss of heat during storage of exhausted dye liquor and the cooling due to water added to make-up the liquor ratio are sufficient to drop the dye bath temperature to a safe level for the next dyeing.

A higher degree of difficulty may be expected from other classes. Thus, for the vat or sulphur dye baths, constant monitoring to keep them in dissolved form is essential and, hence, their quantitative estimation is difficult. In the case of reactive dyes also, after addition of alkali for fixation of the dye on cellulose, the residual dye is hydrolysed and, hence, the reactive dye bath cannot be used again.

The easiest situation to manage is the reuse of a dye bath in the same equipment to repeat the same shade with the same dye. The textile form to be dyed will be of the same fibre type, however, it is also preferable to have it in the same form (i.e. yarn, fabric of same construction etc.) since the mechanical factors deciding the dye penetration will remain identical. Where exactly the same shade depth is not a requirement of this replenished bath dyeing, and only a roughly calculated darker or lighter shade with the same dyestuff is to be obtained, it is easier to achieve. However, this is not always the case and a perfect shade matching may be desired. Most difficult will be the reuse of dye bath by addition of new colorants to reconstitute a dye bath. Rarely, the dye bath shows complete exhaustion and at least a trace of the earlier used dyestuff remains in the bath. In such situations, the remaining colour will definitely have a bearing on the new shade to be developed and hence reuse is not advisable. There will be potential problems with shade matching and metamerism.

The replenishment of dye bath was considered in the past mainly for repeat dyeing with exact reproduction of the first obtained shade and not for dyeing applications to obtain the same colour with a lower depth. The process of reuse of dye bath no doubt helps in giving consideration to the environmental aspects of dyeing by repeated use of water and a part of the chemicals and dyes. However, a more appropriate approach would be to use the partially exhausted dye bath to obtain a lower depth of dyeing. This will serve to further reduce the colour content of the bath and also it may not require replenishing additions of the salt and auxiliaries. In most of the cases, it is conceivable that the dye bath after second dyeing and, exceptionally, after third dyeing, will be almost colourless, thereby decreasing the pollution load drastically.

Textile dyeing is a very complicated heterogeneous process and there are many factors that are likely to hinder implementation of the dye bath replenishment programme. Both theoretical and practical knowledge play important roles in working out the methodology for dye bath replenishment.

Before attempting dye bath reuse, the most basic operation is to analyse the bath for the amounts of unexhausted dye and the residual chemicals. The unexhausted dyestuff must be analysed to determine the exact quantities remaining in the dye bath. This ensures the proper desired shade to be achieved in the next dyeing cycle through replenishment of the exact amount of dye to the reused dye bath. The analysis is performed with a visible spectrophotometer. Such analysis will simplify calculations required for the dyestuff additions. Complications may, however, arise when a mixture of dyes having close λ_{max} values is being used or a component dye in the mixture is in extremely small quantities or when the dyes in the mixture are interacting with each other.

Most auxiliary chemicals used in the dye bath are not added in extremely precise amounts as for the dyes but vary in quantity (e.g. 2–3 g l^{-1}). Because of this and also because they do not exhaust to an appreciable degree during the dyeing process, to estimate the amount necessary for replenishment is difficult. There are no handy and easy techniques such as spectrophotometry to estimate the concentration remaining in the dye bath. These chemicals may be lost by several mechanisms, which include losses due to exhaustion onto the fabric, evaporation from open dyeing machines, chemical reactions and dye liquor carry-off by the dyed material. These losses may be around 10% or higher depending on the components of a blended chemical specialty. As a generalisation, however, their make-up quantity is taken as about 10%, amounting only to their carry off on the textile material. When the auxiliaries are exhaused or partially depleted during dyeing, it is sufficient to estimate the degree of exhaustion and the quantity needed to replenish the bath.

It is possible to save the exhausted dye bath for reuse in two ways. The dye bath is transferred to a separate holding tank, and the textile is rinsed and washed in the same dyeing machine using fresh additions of water. The rinsed material is then removed and the exhausted dye bath from earlier dyeing is returned back for the next dyeing cycle. Alternatively, the dyed material may be transferred from the exhausted dye bath to a rinsing machine. In both cases, care needs to be exercised to avoid spilling of dye liquor while transferring for achievement of environmentally good practice. In both schemes, the dye bath needs to be cooled down. However, as no dilution of bath liquor should occur, indirect cooling methods should be used.

While replenishment of the dye bath is being performed, it should be in terms of the quantities of water adhering to the dyed material that are removed from the dye bath, the auxiliary chemicals consumed during dyeing and the dyestuffs needed for the next dyeing cycle to attain a particular depth of colour.

Addition of water should also take into account the loss through evaporation due to dyeing at high temperature. Auxiliary chemicals that are not consumed during dyeing are added in proportion to the amount of water added. However, those auxiliary chemicals that exhaust during dyeing are added in further quantity to make up for such exhaustion. Exact analysis as in the case of dyes is not required for this purpose. Dyestuff addition is determined on the basis of the exact exhaustion that has taken place in earlier dyeing and the shade required in the reuse of dye bath. Salt additions are generally avoided or may be done in only small quantities of 10% of the amount added during fresh dyeing.

Information is available on dye bath reuse and reconstitution or other pollution prevention techniques,[37] and also from the *Pollution Prevention Pays Program*, Department of Natural Resources and Community Development, Division of Environmental Management, P.O. Box 27687, Raleigh, North Carolina 27611-7687.

The number of cycles that a dye bath can be reused for is limited by the build-up of impurities that occur every time the dyeing is carried out.[38] Since most of the dyeing operations are performed at higher temperature and in the presence of chemicals controlling bath pH, the incompletely removed impurities during the pre-treatment processes may be extracted from the fibre material. These impurities include naturally occurring impurities, waxes and emulsions, sizing chemicals, knitting oils and fibre finishes. The so-called other impurities from a dyeing point of view can also accumulate from dye bath diluents, the build-up of electrolytes, addition of acids and bases for pH control, impurities received through steam if direct steam is used for heating the dye baths and the emulsifier systems from exhausted specialty auxiliary chemicals. Excessive amounts of surfactants also act adversely causing retarding or even stripping of dye during the dyeing from a replenished bath. They also cause increased foaming with increasing number of reuse cycles. Although it is theoretically possible to reuse the dye bath for 20 cycles, the practicalities prevent this.

Batchwise exhaust dyeing is capable of producing small lots in a short time. Although reuse of dye bath in batch-dyeing operations is said to be possible, it requires special scheduling, putting limitations on the flexibility of dyeing varieties. That is why batch dye-bath reuse may not be possible every time. As in batch dyeing, the key to minimising colour discharges in continuous dyeing operations is to maximise dye fixation, which takes place mainly through application of steam, thermofixation, or chemical agents. The proper dwell time and temperature in the steamer or in the stenter used for thermofixation are essential for optimum fixation. Further, in order to minimise dye wastage into effluent, only the required volume and concentration of dye solution should be prepared so that no extra solution remains to be discarded at the end of the run. This is the main source of colour content in wastewater from a continuous dyeing operation. As against batch dyeing, the volume of dye liquor discarded into wastewater through continuous dyeing is much less.

Good quality soft water is scarce in some places and, even after using replenished baths for dyeing, it becomes necessary to treat wastewater in such a manner that it becomes usable either for fresh dyeing or for other purposes such as cleaning. Even after removal of all possible impurities from textile dye house effluent, through primary and secondary treatments and even after removal of colour and heavy metals by various means, the dissolved electrolytes remain present in the wastewater. These cannot be removed by any process other than by reverse osmosis (RO) technique, which is a costly operation as compared with other conventional techniques of treating dyeing effluent.

Reverse osmosis (RO or hyperfiltration) is very effective and efficient for recycling and reuse of wastewater.[39–42] Because of the open character of the membranes, the productivity is high. RO is applied mainly for removal of dissolved salts from water. RO membranes work on the principle of separation of salt molecules by diffusion through the membrane and not by filtration through the pores. The pressure that is required for RO operation is much higher than the pressure required for micro and ultra filtration, while productivity is lower. It is a low-energy process as the liquids have to be pumped through the membrane. (Source of information: Lenntech Water treatment and air purification, Holding BV, Rotterdamseweg 402 M 2629 HH Delft, The Netherlands. http://www.lenntech.com/index.htm.)

The benefits derived by using RO are:

- Energy consumption reduced by 70%
- Water consumption reduced by 90%
- Chemical consumption reduced by 100%
- Time consumption per lot reduced by 60%.

The total amount of energy that is used is minor compared with alternative techniques such as evaporation. Comparison of water reclamation techniques in reactive dyeing of cotton is shown in Table 6.6. Process improvements have resulted from the use of Best Available Techniques (BAT) in the textile industry in Denmark (e.g. Kemotextil A/S).

Table 6.6 Comparison of water reclamation techniques in reactive dyeing of cotton

	Effect of wastewater characteristic on			
Wastewater characteristics	Membrane filtration	Chemical precipitation	Activated carbon	Counter current evaporation
Initial high dyestuff concentration	0	0	+ve	0
High salt concentration	–ve	–ve	+ve	–ve
Detergents and other COD	0*	–ve	0	0
High temperature	+ve	–ve	0	+ve

Note: 0 not influenced significantly, +ve positive influence, –ve negative influence, *specific compounds, e.g. cations, can influence negatively.

6.2.6 Best management practices

The benefits of good management of resources and processes from the point of view of economy may also be viewed for their positive environmental impact. These are as follows:

- Increased profits through:
  - lower material costs
  - lower energy costs
  - lower disposal costs

  (all of these reduce the pollution load)
- Improved quality and productivity, increased staff morale
- Perception as a responsible community member

  (both of which lead to an understanding of better work practices and work culture)
- Less pollution, resulting in:
  - fewer wastes to water
  - fewer wastes to landfill
- Better use of resources.

The right-first-time (RFT) approach for achieving good dyeing and for minimising the wastage of time, money, energy, dyes, water and chemicals is the ideal concept. One of the primary problems in textile dye houses is the low RFT factor, an indicator of the level of precision and accuracy of the process so as to impart the desired quality to the fabric in the first instance of processing. For example, an RFT of 70% means that 30% of the production needs to be reprocessed to achieve the desired quality. It eliminates need for stripping, redyeing or reshading. Ideally, the stripping rate should be below 1%, redyeing below 3% and reshading below 10%. Before giving consideration to the complicated and capital-intensive innovations for cleaner production, the industry should focus primarily on improving its housekeeping. Better working habits of the operators and good housekeeping often account for a significant reduction in the total waste load generated and in the water consumption. This needs implementation of strict administrative and procedural measures for improving the operational management and process efficiency. They generally involve:

- Proper inventory control and material handling
- Material loss prevention
- Production scheduling
- Waste stream segregation.

In all the continuous and semi-continuous dyeing processes, the treatment of unused pad liquor is essential to minimise the BOD and COD loads, as well as the presence of coloured substances, and it is recessary to explore the possibilities for recycling or reuse. For example, exhaust dyeing of knitted goods is less polluting and the pad-batch option does not represent the best option for waste minimisation in cases where a lower fixation is achieved in the pad-batch process and also as a result of the need to ensure that excess pad liquor is available to avoid running out of colour during the padding process. The pad-trough needs to have a minimal volume (minimal application techniques) and the distance from the feed tank must be very small to reduce the extra make-up of dye liquor.

6.3 Waste minimisation in textile dyeing

6.3.1 Wastewater composition and characteristics

The wastewater generated from different dyeing operations shows varying characteristics. The main ingredients in wastewater from dyeing of different dye classes, apart from dyes, are as shown in the Table 6.7. Wastewater ingredient values derived from different combination of dye, substrate and dyeing equipment are shown in Table 6.8.[43] It may clearly be observed that depending on the dye – substrate – dyeing technique, the characteristic parameters of wastewater differ widely.

Thus, the ingredients used during dyeing and the pollutants generated therefrom need to be minimised to reduce the pollution load. Apart from the 'use minimum' technique, it is essential to optimise the design of a dyeing process through better understanding of the theoretical knowledge.

6.3.2 Maximising the exhaustion from dye bath

In order to maximise the dye exhaustion, a knowledge of the relationship between the exhaustion, affinity and liquor ratio is important. These are the three main parameters, which control the dyeing process.

Table 6.7 Main ingredients present in dye baths of various classes

Dye	Main ingredients
Direct	Glauber's salt, sodium carbonate, surfactant
Reactive	Sodium hydroxide, sodium phosphate, sodium bicarbonate, Glauber's salt, urea, surfactant
Acid	Glauber's salt, ammonium sulphate/ acetic acid/sulphuric acid, surfactant
Acid mordant	Acetic acid, Glauber's salt, sodium dichromate, surfactant
Premetallized	Sulphuric acid/sodium acetate/ammonium sulphate, Glauber's salt, surfactant
Cationic	Sodium acetate, sodium carbonate, ammonium acetate, surfactant
Sulphur	Sodium sulphide, sodium carbonate, Glauber's salt
Vat	Sodium hydroxide, hydros (sodium hydrosulphite), Glauber's salt, Turkey red oil
Azoic	Sodium hydroxide, hydrochloric acid, sodium nitrite, sodium acetate, surfactant
Disperse	Carrier, sodium hydroxide, hydros, surfactant

Typical values for affinity, liquor ratio and exhaustion are:

K (affinity) = 50 to 1 000 for various dye/fibre combinations,
L (liquor ratio) = 5 to 50 for various machines,[44] and
E (exhaustion) = 0.50 to 1.00 (50 to 100% exhaustion).[45]
The relationship between these three is given as $E = K\ (K + L)$
where, K is a partition coefficient, or the ratio of the concentration of the dye in solution to the concentration of the dye in the substrate, at equilibrium, i.e. $K = C_f/C_s$

where C_f and C_s are the equilibrium concentrations of dye in fibre and in solution, respectively. When L increases, E decreases and more colour is discharged. The effect is more pronounced on low-affinity dyes (i.e. when K is low). When K decreases, the dye remains in the solution and the colour in the wastewater increases, especially if L is high.

K is an important factor in determining dye exhaustion. Each dye class has affinity for specific types of fibres. Individual dyes within dye classes, however, can show large variations in affinity. Therefore, typical exhaustion data provide only general guidelines. Typical exhaustion/fixation levels for various dye types are given in Table 6.9. The typical K is computed by assuming a liquor ratio of 17:1 (typical for beck dyeing) and solving for $K = EL/(1 - E)$, where E is on a 0 to 1 scale. For acid dyes, the dye exhausted is typically 87%, or $E = 0.87$. Solving $E = K\ (K + L)$ for K results in $K = L/(1 - E) = (17)/(0.13) = 130$.

Thus, at equilibrium, the concentration of dye in the fibre is 130 times greater than the concentration of dye in the bath for a dye that exhausts

Table 6.8 Wastewater characteristics derived from different combinations of dyes, substrate and dyeing equipments[43]

No.	Dye class	Substrate	Method	ADMI* colour	Apparent ADMI	TOC (mg l^{-1})	BOD (mg l^{-1})	pH	Cl$^-$ (mg l^{-1})	Suspended solids (mg l^{-1})	Dissolved solids (mg l^{-1})†
1	Vat	Cotton	Exhaust	1,910	–	265	294	12	190	41	3945
2	1:2 Pre-metallised	Polyester	Exhaust/Beck	370	–	400	570	7	nil	5	1750
3	Disperse	Polyester	Atmospheric/ Exhaust	315	–	300	234	8	33	39	914
4	After coppered direct	Cotton	Exhaust/Beck	525	1280	135	87	5	520	41	2763
5	Reactive	Cotton	Exhaust/Beck	3890	–	150	INT††	11	9800	32	12500
6	Disperse	Polyamide	Exhaust/Beck	100	–	130	78	8	28	14	395
7	Chrome	Wool	Exhaust/Beck	3200	–	210	135	4	33	9	1086
8	Basic	Polyacrylic	Exhaust/Beck	5600	12000	255	210	6	27	13	1469
9	Disperse	Polyester	Exhaust/Beck	215	315	240	159	7	27	101	771
10	Acid	Polyamide	Exhaust/Beck	4000	–	315	240	5	14	14	2028
11	Direct	Rayon	Exhaust/Beck	12500	–	140	15	7	61	26	2669
12	Developed	Rayon	Exhaust/Beck	2730	–	55	12	3	130	13	9.8
13	Disperse/ Acid/Basic	Polyamide	Exhaust/Beck	210	720	130	42	7	10	8	450
14	Disperse	Polyester	HT Exhaust	1245	–	360	198	10	1680	76	1700
15	Sulphur	Cotton	Continuous	450	–	400	990	4	42	34	2000
16	Reactive	Cotton	Continuous	1390	–	230	102	9	57	9	691
17	Vat/ Disperse	Cotton/ Polyester	Continuous	365	1100	350	360	10	167	27	2292
18	Basic	Polyester	Atmospheric/ Exhaust	1300	2040	1120	1470	5	17	4	1360
19	Disperse/ Acid/Basic	Polyamide	Continuous/ Kuster	<50	100	100	100	7	22	49	258
20	Azoic	Cotton	Exhaust/Package	2415	–	170	200	9	7630	387	10900

*ADMI = American Dye Manufacturers Institute †Mostly salt ††INT= High salt or reactive

Table 6.9 Typical exhaustion/fixation rates for various dye classes[45]

Dye class	Typical *K*	Typical fixation, %	Fibres typically applied to
Acid	130	83 to 93	Wool, nylon
Azoic	200	90 to 96	Cellulose
Basic	700	97 to 98	Acrylic
Direct	100	70 to 95	Cellulose
Disperse	120	80 to 92	Synthetic
Pigments	470	95 to 98	Wool
Reactive	50	50 to 80	Cellulose
Sulphur	50	60 to 70	Cellulose
Vat	130	80 to 95	Cellulose

87% at a 17:1 bath ratio. Cellulose dyes typically have poor exhaustion and fixation characteristics. The reactive dye classes exhibit the poorest fixation.[46]

If the dyeing machines are selected with approach to conservation in mind, the pad batch dyeing machine can save up to 80% of energy requirements and about 90% of water consumption. At the same time, it also reduces the dye and salt usage. For knitted goods, however, exhaust dyeing is preferred. Similarly, the jet dyeing machine with a low liquor-to-material ratio of 4:1 to 8:1 should be used instead of winch, with a ratio as high as 15:1, where feasible. Such conservation of water reduces the amounts of chemicals and dyes, which in turn, reduce the amounts of the unutilised chemicals, i.e. the pollutants, to be treated.

6.3.3 Maximising fixation and wash off

For fixation of dyes, different mechanisms are used, which include chemical reaction of the dye with the fibre to form a covalent bond, insolublisation of the dye within the fibre, formation of an ionic bond, formation of solid solution, or the use of cationic dye fixing agents. These different mechanisms determine the colour retained by the fibre material and that released into the wash liquor on completion of dyeing. The better the fixation mechanism, the lower is the colour present in the wastewater. As compared with fibre reactive dyes, the fixation achieved for acid, basic, disperse, direct, vat, sulphur and azoic dye classes is much better. The unfixed dye reduces the much desired fastness properties of the dyed textile and hence it needs to be thoroughly washed out. Thus, washing is a very important step in determining final product quality as its function is to remove completely the unfixed dye from the dyed textile. Large amounts of good quality water are required for the wash off process. Water conservation thus becomes very important. The colour carry over is minimised through adoption of different techniques of efficient washing such as counter current washing and use of water jets impinging on fabric.

The main problems of presence of colour in the effluent result from cotton dyeing. To improve upon the cellulosic batch dyeing processes in terms of quality of dyed material and reduction in pollution, important factors for consideration are:

- Ensuring a good and uniform cloth preparation
- Selecting high-affinity dyes and lower liquor ratio
- Using a correct heating rate
- Optimising the essential process additives like salt
- Maintaining optimum pH for each dyeing, and
- Minimising the use of auxiliaries and surfactants.

For fibre reactive dyes, use of the two-step dyeing is better rather than the all-in process, since this minimises hydrolysis of the dye.[47] Use of cationic dye fixatives is advisable as in the case of direct dyed material. Also, the use of bifunctional reactive dyes is recommended for the same purpose. One additional step to be taken is to maximise the reactive dye bath exhaustion before addition of alkali.

6.3.4 Use of optimum amount of salt

In most of the dyeing processes, especially for dyeing of cellulosic materials, salt is used in sufficiently large amounts to enhance the dye exhaustion. In the past, the use of salt was not considered a threat to the environment as it has low toxicity. Being cheap and effective, it is used in liberal amounts in dyeing without any serious thought to optimise its use. There is no other chemical that could perform all the functions of salt at comparable cost and with such a low toxicity. Removal of the salt from effluent requires special and comparatively costly techniques like use of reverse osmosis membranes. The limit prescribed for chloride in water streams is 250 ppm and hence its removal becomes essential.[47] It is not possible to eliminate salt usage completely. However, several approaches to reducing use of salt are made available. The general approaches to minimise the use of salt during dyeing are as given below:

- Use of the lowest possible liquor ratio in batch dyeing
- Optimisation of salt use for each individual dyeing
- Use of continuous dyeing or pad-batch dyeing whereever possible
- Minimisation of colour changes and discards in continuous dyeing
- Reuse of dye baths
- Ensuring proper handling of dyes and fabrics
- Selection of dyes that exhaust with minimum salt
- Optimisation of dyeing temperature individually for each recipe.

Each dye class requires characteristic amounts of salt but dyes within a class vary widely in their salt requirement during dyeing. Thus, the order of salt requirement is hot brand reactive dye > cold brand reactive dye > direct > vat. As an example, each individual direct dye has a temperature of maximum affinity. Therefore, maximum exhaust with minimum salt can occur at a specific temperature, thereby reducing the amount of salt required.[48] However, a dyer hardly sets the precise final exhaustion temperature for a particular recipe and follows the general ranges of temperature, the salt addition and other chemicals given in the dyestuff manufacturer's literature. No consideration was given earlier to find out the optimum requirements of each individual dyeing. Setting the requisite temperature and adding only the optimum quantities of chemicals including salt as per the already set time–temperature profile is no longer difficult with modern microprocessor controlled machines used for dyeing. Using the optimum exhaust temperature for dyeing not only produces maximum exhaustion with minimum salt use but also ensures consistent shade repeats and better quality.

6.3.5 Low liquor ratio baths

In the last decade, dyeing systems with lower liquor ratio have been developed with the aim of water and energy conservation as well as saving in quantities of chemicals. These machines can also minimise the use of salt as it is added on the basis of liquor (owm) and not on fabric (owf). The rule is: (owf) × (bath ratio) = (owm). For example, at a 5:l liquor to fabric ratio, 50 g l^{-1} of salt is 25% owm, but at 40:l ratio, the same concentration of salt is 200% owm.

6.4 Future trends

There are further developments in combined radio frequency (RF) and hot air drying machines for dyeing or for drying after yarn/loose stock dyeing, which has improved the speed and uniformity. The integrated dyeing and heat recovery systems are also commercially successful, since they use less water and energy and help to reduce dye cycle times. The fill and drain mechanisms using pumps, reel-less jet dyeing machines, jigs with built in padding mangles, low liquor usage, additional spray bars and vacuum slots for more effective dyeing and rinsing are now becoming options worthy of serious consideration.

Fully automated yarn and package dyeing plants with microprocessor control, which monitor and control the use of water and energy, have also been introduced recently.

Dyeing under supercritical conditions is now being looked upon with promise. A supercritical fluid is defined as a substance above its critical temperature and pressure. At this condition, the fluid has unique properties and does not condense or evaporate to liquid or gas.[49] Use of supercritical carbon dioxide technology, which does not require water as a dyeing vehicle, has been tested mainly on dyeing of disperse dyes on polyester. Carbon dioxide flashes off upon release of supercritical pressure and the dyed fabric is ready without any contaminants or unfixed dye to pollute. Commercially available disperse dyes can be used and no special colorants need to be developed. Such processes are totally environmentally friendly and cause no pollution at all. The unutilised dyestuff is available as such for further dyeing and does not require any tedious recovery process. This technique has the advantages of low cost, non-toxicity, non-inflammability, no water discharge and low critical parameters.

A German patent was granted in 1994 for a process in which a dye, free of additives, is generally dissolved in a supercritical fluid and the substrate to be dyed is suffused with it. A small production plant has also become commercially viable (Critical Processes Ltd., Roecliffe, North Yorkshire). The advantages of this process are:

1. No requirement of dispersant addition for solubilising disperse dye in water.
2. Solubility of dye is controlled by pressure that allows control of dyeing intensity and colour.
3. Mass transfer in the fluid is faster due to higher diffusivity.
4. Carbon dioxide causes swelling of fibre allowing faster dye diffusion.
5. Lower viscosity of fluid with dye dissolved in it makes the circulation easier.
6. Dye penetration is fast due to low surface tension and extremely good miscibility of air with CO_2 under pressure.

Supercritical dyeing of synthetic fibres has been reported to be successful.[50] Dyeing of natural fibres such as cotton, can also be performed from supercritical carbon dioxide after modifying it by reacting the –OH groups on its surface with an organic compound, such as benzoyl chloride.[51,52] Polyester[53] and modified cotton[54, 55] may be dyed with disperse dyes by this method. It has also been reported that better qualities are obtained in such dyeing.[56–58]

6.4.1 Chemical substitution

Carriers are used in dyeing of polyester at boil. However, a number of disadvantages are associated with the use of carriers, including their toxicity.[59] Liposomes[60] having a hydrophobic part of a maximum of up to two hydrocarbon chains and a hydrophilic part composed of phosphates and chorine, have been reported to be an environmentally safe alternative to the hazardous carriers for disperse dye exhaustion and colour uniformity in polyester dyeing.[61] Low temperature polyester dyeing is also possible assisted by soya lecithin, a double-tailed natural phospholipid. A synthetic cationic double-tailed surfactant has similarly been used in the disperse dyeing of nylon and polyester.[62] Liposomes have been used as vehicles for oxidative reagents in wool chlorination.[63,64] Attempts have been made to improve the dyeing of wool using liposomes.[65–68] Application of metal complex dyes has also been assisted by liposomes.[69,70] Such studies have been extended recently even to the dyeing of polyester–wool blends.[71]

6.5 Sources of further information and advice

The following contact details may prove useful in getting further information:

1. US Environmental Protection Agency, Office of Research and Development, National Risk Management Research Laboratory, Centre for Environmental Research Information, Cincinnati, Ohio.
2. North Carolina Division of Pollution Prevention and Environmental Assistance (DPPEA), 1639 Mail Service Centre, Raleigh NC.
3. Case assessment or other activities sponsored by EP3, EP3 Clearinghouse. E-mail: apenderg@habaco.com.
4. The Green Lane™ Environment Canada's worldwide website: http://www.ec.gc.ca/ee-ue/default.asp?lang=En&n=8A6C8F31-1.
5. Office of Enforcement and Compliance Assurance, US Environmental Protection Agency, 401 M St., SW, Washington, DC 20460, Website: http://www.epa.gov/oeca/sector/index.html.
6. To download the technical amendment from the EPA's website, go to 'Recent Actions' at the following address: http://www.epa.gov/ttn/oarpg/. For general information about the standards, contact: EPA's Office of Air Quality Planning and Standards, Emission Standards Division, Coatings and Consumer Products Group by e-mail: almodovar.paul@epa.gov. or website: http://www.epa.gov/ttn/atw/coat/fabric/. The EPA's Office of Air and Radiation (OAR) homepage on the internet contains a wide range of information on the air toxics program and many other air pollution programs and issues. The OAR's home page address is: http://www.epa.gov/oar/.
7. The Office of Waste Reduction (North Carolina Board of Science and Technology) PO Box 29569, Raleigh, NC 27626-9569.
8. National Office of Pollution Prevention Environment, Canada, 351, St. Joseph Boulevard, 13th Floor, Gatineau, QC K1A OH3, e-mail: CEPAP2Plans@ec.gc.ca.
9. ITT Technologies, Inc., 1 Caledon Court Suite C, Greenville, SC 29615. Web: www.it3-services.com.
10. The Pollution Prevention Assistance Division (P^2AD) is available to help Georgia companies reduce waste and increase profits through

pollution prevention. Services range from telephone assistance to on-site evaluations and consultations. The service is free, confidential and non-regulatory. Contact Jancie Hatcher. e-mail: p2ad@ix.netcom.com.

11. Pollution prevention and abatement handbook: *Sources of pollution, prevention and abatement: textiles industry*, technical background document. Web: www.miga.org/miga_documents/Textiles.pdf.
12. Envirowise – practical environmental advice for business, a Government programme managed by Momenta, an operating division of AEA Technology Plc, and TTI, an operating division of Serco Ltd.
13. Scottish environment protection agency (SEPA) SEPA corporate office, Erskine Court, Castle Business Park, Stirling, FK9 4TR, Web: http://www.sepa.org.uk/contact/index.htm.
14. The environment agency UK, e-mail: enquiries@environment-agency.gov.uk.
15. Highly informative and with case studies: *Best management practices for pollution prevention in the textile industry*, EPA/625/R-96/004, September 1996.

Advice

There is a growing concern about ever-increasing environmental loads and processors have to face stringent norms and conditions. The maximum levels for indirect discharge of effluents are shown in Table 6.10.[72]

Ecolabelling

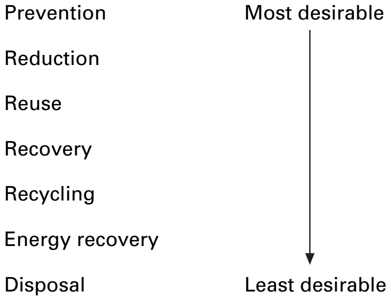
Ecolabelling schemes developed in recent years have had an impact on both the dyestuff industry and its customers. The plethora of schemes now in existence contribute greatly to customer confusion and remarkably little to reducing environmental impact. Many schemes are more easily understood in terms of trade protection and opportunism. This is unfortunate, as many new products can offer significant benefits, e.g. bifunctional reactive dye systems with high levels of fixation.[73,74] The more rigorous approach required in the EU (Council regulation no. 880/92 of 23 March 1992) for the award of the EU ecolabel appropriately incorporates the full life cycle of the product. It is unlikely that the actual choice of colorant will be a determinant for the award of an EU Ecolabel for finished consumer goods. A comparison of the norms/criteria stipulated for Eco parameters of different eco-labels is shown in Table 6.11.[7]

On a priority basis, pollution should be dealt with as depicted in Fig. 6.4. Pre-screening of chemicals can be done using the product's MSDS. Quality control and pre-screening before use of the incoming raw material, practices for pollution prevention, include a comprehensive programme to pre-screen

Table 6.10 Maximum levels for the indirect discharge of effluents[72]

Pollutant	Limits
AOX*	0.5 ppm
Arsenic	0.0 ppm
BTX†	0.1 ppm
Chromium vi	0.1 ppm
Total chromium	0.5 ppm
Colour 436 nm	7.0 l/m
Colour 525 nm	5.0 l/m
Colour 620 nm	3.0 l/m
Toxicity to fish	dilute< ×2
Free chlorine	0.3 ppm
Copper	0.5 ppm
Nickel	0.5 ppm
Mercury	0.0 ppm
Sulphide	1 ppm
Zinc	2 ppm

*Absorbable organic halogens.
†Benzene, toluene, xylene.



6.4 Hierarchy of pollution control measures.

all chemicals. For air emissions, the stock of chemicals should receive special attention. Chemical inventory managers should seek maintenance and process chemicals that will not contribute to air emissions (i.e. non-volatile, non-halogenated and non-photoreactive chemicals and those not on the list of toxic or hazardous air pollutants (TAPS or HAPS, respectively). Dye and auxiliary suppliers should be reliable and environmentally conscious. For pre-screen fibres for volatile finishes, incoming QC should also be performed on synthetic fibres to identify spin finishes having components that could vaporise during heat setting. Sampling can be performed using various methods already described.[3–7]

Table 6.11 Comparison of the norms/criteria stipulated for eco-labelling[7]

	Criteria/norms stipulated (ppm)					
	MST*	OTN 100	Clean Fashion	Steilmann	COMITEXTIL**	Indian eco-levels
Formaldehyde						
Baby clothing	20	20	20	50	20	20
Close to skin	75	75	75	300	75	75
Outer wear	300	300	300	500	300	300
Toxic pesticides	1	5	1	1	0.1 – 1	1
Pentachloro-phenol	0.5	–	0.5	Ban	0.05 – 0.5	0.5
Heavy metals						
Arsenic	0.01 – 0.2					
Lead	0.04 – 0.8					
Cadmium	0.005 – 0.1					
Mercury	0.001 – 0.1					
Copper	3 – 100					
Chromium	0.1 – 20					
Cobalt	0.2 – 20					
Zinc	5 – 100					
Nickel	0.2 – 10					
Azo dyes containing carcinogenic amines	Ban	Ban	Ban	Ban	Ban	50
Halogen carrier	Ban	–	–	Ban	Ban	200
Chlorine bleaching	–	–	–	To avoid	Ban	–

*MST, German Textile Association; [†]OTN 100, OEKOTEX Institute from Austria; [††]Clean Fashion and Steilmann are two private eco-label issuing organisations in Germany and popular in European countries; [**]COMITEXTIL, coordination committee for the textile industries, Europe.

In summary, it may be stated that significant opportunities exist for preventing pollution in textile dyeing operations. Pollution prevention measures in textile dyeing can be outlined as follows:

1. Selecting quality raw material with pre-screening;
2. Selecting dye with pre-screening for right-first-time dyeing having maximum exhaustion;
3. Selecting ecofriendly chemical substitutes;
4. Process optimisation for maximum dye exhaustion;
5. Optimising salt and auxiliaries for each recipe;
6. Understanding the application classes and subclasses of dyes, and site-specific features and limitations (e.g. equipment, control systems and facility layout) to design efficient processes;
7. Modifying process to reduce environmental load;
8. Optimising material handling, auditing, maintenance and employee training;
9. Implementing better management practices;
10. Practising reuse and conservation.

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7

Decolorisation of effluent with ozone and re-use of spent dyebath

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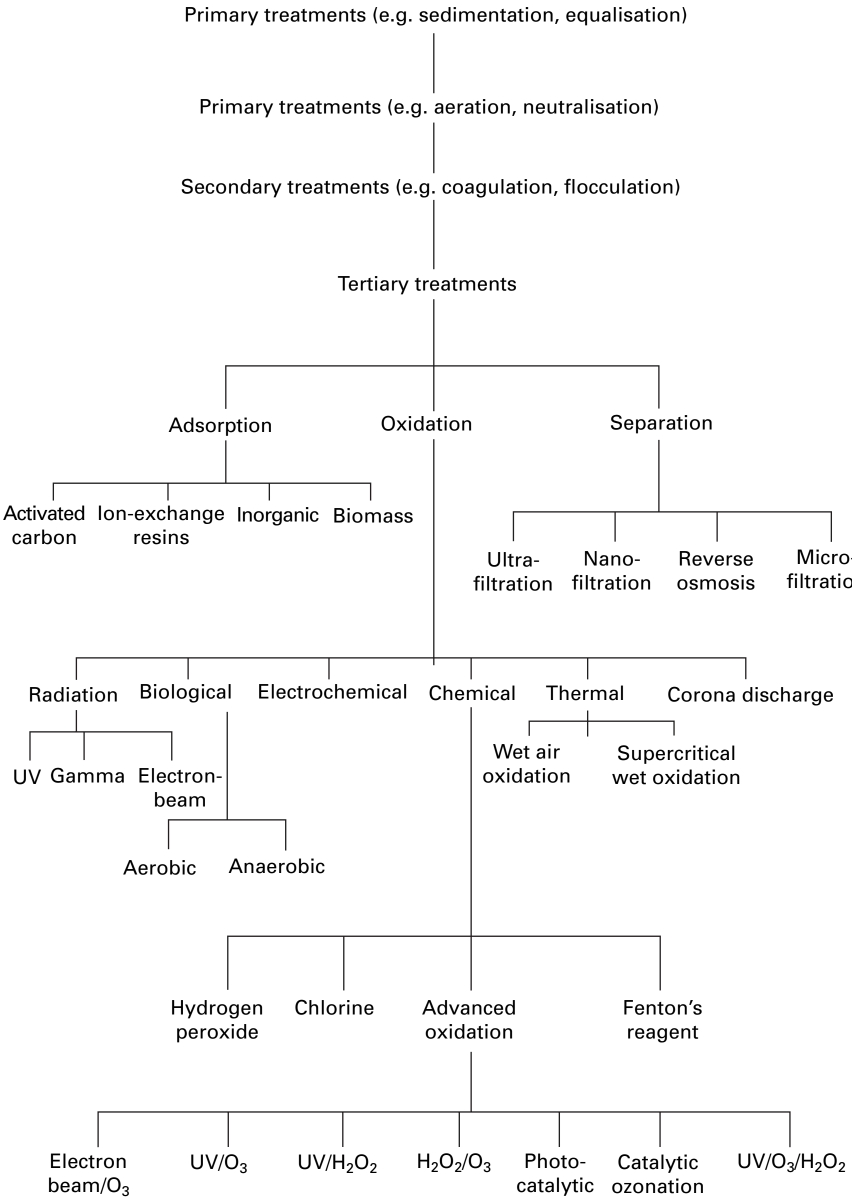
7.1 Introduction

Industrial effluents have usually been discharged into municipal sewage systems in developed countries since the 1920s. Previously, the majority of sewage was discharged to tidal waters without any treatment. Little attention was paid to the colour of wastewater until the 1980s and, even then, the objections were on aesthetic grounds, since it was known that modern dyestuffs are relatively non-toxic.

At the beginning of the 1970s, only physical treatment methods such as sedimentation and equalisation were applied to maintain the pH, total dissolved solids (TDS) and total suspended solids (TSS) of the discharged water. There were no obligatory discharge limits for the colour of the effluent at that time. Secondary treatments such as the use of filter beds for biodegradation and, more recently, the introduction of the activated sludge process (aerobic biodegradation) have reduced the toxicity of sewage water considerably. As a result, much of the water is now discharged to local rivers. However, sewage treatment works have often been unable to remove the colour from dyehouse effluent completely, especially when reactive dyes are included, and this causes the receiving river water to become coloured. As a result, there have been complaints by the public, who are becoming increasingly aware of environmental issues.

Wastewater treatment methods can be classified as shown in Fig. 7.1. Treatment of large volumes of effluent is a very costly process and investment in effluent treatment is often considered a waste of money as it makes no contribution to profit for an industrial company. However, textile wet processing is now under threat in many countries because of the tightening of discharge limits for effluents by environmental agencies. The viability of many textile dyeing, printing and finishing plants is already in danger and the future of many of them will depend on their ability to treat effluent economically to eliminate colour and reduce chemical oxygen demand (COD) and biological oxygen demand (BOD). Although effluent treatment costs can be reduced by



7.1 Wastewater treatment methods.

selecting low COD-contributing surfactants, dispersants, dyes and other auxiliary chemicals,[1] these chemicals are considerably more expensive than conventional ones. In-house treatment and reuse of treated effluent is an alternative way to tackle this problem.

7.1.1 Biological treatments

Biological treatments have been investigated for colour removal from wastewater by many researchers. They can be aerobic or anaerobic treatments, i.e. with or without the presence of oxygen. In aerobic conditions, enzymes secreted by bacteria present in the wastewater break down the organic compounds. Various micro-organisms including the wood-rotting fungus, *Rhyzopus oryzae*, and other micro-organisms have been investigated for colour removal from textile and pulp bleaching effluents.[2–6]

Many factors including concentration of pollutants, e.g. dyestuff concentration, initial pH and temperature of the effluent, affect the decolorisation process. After the fungal treatment, an improvement in the treatability of the effluent by other micro-organisms was observed. Investigations showed that they are not only capable of eliminating colour, but also capable of reducing COD, AOX (adsorbable organo-halogen) and toxicity. Although biological treatments are suitable for some dyes, some of them are recalcitrant to biological breakdown.[7]

Pavlosthasis and co-workers[8] investigated colour removal from simulated reactive dye wastewater by biological treatment. They found that more than 83% colour removal was achieved for CI Reactive Yellows 3 and 17, Black 5, Blue 19 and Red 120, but only marginal colour removal was achieved with Blue 4, Blue 7 and Red 2. Moreover, the breakdown products of Blue 19, Blue 4 and, to a lesser extent, Black 5 were inhibitory to the anaerobic culture. No information is available about the stability of bacteria in the presence of high concentrations of salt, which might affect the decolorisation process, as high amounts of salt could be toxic to bacteria.

7.1.2 Adsorbents and adsorption

Dyes that are recalcitrant to biological breakdown can often be removed by using adsorbents. The adsorbents most investigated for various types of effluent treatment are dead plants and animal residues, known as biomass, which include charcoals, activated carbons, activated sludge, compost and various plants.

Activated sludge

The most widely used adsorbent is activated sludge. Important factors affecting the optimum adsorption of colour with activated sludge are its quality and concentration, the hardness of the water and the duration of the treatment. Pagga and Taeger[9] investigated the application of activated sludge for the removal of water-soluble acid and reactive dyes and water-insoluble disperse dyes. They found that the concentration of sludge, water-hardness and dwell time for optimum removal of colour were 3 g l^{-1}, 80 mg l^{-1} Ca^{2+} and 1–2 days, respectively. Although activated sludge is suitable for removal of various textile dyes, it alone cannot satisfy modern day's tight consent limits.[10]

Clays

Different types of clays and diatomaceous earth, including activated bleaching earth, montmorillonite, bauxite, alumina pillared clays, mesoporous alumina, aluminium phosphates and bentonitic or kaolinitic clays, were investigated for wastewater treatment.[11,12] Their use encourages flocculation of organic impurities. The feasibility of using peat and lignite as adsorbents for the removal of basic dyes was studied by Hamed.[13] A two-resistance model based on external mass transfer and pore diffusion was developed to predict the performance of agitated-batch adsorbers, but the validity of the model was not tested against a real industrial effluent.

Fly-ash adsorbents

At the Harbin Dyeworks in China, the possibility of using cinder ash for the treatment of wastewater containing disperse dyes has been investigated[14] and found to be effective for their removal. Malik and Taneja[15] investigated the possibility of using silica, alumina and other oxide-rich fly-ash for decolorisation of dyehouse effluents. Their investigation showed better colour removal with dyes containing few ionisable chlorine groups. For reactive dyes, fly-ash with a high silicon oxide content facilitated colour removal.

Activated carbon

Another adsorbent is activated carbon, but it is very expensive and, for re-use, needs to be treated with solvent. However, the solvent is also expensive and alternative treatments, such as thermal and homogeneous advanced oxidation treatments (UV/H_2O_2 and H_2O_2/O_3) have been investigated for this purpose.[16] Unfortunately, thermal treatment was found to be ineffective and homogeneous treatments were also impractical in terms of cost. The regeneration action was much faster for smaller particle-size adsorbents in the H_2O_2/O_3 process and in some cases 100% of the virgin capacity was recovered, but they consumed more oxidants than would be required theoretically.

Activated carbon adsorbents are applicable within a wide range of pH, but colour removal is mainly effective for non-ionic and cationic dyes. Unfortunately, most of the dyes used in the textile industry are anionic in their soluble form. Prabu and Sivakumar[17] investigated the possibility of using activated charcoal for the removal of colour for a wide range of dye classes including acid, direct, metal complex, vat, basic and reactive dyes. They found that pH has a mixed effect for the removal of colour, i.e. the pH for maximum removal of colour varies from one class to another.

One of the main disadvantages of activated carbon is fouling by natural organic matter (NOM). It competes with other organic pollutants for adsorption sites and prevents them from entering the micro-pores by blocking them. Hopman *et al.*[18] has investigated the possibilities of using activated carbon fibre (ACF) as an alternative to granular activated carbon and claimed it to be less affected by the presence of NOM. The use of alternative cheaper carbonaceous adsorbents, including coconut husk charcoal and pyrolyzed bagasse char, was also investigated[19] for decolorisation and reduction of COD and found to be as efficient as activated carbon.

Ion-exchange resins

As activated carbon is expensive and activated sludge alone is not efficient enough for complete colour removal, the search for alternative and cheaper adsorbents continued. Various ion-exchange resins derived from sugar cane bagasse, waste paper, polyamide wastes, chitin, etc., were applied as adsorbents for removal of colour and other organics.[20–24] Colour-removal efficiency with these ion-exchange resins was comparable with that achieved using activated carbon.

Most of the dyes used in the textile industry are either anionic (such as acid, reactive, direct and metal complex) or cationic (e.g. basic dyes). These dyes form complexes with ion-exchange resin and form large flocs, which can be separated by further filtration. Quaternised sugar cane bagasse is another ion-exchange resin derived from natural products and it has excellent colour removal capacity for hydrolysed reactive dyes. Investigation shows that high salt content in the reactive dye wastewater has a minor influence on colour removal with this resin. Chitosan is also a good adsorbent for the removal of dyes and is most efficient for absorbing dyes of small molecular size.[25]

Most ion-exchange resins have poor hydrodynamic properties compared with activated carbon, and it is difficult for them to tolerate the high pressures required to force large volumes of wastewater through the bed at a high flow rate. Among the aforementioned adsorbents, only a few have characteristics that make them suitable for use in a commercial wastewater treatment plant. The demerits of adsorbents are not only the added cost for making them re-useable, but also the production of large volumes of sludge. This requires further treatment, such as incineration or dumping. Incineration causes air pollution and in some countries where land availability is not abundant, dumping will be expensive.

McKay[26] carried out a detailed study on colour removal by chitin, which is a by-product of the shellfish industry. Chitin contains —OH and —NH_2 groups and has affinity for dyes. Investigation showed that chitin is only suitable for those dyes that are strongly anionic or weakly anionic in nature, but, even then, the dye separation is too low (only fractions of a milliequivalent per gram of chitin used). It works as a weak-base anion-exchanger, but there is a problem of instability at low pH. Although this can be overcome by forming cross-links within the polymeric structure (chitin), this, in turn, results in a lowering of its dye binding capacity. Moreover, mixing of different classes of dyes and addition of surfactants reduces the colour removal efficiency.

A large number of agricultural residues including waste banana pith, sunflower stalks, rice hulks, water hyacinths, maize cob, sawdust, coir pith, soybean pulp, sugar beet fibre and eucalyptus bark have been investigated for decolorisation of textile wastewater because of their low price.[27–33] All of the adsorbents were claimed to be effective for colour removal, but none have the characteristics for practical application by comparison with activated carbon.

Microbial biomass

A large number of biomasses of different origin including microbial biomass, unmodified lignocellulose and lignocellulose were studied by several researchers[34–36] for the removal of acid, direct and reactive dyes and were found to be effective as adsorbents. Microbial biomass also has the potential to remove metal ions such as chromium and copper, which are integrated with metal complex dyes and some of them were found to be effective for the removal of acid dyes.[34] Living fungi such as *Anabaena variabilis* were found to be effective for the removal of two reactive dyes (C.I. Reactive Blue 19 and Black 5) and one sulphur dye (C.I. Sulphur Black 1) from simulated dyehouse effluent,[36] for which the maximum colour removal occurred under neutral conditions.

7.1.3 Separation techniques

Various separation techniques including microfiltration, nanofiltration, ultrafiltration and reverse osmosis have been applied in the textile industry for the recovery of sizing agent from effluent[37–38] and some of these methods have also been investigated for colour removal. Among them, microfiltration is no use for wastewater treatment because of its large pore size, and the other separation systems have very limited use for textile effluent treatment. Marmagne and Coste[39] found that ultrafiltration and nanofiltration techniques were effective for the removal of all classes of dyestuffs, but dye molecules cause frequent clogging of the membrane pores. High working pressures, significant energy consumption, high cost of membrane and a relatively short membrane life have limited the use of these techniques for dyehouse effluent treatment.

7.1.4 Oxidation treatments

Oxidation treatments are the most commonly used decolorisation processes as they require low quantities and short reaction times. In the oxidation process, dyestuff molecules are oxidised and decomposed to lower molecular weight species such as aldehydes, carboxylates, sulphates and nitrogen, the ultimate goal being to degrade them to carbon dioxide and water. Various types of oxidant including chlorine, hydrogen peroxide, ozone and chlorine dioxide are used for colour removal from wastewater.

Chlorine and chlorine dioxide

Chlorine in the form of sodium hypochlorite has long been used for bleaching of textile materials. Water-soluble dyes such as reactive, acid, direct and metal complex dyes are decolorised readily by hypochlorite, but water-insoluble disperse and vat dyes are resistant to decolorisation in this process.[40–41] Decolorisation of reactive dyes require long reaction times, while metal complex dye solution remains partially coloured even after an extended period of treatment.

Dyes that contain amino or substituted amino groups on a naphthalene ring, are most susceptible to chlorine and decolorise more easily than other dyes.[42] Subsequent biological clarification results in a considerable reduction of COD. Although the use of chlorine gas is a cost-effective alternative for decolorising textile wastewater, its use causes unavoidable side reactions, producing organochlorine compounds including toxic trihalomethane, thereby increasing the AOX content of the treated water. Metals, including iron, copper, nickel and chromium, are liberated by the decomposition of metal complex dyes. These liberated metals have a catalytic effect that increases decolorisation but also cause corrosion in metallic vessels.

Fenton's reagent

Hydrogen peroxide alone is not effective for decolorisation of dye effluent at normal conditions, even at boil.[43] However, incorporation with ferrous sulphate (known as Fenton's reagent), peroxomonosulphuric acid, manganese dioxide, ferrous sulphate, ferric sulphate, ferric chloride or cupric nitrate, generates hydroxyl radicals, which are many times stronger than hydrogen peroxide. In acidic conditions, hydrogen peroxide generates hydroxyl radicals ($^\bullet$OH) in the presence of ferrous ions in the following way.[44]

$$H_2O_2 + Fe^{++} \rightarrow Fe^{+++} + OH^- + {}^\bullet OH \qquad [7.1]$$

$$RH + {}^\bullet OH \rightarrow H_2O + {}^\bullet R \qquad [7.2]$$

$${}^\bullet R + Fe^{+++} \rightarrow R^+ + Fe^{++} \qquad [7.3]$$

$$R^+ + H_2O \rightarrow ROH + H^+ \qquad [7.4]$$

In this scheme, RH is any organic compound.

The $^\bullet$OH radicals generated in the reaction attack organic molecules (here unsaturated dye molecules) and thus render the dye colourless. The ferric ions generated in the above redox reactions can react with OH^- ions to form a ferric hydroxo complex, capable of capturing the decomposed dye molecules or other degradation products of dye and precipitating them.[45]

Kim *et al.*[46] found that Fenton's reagent was effective for reactive and disperse dye decolorisation and reactive dyes decolorised more easily than the water-insoluble disperse dyes; about 90% of COD and 99% of dye removals were obtained at the optimum conditions. Gregor's[47] investigation showed that Palanil Blue 3RT was resistant to oxidation by Fenton's reagent, but other colorants, including Remazol Brilliant Blue B, Sirrus Supra Blue BBR, Indanthrene Blue GCD, Irgalan Blue FGL and Helizarin Blue BGT, were significantly decolorised. Some dyes decolorise by $^\bullet$OH radicals and some are removed by simply complex formation with ferrous hydroxide. In this process, not only is colour removed, but also (COD) total organic carbon TOC and toxicity are reduced. As the mechanism involves, simultaneously, oxidation and coagulation, pollutants are transferred from the aqueous phase to the sludge, which cannot be freely dumped because it has adsorbed toxic degraded organic products. To overcome this problem, Peroxid-Chemie GmbH, Germany, developed the fenton sludge recycling (FSR) system, in which ferric sludge deposition was eliminated. Usually, Fenton's process is preferred for wastewater treatment when a municipality allows the release of Fenton's sludge into sewage. From a biological point of view, not only is the quality of the sludge improved, but also phosphates can be eliminated. It is suitable for decolorisation of acid, reactive, direct, metal complex dyes, but unsuitable for vat and disperse dyes.

To overcome sludge generation, another alternative process has been developed in which oxidation is carried out at a higher temperature with a reduced ferrous sulphate concentration.[48–49] In this way, it is possible to decolorise textile wastewater without generation of any sludge and the treated water may be reused for dyeing. Continuous Fenton's treatments were also investigated and showed good prospects, but have the disadvantage of longer processing times.

Hydrogen peroxide/peroxidase

Hydrogen peroxide can also be activated by peroxidase enzyme. Klibanov and co-workers[50] first reported a horseradish peroxidase (HRP) method for the removal of aromatics from aqueous solution. HRP can catalyse the oxidation of organic molecules in the presence of hydrogen peroxide and generates free radicals, which diffuse from the active centre of the enzyme into solution.[51] Then they form dimers and trimers with the organic molecules, which ultimately result in the formation of water-insoluble oligomers.[51] The colour removal efficiency depends on pH, peroxidase concentration, reaction temperature and type of peroxidase used.

Temperature of the effluent is important as it was reported that high-temperature effluent from bleaching plant substantially affected the stability of HRP and thus their oxidation capability.[52] Apparent inactivation of peroxidase during high-temperature polymerisation reactions is mainly due to unfolding of the protein backbone. The catalytic lifetime of HRP at high temperatures could be extended by chemical modification of lysine ε-amino groups by reacting with succinimides.[52] Morita *et al.*[53] investigated the decolorisation of acid dyes using three types of peroxidase, namely, HRP, Soybean (SPO) and *Arthromyces ramosus* peroxidase (ARP). ARP was the most effective among them for colour removal and maximum decolorisation occurred at pH 9.5. Peroxidase enzymes are very expensive and the effectiveness of this system for genuine effluent is unknown. Moreover, it generates sludge.

Electrochemical oxidation

Electrochemical treatment also plays an important role in wastewater treatment. It has a wide range of applications including the treatment of toxic wastes, effluent treatment to control pollution, the economic and clean recycling of chemical streams or their components, and the clean and cheap synthesis of organic and inorganic chemicals. The process involves the use of a sacrificial iron electrode, the anode dissolving to form ferrous hydroxide. The typical electrochemical cell consists of two electronically conducting materials put into an electrolyte solution. When iron electrodes are used as both the cathode and anode, and electricity is applied, the following reaction takes place:
At the anode (oxidation):

$$Fe \rightarrow Fe^{2+} + 2e^- \qquad [7.5]$$

At the cathode (reduction):

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \qquad [7.6]$$

This treatment process is especially suitable for acid dyes and the maximum colour removal takes place in acidic conditions. The colour removal mechanism is still unknown, but the most widely accepted theory is that colour is removed by adsorption with ferrous hydroxide floc.

$$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2 \qquad [7.7]$$

It was reported that the azo group ruptured and produced an amino compound during electrolysis of an acid dye.[54] Naumczyk *et al.*[55] also observed that the azo groups of the dyes ruptured by anodic oxidation and produced various chloroorganic compounds, but no report was given concerning further decomposition of those products or about other dyes with different chemical structures.

Advanced oxidation processes

When it was realised that a single oxidation system is not enough for the total decomposition of dyes into carbon dioxide and water, investigation continued into the simultaneous application of more than one oxidation processes. Simultaneous use of more than one oxidation processes are termed Advanced Oxidation Processes (AOPs). All AOPs are based mainly on $^{\bullet}OH$ chemistry, which is the major reactive intermediate responsible for organic substrate oxidation.

H_2O_2/UV

The UV radiation system has been used for destroying bacteria in potable water for a long time, but is not effective for wastewater that contains high quantities of solids. For UV radiation treatment to be effective, wastewater must be free from turbidity, as the chemicals that cause this can absorb UV light. Unfortunately, textile wastewaters are usually highly turbid, so it is usually applied along with ozone or hydrogen peroxide, or with both of them.

Hydrogen peroxide can be activated by ultra-violet (UV) light, generating $^{\bullet}OH$ radicals.

$$H_2O_2 + h\nu \rightarrow 2\ OH^{\bullet} \qquad [7.8]$$

The important factors that influence colour removal in the H_2O_2/UV treatment are peroxide concentration, time of treatment, intensity of UV radiation, pH, chemical structure of the dye and dyebath additives. In general, the optimum pH for decolorisation is pH 7. The treatment of disperse, reactive, direct, metal complex and vat dyes in the UV/H_2O_2 process showed excellent decolorisation,[56] but yellow and green reactive dyes needed longer treatment times than others. In one paper, it was reported that only 10–20% colour removal was achieved with UV alone, but in conjunction with peroxide, colour removal increased to 90%.[57] Marechal *et al.*[58] found this process effective for chlorotriazine-based azo reactive dye decolorisation. Colonna *et al.*[59] studied decolorisation of five acid dyes and one reactive dye by ultraviolet radiation in the presence of hydrogen peroxide and all of them completely decolorised and mineralised in a relatively short time. TOC decreased at a markedly slower rate than colour removal but, within three hours, TOC was significantly reduced by the conversion of the dyes into carbon dioxide and water.[60]

Photo-Fenton process

Photo-Fenton and Fe^{3+}-based Fenton-like oxidation processes were found to be highly effective for a diazo dye (Reactive Black 5) in terms of colour removal efficiency and COD reduction.[60] However, the same process was found to be ineffective for a copper phthalocyanine dye as only a limited fraction of that dye underwent oxidative degradation. The sequential ozonation followed by oxidation with Fenton's reagent has been investigated for the decolorisation of acid and reactive dye effluent. We found that pre-ozonation considerably accelerated decomposition of dyestuffs in the subsequent treatment with Fenton's Reagent.[61]

Photocatalytic oxidation

Research in the field of the photo-catalytic oxidation method began with the work of Carey,[62] who showed that the irradiation of an aqueous solution of polychlorinated biphenyl (PCB) in the presence of titanium dioxide resulted in the removal of PCB and the appearance of Cl^- ions. Various semiconductors including TiO_2, ZnO, CdS, WO_3 and SnO_2, can be used in the photocatalytic process. The basic mechanism of the process has been described by several researchers.[63–65] When TiO_2 particles are irradiated by UV photons, photon energy exceeding the band gap energy excites an electron on the TiO_2 surface from the valence band to the conduction band (e^-_{CB}) generating electron deficiency or a so-called 'positive hole' (h^+_{VB}) in the valence band. If electron donors such as OH^- ions and H_2O molecules are available, then the photo-generated 'hole' extracts electrons from them, generating $^\bullet OH$ radicals and superoxide ions according to the following equations:

$$TiO_2 + h\nu\ (UV) \rightarrow e^-_{CB} + h^+_{VB} \qquad [7.9]$$

$$h^+_{VB} + OH\ (surface) \rightarrow {}^\bullet OH \qquad [7.10]$$

$$h^+_{VB} + H_2O\ (adsorption) \rightarrow {}^\bullet OH + H^+ \qquad [7.11]$$

$$e^-_{CB} + O_2\ (adsorption) \rightarrow O_2^- \qquad [7.12]$$

The superoxide ions produce hydrogen peroxide through disproportionation as follows:

$$2O_2^- + 2H^+ \rightarrow H_2O_2 + O_2 \qquad [7.13]$$

Then the $^\bullet OH$ radicals generated react with the dye molecules and rupture the azo linkage.

Photocatalytic processes are suitable for a wide range of dyes including direct, reactive, vat and disperse. Colour removal usually occurs in acidic conditions and decreases with increasing pH. The decolorisation of azo dyes by TiO_2-based photocatalytic oxidation showed that degradation kinetics is greatly influenced by the electrical nature of the catalyst, pH, the number of azo groups in the dye structure and the radicals attached to them.[66] Colour removal decreases if the dye contains a conjugated naphthalene group. The azo bond was reductively cleaved by gaining electrons from the conduction band of TiO_2 and cleavage was favoured at pH 3. The reason for the difficulty in decolorising when naphthalene groups are present may be steric constraint, because the larger the two radicals attached to the azo bond are, the more difficult it will be to form a covalent bond with the TiO_2 particle. The optimum pH of colour removal varies from dye to dye depending on their chemical structure, e.g., the oxidation rate of monoazo C.I. Basic Yellow 15 was faster than diazo C.I. Reactive Red 120 which in turn was faster than triazo C.I. Direct Blue 160.[66] The photocatalytic process was found to be not only effective for colour removal but also for COD reduction,[67–68] although there was an increase in BOD.

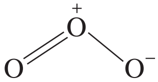
O_3-based AOPs

O_3-based AOPs such as ozonation in combination with γ-radiation was found to be effective for decolorisation of wastewater.[69] It was reported that the use of hydrogen peroxide with ozone for the decolorisation of metal–complex dyes could not improve colour removal efficiency and added cost.[70] The combined process was also found to be more susceptible to the negative impacts of added alkalinity, as OH^-, CO_3^{2-} and HCO_3^- decompose the $^\bullet OH$ radicals. Moreover, release of free metals during ozonation of metal complex dyes increased the pollution load to the environment.[71] Other researchers also found similar results.[73–3] It was reported that $O_3/H_2O_2/UV$ treatment of disperse dye containing polyester dyeing effluent resulted in 99% reduction in COD.[74]

7.1.5 Ozone

Ozone is ambiguously called an allotropic form of oxygen with an oxidation potential of 2.07 V, which means only fluorine and hydroxyl radical have higher oxidation potentials than ozone. It exists as a slightly bluish gas at room temperature and has a distinct pungent odour readily detectable at concentrations as low as 0.02 to 0.05 ppm (by volume), which can be very useful as ozone is very reactive and toxic.

Ozone is composed of triatomic oxygen molecules. An electron diffraction study has revealed that, in the gas phase of ozone, the three oxygen atoms form an isosceles triangle with a vertex angle of 127° ± 3°, the length of the equal sides being 0.126 + 0.002 nm and the base being about 0.224 nm.



Ozone is a very unstable gas and, because its half-life in water is about 20 min depending upon pH, temperature and the presence of ozone scavengers, it requires generation on site. An ozone treatment plant consists of a gas preparation plant, an ozone generator, an ozone–water contactor and an ozone off-gas destruction unit.

Ozone was first used for the disinfection of drinking water in 1893 in the Netherlands. Later use of ozone for the same purpose spread to other European countries. In 1991, approximately 40 water treatment plants each serving more than 10000 people utilised ozone in the United States.[75] Ozone is suitable for decolorising textile dyehouse wastewater because of its high oxidation potential and because in alkaline conditions it produces $^{\bullet}OH$ radicals, which have an even higher oxidation potential than ozone. Ozone is highly selective in its reaction with organic compounds, but $^{\bullet}OH$ radicals are highly reactive and their reaction with organics is not selective.

Some decolorisation systems such as adsorption, Fenton's reagent and electrochemical oxidation are effective as phase transfer processes in transferring toxic pollutants from liquid phase to solid phase, but they produce a large volume of sludge, which needs either incineration or dumping. Chlorine treatment increases toxicity by generating trihalomethane in the wastewater, as mentioned earlier. Biological treatment takes months for colour removal and some dyes are recalcitrant to biological breakdown. In these respects, ozone seems to be the most convenient alternative because it does not produce any sludge or toxic by products. In the ozonation process, the half-life of ozone is very short, only minutes, and it then decomposes to produce environmentally friendly oxygen. For this reason, research over recent years has focused on this system.

Colour removal by ozone is influenced by many parameters, including temperature, pH, dye bath admixtures, chemical structure of the dyestuff, gas sparging systems (as it affects ozone mass transfer from gaseous phase to liquid phase) and initial concentration of the organic matter in the wastewater. Some classes of dyestuffs decompose more easily in the ozonation process than in the other oxidation processes. Horning[76] found that reactive dyes decolorised more readily than other classes of dye, but water-insoluble disperse and vat dyes were very difficult to decolorise by this process.

Effect of ozonation on TOC, BOD and COD

The effectiveness of ozonation is often characterised by its effect on BOD, COD and TOC, as these are among the common parameters that determine the hazard and toxicity level of wastewater. Low values in the above-mentioned tests indicate better performance of the treatment process. Although several researchers found that COD and BOD decreased after ozonation,[74,77–80] the level of COD reduction was very poor at only 10%.[79] After ozonation, some previously non-biodegradable waste can be converted into a form that is biodegradable. Ozonation can only reduce COD if purified dyestuffs are used but, for genuine wastewater, COD remains unchanged[80] and also there is no effect on the reduction of TOC.[81] This indicated that the dye chromophore had degraded to a form that could not be decomposed further by ozone. Dyestuffs usually make little contribution to the COD load in the effluent of textile finishing plants, other additives being more important in this respect.

There is also debate about the fate of the ozonation metabolites of dyestuffs and whether ozonation by products are more toxic than the parent dyes. Cooper[82] reported that ozonation metabolites of dyestuffs could be more toxic than the parent dyestuff, which may be true for all oxidation treatments that involve colour removal through decomposition of dyes. Another important factor to consider for ozone-based oxidation is that it can release metals bound with the dye during its decomposition, which can increase the total toxicity of the effluent. In a chromium-complex dye, Cr(III) is bonded in a ligand system with two oxygen atoms and two unpaired electrons donated by the —N=N— bond. During ozonation, this azo bond is broken down and releases chromium into solution that may exists in an anionic Cr(VI) form, which is more toxic than Cr(III).

A number of factors, such as temperature, pH and various additives used during dyeing can affect decolorisation efficiency of dyehouse effluent by ozone.

Effect of temperature

Mass transfer of ozone from the gaseous phase to the liquid phase decreases with increasing temperature as its solubility decreases. Sotelo *et al.*[83] found that the dissolved ozone concentration at 10 °C was 11.52 mg l^{-1} (2.4×10^{-4} mol l^{-1}), but at 35 °C it reduced to 4.8 mg l^{-1} (1×10^{-4} mol l^{-1}. On the other hand, it was reported that acid dyes were decolorised much faster at 80 °C than at 25 °C,[84] although the solubility of ozone at 80 °C is less than at 25 °C. No significant reduction in the time necessary for the decolorisation of disperse dyes was observed above 80 °C. This means that the oxidation of organic dyestuffs accelerates with increasing temperature. However, during ozonation of vat and reactive dyes, it was found that temperature had no effect on decolorisation rate, which is obvious for vat dyes as they are in an insoluble form in that condition. This may indicate that the increased reaction rate at higher temperatures is counter-balanced by the lower solubility of ozone and the higher likelihood of its decomposition for dyes that are harder to degrade.

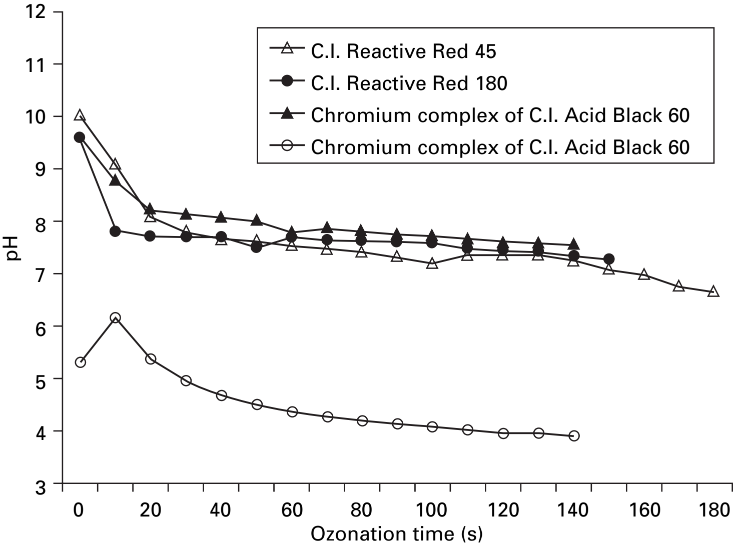
Effect of pH

The study of the effect of pH on decolorisation by ozone is very important, as several researchers have found that the pH of water in single-phase ozonation affects O_3 decomposition; as the solution becomes more basic, the rate of ozone decomposition significantly increases.[85–87] The decolorisation of dye should increase with increasing pH of the solution as higher fractions of ozone are decomposed to form $^{\bullet}OH$ radicals at higher pH values[88] and those are stronger oxidants than molecular ozone. Several researchers observed that pH had little or no effect on the rate or efficiency of decolorisation of acid, reactive, disperse and reactive dyes during ozonation.[81,89] During the study of the self-decomposition of ozone in aqueous solution for a pH range from 1 to 13.5, it was observed that the rate was related to the total amount of ozone consumed.[90] It was noticed that decolorisation efficiency was strongly dependent on the pH of the solution during decolorisation of dyes other than Naphthol Yellow, for which the rate of decolorisation was almost independent of the pH.[90]

Interestingly, one acid dye, C.I. Acid Red 158 showed that at a temperature of 10 °C, the rate of decolorisation efficiency was independent of pH, but, at 30 °C, the decolorisation reaction was significantly faster at pH 10 than at pH 4.[9] This means that the effect of pH is related to the treatment temperature. In the case of pentachlorophenol, it was observed that its removal increased with increasing pH and the maximum removal was achieved at pH 11.[92] Similar behaviour was also observed in the case of C.I. Fluorescent Brightener 28 at pH 3–11, but, at pH >11 its removal decreased.[93] During the decolorisation of C.I. Reactive Black 5, it was observed that hydrolysed C.I. Reactive Black 5 solution decolorised more rapidly and consumed less ozone per unit colour loss in alkaline conditions than in acidic conditions.[94] It was observed that better decolorisation was achieved in acidic conditions than neutral or slightly alkaline conditions during ozonation of direct dyes.[95] The reason for these conflicting results may be that some researchers used buffer solution to control the pH and some researchers simply adjusted the pH with a diluted solution of acid or alkali. However, it is very difficult to maintain a constant pH for a long period of ozonation with diluted H_2SO_4/NaOH solution; also the interaction between ozone and the buffering chemicals has to be considered.

Adams *et al.*[70] observed that, in the case of ozonation of unbuffered dye solution, when the ozonation reaction was started at pH 4, initially the pH increased after absorbing 1 mmol l^{-1} ozone, but the final pH fell to 3 after absorbing 5 $mmol^{-1}$ ozone. Similarly, when the ozonation reaction was started at pH 7, the pH decreased very rapidly to about 4.8 after 1 mmol l^{-1} of ozone had been absorbed, but, after addition of more ozone, it reduced to a steady state at pH 3.1 to 3.2. When ozonation of unbuffered aqueous solution of C.I Reactive Red 45 was started at pH 10 and C.I. Reactive Red 180 and chromium complex of Acid Black 60 were started at pH 9.6, the pH dropped to 6.6, 7.2 and 7.5, respectively, within 3 min of ozonation,[96] as shown in Fig. 7.2. When ozonation of chromium complex of C.I Acid Black 60 was started at pH 5.3, the pH dropped to 3.9 after 140 s of ozonation. Therefore, after starting ozonation at pH 4–7, if ozonation is continued for a long time, the ozonation reaction will take place predominantly at pH 3–3.2, whatever is the initial pH.

The nature of the alkali used for setting alkaline pH can also affect the decolorisation efficiency. When sodium hydroxide is used to set the pH, ozone decomposition is accelerated by the presence of OH^-, which acts as a radical initiator, and forms $^{\bullet}OH$ and $^{\bullet}O_2^-$ radicals, which act as propagators in a series of chain reactions. Conversely, CO_3^{2-} acts as an inhibitor in the free-radical reaction, as it attacks $^{\bullet}OH$ radicals without generating superoxide anions O_2^-, and therefore decolorisation efficiency decreases when sodium carbonate is used. However, during ozonation, it was observed that more decolorisation was achieved when sodium carbonate was used to set the alkaline pH rather than when using sodium hydroxide.[96]



7.2 Effect of ozonation time on the pH in decolorisation of aqueous dye solution.

It can only be concluded from the wide variation in the above observations that the effect of pH on decolorisation efficiency is dependent on the chemical structure of the dye and the type of alkali being used to set the initial pH.

Effect of dyebath additives

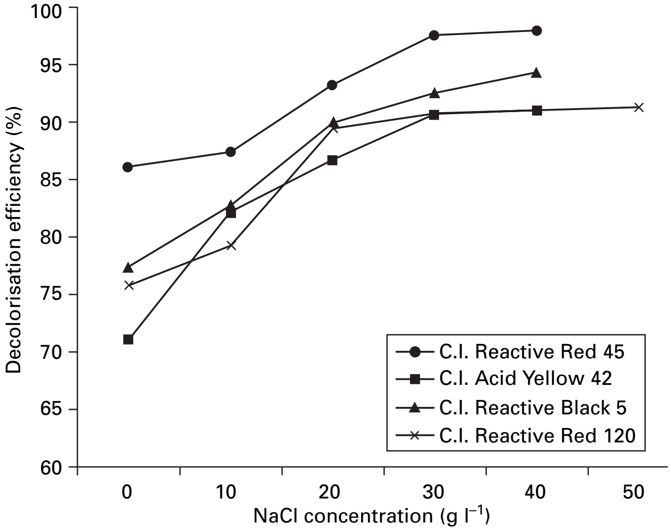
The admixtures present in dyehouse wastewater can greatly influence the efficiency of the decolorisation process, since they may also react with ozone, thereby increasing its consumption.

Dyeing usually requires the addition of auxiliaries, such as wetting agents, dispersing agents, levelling agents, electrolytes, acids or alkalis, reducing or oxidising agents and buffering chemicals, depending upon the dyeing method, dyestuff class used and fibre to be dyed.[97] When the cloths to be dyed are introduced into a dyebath, they pollute it by addition of foreign substances, surfactants and fluff. Printing also causes pollution, as pastes contain thickeners, dyes or pigments, binders, bicarbonates, citric acid, urea and kerosene oil, and all of these substances have to be washed off at the end of the production process.

Schultz *et al.*[98] reported that addition of sodium alginate increased the consumption of ozone during ozonation of reactive dye solution. Similarly, more time was required for decolorisation when guar gum was present in the wastewater; ozone consumption being 60% higher than it was without it.[99] It was observed that addition of the chelating agents EDTA (ethylenediamine tetra-acetic acid) and diethylenetriamine penta-acetic acid, surfactants (C12–C15 alcohol ethylene oxide) and carrier (butyl benzoate) increased the time for the removal of colour, along with increasing ozone consumption.[41] It was also observed that the addition of 1 g l^{-1} silicone-based antifoaming agent in the ozonation process decreased decolorisation by 50%, but the chelating and lubricating agent had an insignificant effect.[100]

In our laboratory, we studied the effect of five dyebath additives, i.e., electrolytes (sodium chloride and sodium sulfate), chelating agent (EDTA), reducing agent (sodium dithionite), optical brightener (Uvitex BHT) and dispersing agent (Zetex DN-VL). It was found that addition of sodium chloride, sodium dithionite and Zetex DN-VL markedly improved decolorisation efficiency, but EDTA and optical brightener showed a negative effect.[101] Sodium sulphate did not show any positive or negative effect on decolorisation efficiency. Among them, addition of NaCl showed very significant improvement in decolorisation compared with the other additives studied.

In Fig. 7.3 it can be seen that decolorisation considerably increased with increasing sodium chloride concentration for all of the dyes studied. The mechanism of decolorisation in the presence of NaCl was not clear, but one possible explanation is that ozone reacts with NaCl forming hypochlorous ions (OCl^-) and this, along with ozone, then decomposes the dye.

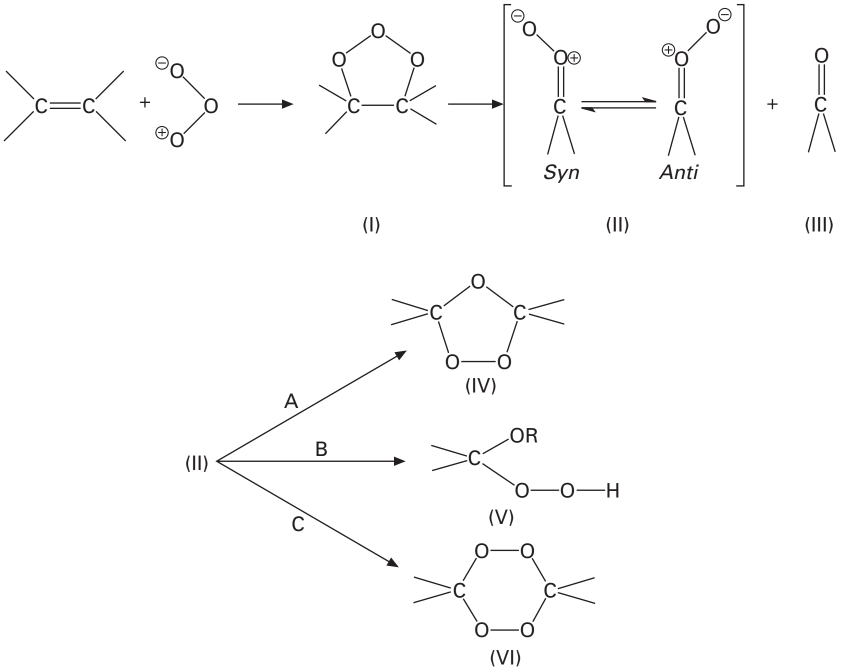


7.3 Effect of NaCl concentration on decolorisation of various reactive and acid dyes in the ozonation process.

7.2 Decolorisation mechanisms with ozone and ozone-based AOPs

Ozone can react with compounds in two ways, either by direct oxidation, as molecular ozone can react with various organic compounds, or by oxidation with hydroxyl free radicals produced during the decomposition of ozone, or both.[102] Direct oxidation with aqueous ozone is relatively slow compared with hydroxyl free radical oxidation but the concentration of ozone is higher. On the other hand, the hydroxyl radical reaction is very fast, but the concentration of hydroxyl radicals under normal ozonation conditions is relatively low. Oxidation takes place mainly by molecular ozone in acidic conditions, but in alkaline conditions $^{\bullet}OH$ radicals play the major role.

The spontaneous decomposition of ozone occurs through a series of steps; the exact mechanism and associated reactions have yet to be established. Ozone can decompose in water and forms, not only unstable $^{\bullet}OH$ radicals, but also peroxide anion, superoxide anion, singlet oxygen and oxygen radical anion. The direct reactions of molecular ozone with organic compounds are selective and slow; they can be divided into three classes namely cycloaddition (Criegee mechanism), electrophilic substitution, and nucleophilic reaction. Owing to its dipolar nature, the ozone molecule reacts with compounds having unsaturated carbon–carbon bonds by 1,3-dipolar cycloaddition, with the formation of a primary ozonide that decomposes into a carbonyl compound in the presence of protonic water.[103] According to this mechanism, ozone reacts with a carbon–carbon double bond via 1,3-cycloaddition to form the 1,2,3-trioxolane intermediate (I) as shown in Fig. 7.4. Then, decomposition

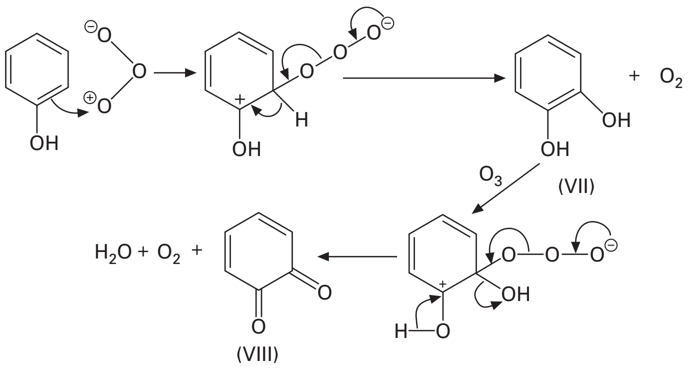


7.4 Probable mechanism of olefin ozonolysis.[103,106–7]

of (I) via a 1,3-cycloreversion yields the syn- and anti-isomers of zwitterion (II) and a carbonyl compound (III).[104–5] One of three routes may then be followed depending upon the reaction conditions.

1. A final ozonide (IV) can be produced by another 1,3-cycloaddition in which (II) and (III) recombine.
2. Zwitterion (II) may react with a participating solvent to form a hydroperoxide intermediate (V). This appears to be the dominant route when employing protic solvents.[103,108]
3. Dimerisation and polymerisation of (III) may occur to form diperoxides (VI) and polymeric peroxides. This path is the most probable in nonprotic solvents when (III) is a ketone.

In the electrophilic substitution reaction, ozone attacks organic compounds that have molecular sites with high electronic density (such as OH, NH_2 and similar groups) leading first to the formation of ortho- and para-hydroxylated by-products, which further decompose to quinoids. These quinoids again decompose to aliphatic products with carbonyl and carboxyl groups due to opening of an aromatic ring.[109] Ring hydroxylation and quinone formation are likely results of this mode of attack and, thus, ozonation of phenol produced catechol (VII) and *o*-quinone as intermediate products upon ozonation as shown in Fig. 7.5.[110–111]



7.5 Ozone attack on phenol via electrophilic substitution.[109]

Ozone can also attack molecular sites with an electron deficit (such as —COO^-) and, more frequently, at sites with carbon carrying electron-withdrawing groups (such as —NH_3^+, —NO_2, —CN, —SO_3H, etc).

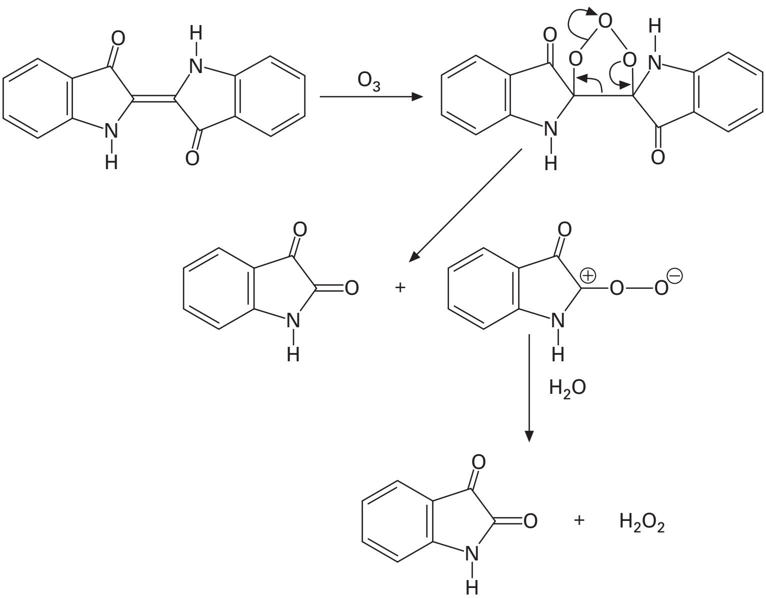
7.2.1 Reaction with dyestuffs

The reaction mechanism of ozone with azo and indigo dyes was discussed in several published reports.[39, 112–113] Marmagne *et al.*[41] described the reaction mechanism of an indigo dye with ozone as shown in Fig. 7.6.

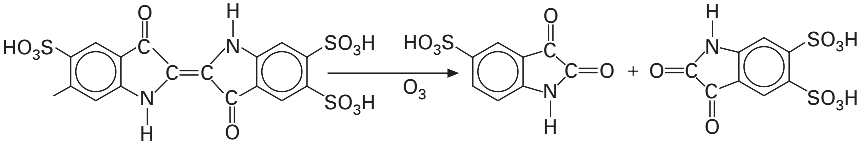
Similarly, ozonolysis of >C=C< double bonds in dye molecules of C.I. Basic Violet 14 produces (>C=O) groups in the following way as shown in Fig. 7.7.[114]

The mechanism of ozonation of 1-phenylazo-4-naphthol dye was described by Matsui[112,115] as shown in Fig. 7.8. It is acknowledged that hydroxyazobenzene exists as azo–hydrazo tautomers in aqueous solutions and that equilibrium is established between them. Initially, the carbon atom in the 4 position of the hydrazo tautomer is electrophilically attacked by ozone to form unstable ozone adduct (iv). The ozone adduct (iv) decomposes to 1,4-naphthoquinone (vii), perhydroxyl ion (viii) and benzene diazonium ion (vi) through the 'ene' reaction. Then benzene diazonium ion hydrolyses to phenol (ix), nitrogen (x) and hydronium ion (xi).

The reaction of ozone with aromatic azo compounds is very complicated, as shown in the Fig. 7.9. Ozone acts as a 1,3-dipole electrophile and an electron acceptor. It electrophilically attacks not only aromatic rings (Path A), but also nitrogen atoms (Path B). When an electron-donor substituent is present in azobenzenes, ozone attack on the aromatic ring is enhanced. In Path B, ozone predominantly attacks the more electron-rich nitrogen atom and the azoxy isomers are produced via corresponding ozone adducts. The azoxy compounds are then further ozonised to give glyoxals and hygroscopic compounds. Matsui found evidence that indicated the validity of the above-mentioned reaction mechanism.[113]

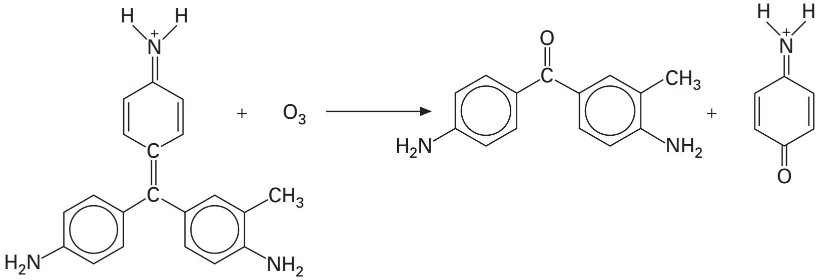


7.6 Reaction of ozone with indigo.[41]



Indigo trisulphonate (a derivative of Vat Blue)

Carbonyl products (colourless)



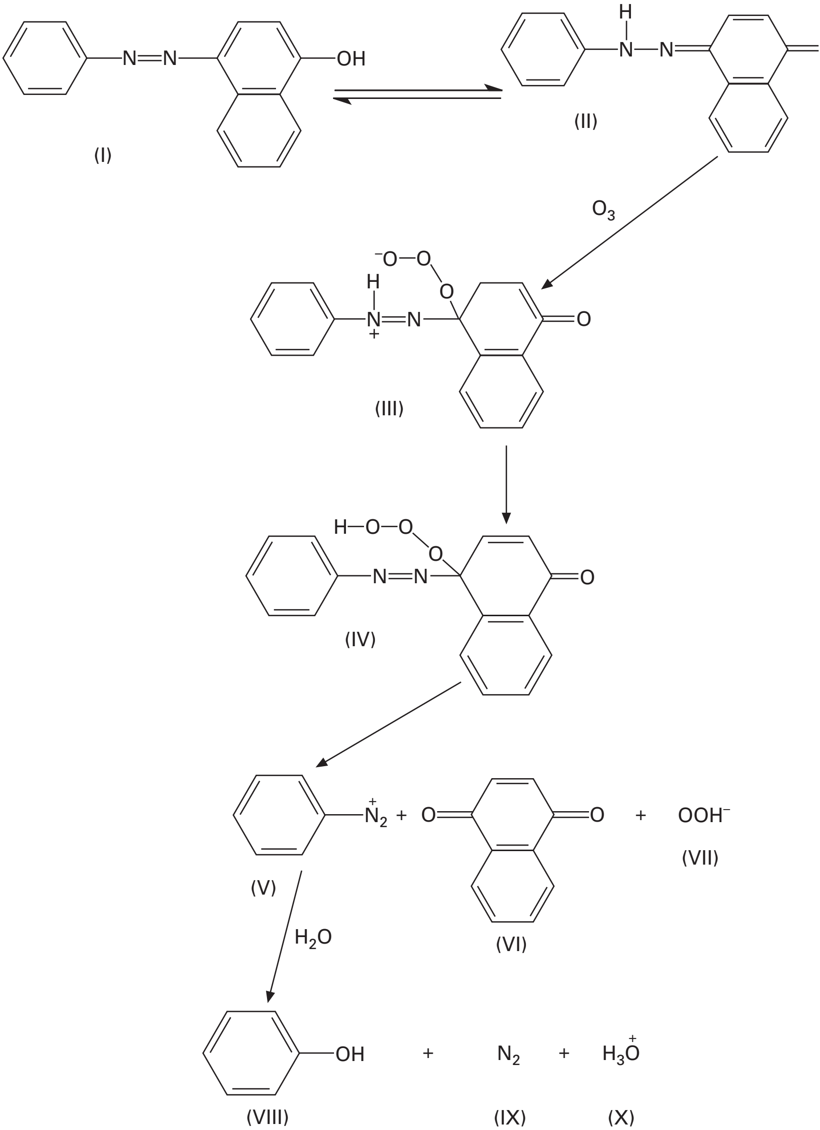
C.I. Basic Violet 14

Carbonyl products (colourless)

7.7 Reaction of ozone with indigo trisulphonate and C.I. Basic Violet 14.[114]

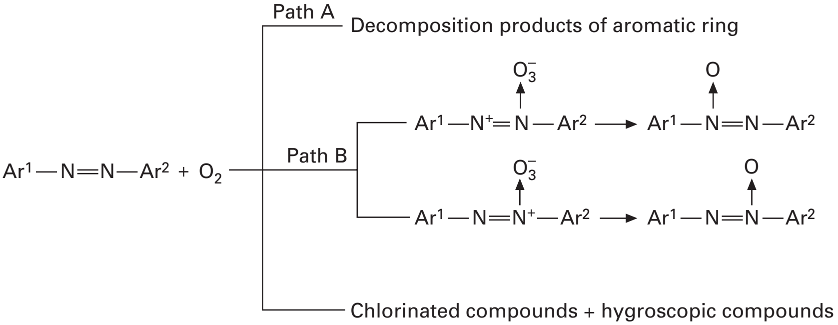
7.2.2 Hydroxyl radical generation in AOPs

To increase the concentration of hydroxyl radicals, ozone is activated with UV, H_2O_2, and various catalysts such as activated carbon, alumina, Ferral, platinised TiO_2. Simultaneous application of ozone and ultraviolet radiation



7.8 Mechanism of ozonation of 1-phenylazo-4-naphthol dye.[112,115]

generates hydroxyl radicals and the mechanism of decomposition of organics by this method has been described.[116] Photolysis of ozone produces hydrogen peroxide as the initiation step in a series of reactions. Then UV radiation decomposes H_2O_2 into $^\bullet OH$ radicals. Hydrogen peroxide also auto-dissociates into perhydroxyl ions and hydrogen ions. Then perhydroxyl ion reacts with ozone to generate a series of free radicals including $^\bullet OH$ radicals.



7.9 Reaction of ozone with aromatic azo compound.

$$O_3 + H_2O + h\nu \rightarrow H_2O_2 + O_2 \quad [7.14]$$

$$H_2O_2 + h\nu \rightarrow 2^{\bullet}OH \quad [7.15]$$

$$H_2O_2 \rightarrow HO_2^- + H^+ \quad [7.16]$$

$$HO_2^- + O_3 \rightarrow {}^{\bullet}HO_2 + {}^{\bullet}O_3^- \quad [7.17]$$

$$O_3 + {}^{\bullet}O_2^- \rightarrow {}^{\bullet}O_3^- + O_2 \quad [7.18]$$

$$^{\bullet}O_3^- + H^+ \rightarrow {}^{\bullet}OH + O_2 \quad [7.19]$$

Hydroxyl radicals are believed to be the prime oxidant in processes involving the catalytic decomposition of ozone.[116] Moreover, they readily undergo reactions with the organic components (here dye molecules) and remove them from wastewater. In alkaline conditions, scavengers like HCO_3^- and CO_3^{2-} present in the wastewater react with hydroxyl radicals and produce carbonate radicals. Thus, the consumption of ozone increases.

$$^{\bullet}OH + \text{dye molecules} \rightarrow \text{decolorised products} \quad [7.20]$$

$$^{\bullet}OH + HCO_3^- \rightarrow {}^{\bullet}CO_3^{2-} + H_2O \quad [7.21]$$

$$^{\bullet}OH + CO_3^{2-} \rightarrow {}^{\bullet}CO_3^{2-} + OH^- \quad [7.22]$$

The carbonate radicals formed could then react with H_2O_2 and organic scavengers (S).

$$^{\bullet}CO_3^{2-} + H_2O_2 \rightarrow {}^{\bullet}HO_2 + HCO_3^- \quad [7.23]$$

$$^{\bullet}CO_3^{2-} + S \rightarrow \text{Products} \quad [7.24]$$

7.2.3 Catalytic ozonation

As ozonation is very expensive and not very effective for COD and TOC reduction, investigation was continued in order to determine whether catalysts could be used to reduce ozone consumption while simultaneously lowering

COD and TOC. In the early 1980s, it was found that the use of certain catalysts could accelerate the oxidation reaction of ozone with organic compounds and reduce ozone consumption.[117] It was also observed that some catalysts such as $CoSO_4$, $TiCl_3$, $MnSO_4$, $NiSO_4$ and $FeSO_4$ reduced the TOC of wastewater.[118]

Several researchers found ferric oxide effective as a catalyst in ozonation.[119–121] During ferric oxide-catalysed ozonation of industrial and domestic wastewater containing phenol and ethyl acetoacetate, a substantial reduction of TOC was also observed.[120] It was reported that, during Fe_2O_3-catalysed decomposition of ozone, a high degree of initial ozone decomposition was observed, but the catalytic activity decreased after a certain time.[121]

In recent years, manganese-catalysed ozonation has been extensively investigated. Manganese salts and manganese dioxide have been found to be effective catalysts, thereby increasing pollutant destruction efficiency in the ozonation process.[122–124] Ma *et al.* reported that addition of manganese oxides (MnO_x) supported on activated carbon enhanced the oxidation of nitrobenzene by ozone.[125] We have investigated several catalysts such as potassium permanganate, Ferral (a natural earth-derived material composed of ferric aluminium oxide and sulphate), hydrated alumina, activated carbon and ferric oxide supported on silica for the improvement of decolorisation efficiency in the ozonation of dyehouse effluent.[126–128] Of them, Ferral, hydrated alumina and activated carbon showed best results for the decolorisation of dye effluent. Ferral showed excellent catalytic activity under acidic conditions but, in alkaline conditions, its catalytic activity diminished. Hydrated alumina and silica-supported ferric oxide showed excellent catalytic activity under acidic conditions, whilst activated carbon was found to be effective in both acidic and alkaline conditions.

7.3 Decolorisation by ozonation

Increasingly, ozone is being used both for water purification and effluent decolorisation. This is partly due to environmental considerations but also to improvements in the design of ozone generators.

7.3.1 Methods of ozone generation

Ozone can be generated by corona discharge, thermal, photochemical or chemical processes or by the electrolysis of water. Among these only the corona discharge system is now employed for commercial ozone production. Ozone is produced from oxygen or air (as air contains oxygen gas) through corona discharge, which is silent electrical discharge. In this method, an oxygen-containing air is passed through two electrodes separated by a dielectric and a discharge gap. When high voltage is applied to the electrodes, an electron flowthrough occurs across the discharge gap and these electrons provide the energy to disassociate the oxygen molecules, leading to the formation of ozone. Figure 7.10 shows a basic ozone generator.

At very high voltages, the electrons in the discharge, having high kinetic energy, collide not only with each other, but also with oxygen molecules, and break the molecular bonds to generate free oxygen atoms. At the same time, ozone is formed from oxygen atoms formed by the dissociation of oxygen molecules due to inelastic collision of electrons and when a free oxygen atom collides with a molecule of oxygen in the presence of a third molecule (M) which accepts the vibrational energy. The following simplified scheme shows the most important processes for the formation and decomposition of ozone.

$$e^- + O_2 \rightarrow 2O + e^- \qquad \text{(i)} \qquad [7.25]$$

$$O + O_2 + M \rightarrow O_3 + M \qquad \text{(ii)} \qquad [7.26]$$

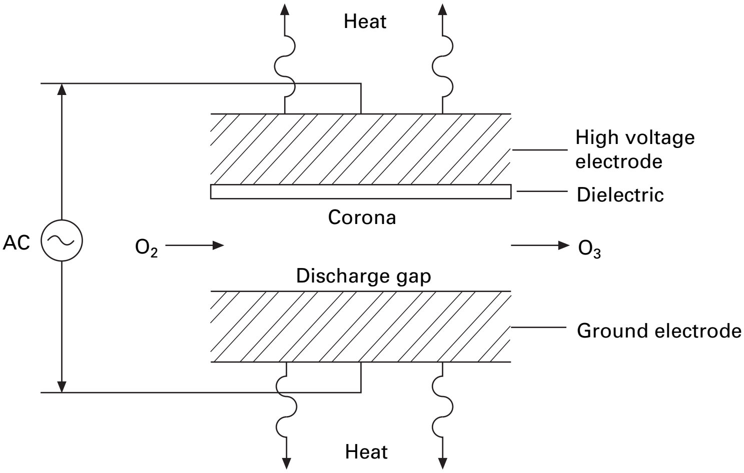
$$O + O_3 \rightarrow 2O_2 \qquad \text{(iii)} \qquad [7.27]$$

$$e^- + O_3 \rightarrow O_2 + O + e \qquad \text{(iv)} \qquad [7.28]$$

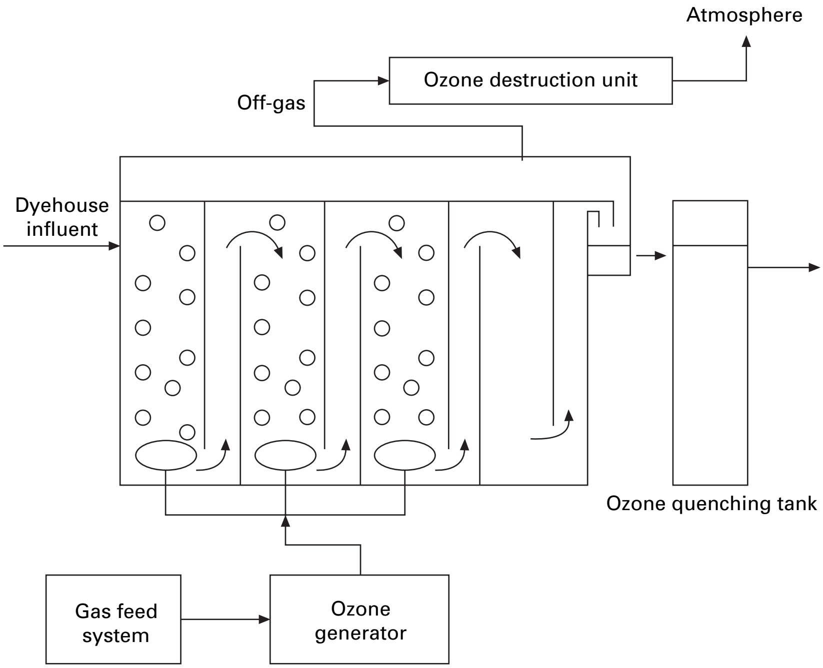
Since the half-life of O atoms is 10^5 times less than that of oxygen, the stationary conditions in the discharge according to the second equation above are quickly established even in the case of a relatively high flow velocity.

7.3.2 Ozonation treatment system for the decolorisation of spent dyebath

Figure 7.11 shows the schematic of an ozonation system plant for the decolorisation of textile wastewater. As shown in the Fig. 7.11, the ozonation



7.10 Basic ozone generation method.



7.11 Ozonation system for the decolorisation of effluent.

plant has four basic components: a gas feed system, an ozone generator, an ozone contactor where it reacts with effluent and an off-gas destruction system.

Gas feed system

Ozone is produced from oxygen or dry air or a mixture of both. When oxygen is used as a feed gas, higher ozone concentrations (8–14%) can be achieved, but there are safety concerns. On the other hand, if air is used, it should be properly conditioned to prevent damage to the ozone generator. The air supply should be clean and dry, with a maximum dew point of –60 °C. Although air is almost free, initial investment for the air preparatory system is high and it consumes a great deal of electrical energy. Typically, the air feed system consists of air compressors, filters, dryers and pressure regulators.

Ozone generator

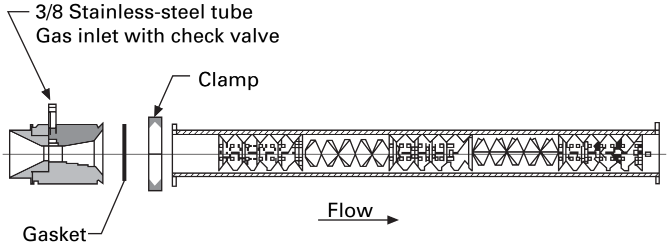
A typical industrial ozone generator uses oxygen as the feed gas rather than air, and converts it by means of corona discharge to ozone. Two different geometric configurations for the electrodes are used in commercial generators:

concentric cylinders and parallel plates. The parallel plate configuration is commonly used in small generators and can be air cooled. On the other hand, the concentric cylinder configuration is used for large generators and the glass dielectric/high voltage electrode used in them looks like a fluorescent light bulb and is commonly referred to as a 'generator tube'. Most of the electrical energy input to an ozone generator (about 85%) is lost as heat.[129] Because of the adverse impact of temperature on the production of ozone, adequate cooling should be provided to maintain generator efficiency. Excess heat is usually removed by water flowing through the stainless-steel ground electrode. Ozone generators are classified into three classes according to the frequency of power applied to the electrodes, low frequency (50–60 Hz), medium frequency (60–1000 Hz) and high frequency (over 1000 Hz). Low and medium frequency generators are the most common found in the effluent treatment industry.

Ozone contactor/reactor

Ozone is then transferred to an ozonation reactor, known as ozone contactor, where ozone is reacted with dyehouse effluent. Transfer efficiencies of greater than 80% typically are required for using ozone as an efficient oxidant.[130] Various types of ozone contactors based on bubble diffuser, venturi type injector or turbine mixer are used for efficient transferring of ozone to aqueous systems. The bubble diffuser contactor is commonly used for ozone contacting in the United States and throughout the world.[131] This method offers the advantages of no additional energy requirements, high ozone transfer rates, process flexibility, operational simplicity and no moving parts.

The injector contacting method is commonly used in Europe, Canada and also in the United States.[131] Ozone is injected into a water stream under negative pressure, which is generated in a venturi section, as shown in Fig. 7.12, thereby pulling the ozone into the water stream. In many cases, a sidestream of the total flow is pumped to a higher pressure to increase the available vacuum for ozone injection. Ozone is injected into the sidestream,



7.12 Venturi-type static mixer.

which is then combined with the remainder of the plant flow under high turbulence to enhance dispersion of ozone into the water.

Turbine mixers are used to feed ozone gas into a contactor and mix the ozone with the water in the contactor. Ozone transfer efficiency for turbine mixers can be more than 90%, but the power required to achieve this efficiency is 4.85 to 5.95 kWh of energy per kg of ozone transferred.[132]

Off-gas destruction

The concentration of ozone in the off gas from a contactor is usually well above the fatal concentration. For example, at 90% transfer efficiency, a 3% ozone feed stream will still contain 3000 ppm of ozone in the off gas. Therefore, ozone in the off gas needs to be converted back to oxygen before release to the atmosphere. Ozone is readily destroyed at high temperature (>350 °C or by a catalyst operating above 100 °C to prevent moisture buildup). The off gas destruction unit is designed to reduce the concentration to 0.1 ppm of ozone by volume.

7.4 Reuse of spent dyebath

The feasibility of reusing dyebath effluent has been the subject of many previous investigations.[133–135] Depending on the classes of dyes used, reuse of spent dyebath methods can be divided into two classes.

1. Use of spent dyebath through reconstitution.
2. Use of spent dyebath through decomposition of dyes.

7.4.1 Use of spent dyebath through reconstitution

As mentioned earlier several classes of dyestuffs are used in the textile dyeing and printing industries depending on the substrate, fastness properties, brightness required and cost considerations. Among them, some, such as acid, basic, direct and disperse dyes, are not decomposed during dyeing and do not undergo chemical modifications. As a result, their spent dyebaths can be reused through reconstitution for particular shades. This is an attractive method especially in terms of cost, as no chemical treatment of spent dyebath is required and the same dyebath can be reused several times. In this method, not only dyes, but also auxiliaries added during dyeing, can be reused.

In practice, the absorbance of the spent dyebath is measured at different wavelengths and the software that accompanies the spectrophotometer calculates the addition of dyes required to achieve a particular shade. It becomes highly successful if the same shade is produced time after time using the same dye/dyes. Dyebath reuse is limited by yarn/fabric impurities that are not removed during preparation and by impurities that accumulate from dye diluents, salt build-up, steam contaminants and surfactants. In addition, dyebath additives may be lost by several mechanisms such as losses due to vaporisation from open dyeing machines, exhaustion onto the fabric, chemical reaction and dye liquor carry-off by the substrate.

Early trials were carried out using untreated spent dyebaths for dyeing nylon with acid dyes. The high exhaustion levels achieved in the process favoured this approach. An automated technique was developed based on spectrophotometric analysis for measuring residual dye concentrations in the spent dyebath and reconstitution by addition of fresh acid dyes for dyeing nylon carpet of the same shade.[133–135] Reuse of spent dyebath using the same method was also demonstrated with disperse dyes on polyester knitted fabric.[136]

Reuse of residual dyes left in the spent bath using the above technique is only suitable for dye classes that are not chemically changed during the dyeing process; these include acid, disperse and direct dyes. On the other hand, reactive, vat and azoic classes of dyes are unsuitable as they undergo chemical modifications during dyeing. For example, in an investigation into the dyeing of cotton fabric with reactive dyes, use of recycled exhausted reactive dyebath without further treatment (other than neutralisation with acid) demonstrated that dyeing properties were affected by the presence of residual hydrolysed and unhydrolysed dyes.[137] Dye sorption and fixation were found to be significantly lower with recycled dyebaths than with a new dyebath. Hydrolysed dye from the previous dyeing process occupied dye sites and affected exhaustion of the freshly added dye.

Although the reuse of untreated dyebaths was found to be feasible for dyeing cotton with direct dyes, reproducibility in some dyeings was affected by the build-up of metal ions released from metal–complex dyes.[138] Moreover, it was observed that, whilst reuse of the spent bath was possible for the same shade, for other, lighter and brighter, shades, its use was precluded, as the presence of trace amounts of other dyes affected brightness.

7.4.2 Use of spent dyebath through decomposition of dyes

As mentioned above, vat and azoic dyes undergo chemical modification during dyeing, and reactive dyes are unsuitable for reuse, as during dyeing they undergo chemical modification by alkaline hydrolysis. It is therefore necessary to decompose and decolorise these dyes for the reuse of their spent dyebath. A variety of decolorisation techniques such as adsorption, biological oxidation, photo-oxidation, chlorine, ozone, Fenton's reagent and various advanced oxidation processes (AOPs) are applied for the removal of colour from effluent and these can also be applied for the decomposition of dyes in the spent dyebath. This is an expensive process and, therefore, less desirable in dyehouses.

Although Pavlosthasis *et al.*[139–141] investigated biological oxidation for the decolorisation of dyehouse effluent and successfully reused the treated water for successive dyeing, it can be less attractive as decolorisation will take place in days to months. Also, a large reservoir is needed to hold the effluent whilst it is being treated. Rapid treatments such as chemical oxidation and membrane filtration will be preferable in dyehouses compared with biological and adsorption processes. In one case, it was shown that decolorisation using Fenton's reagent in combination with a membrane system produced a concentrate containing the reclaimed salt that could be successfully reused in the dyeing of cotton fabric with reactive dyes, although some defective dyeings were reported.[142]

An investigation into the reuse of recycled reactive dyebath decolorised by ozone showed that reproducible dyeing could be achieved for up to five repeated cycles.[41] Dyebath reuse studies were conducted using three reactive dyes, C.I. Reactive Yellow 145, Red 195 and Blue 221. Cotton fabric samples were dyed with the individual dyes at 2% o.w.f. and used as standards. The dyebath was collected after each dyeing and ozonated to remove residual colour. The recycled water was then reused in subsequent dyeings with the same dyes, after raising its pH to 11 by addition of alkali. Five successive dyeing were conducted with recycled dyebath without addition of salt and the shades reproduced were comparable with the standard dyeing. The same applied to a dark brown shade produced by using a trichromatic mixture of blue, red and yellow containing 2% o.w.f. of each of the dyes. However, in the case of dichlorotriazinyl reactive dyes it was shown that the colour strength of the dyed fabric decreased in the successive dyeing cycles.[143] It was reported that a hydrolysable organic ester could be used for controlling acid dyebath pH when a reconstituted bath was used; ten recycles also gave good reproducibility of shade without affecting the dyed fabric's fastness properties.[144]

7.4.3 Spent dyebath reuse techniques

Different reuse techniques are used depending on whether the dyes are chemically changed or not during the dyeing process. Those dyes that are chemically unchanged during dyeing can be reused directly without any decolorisation for duller shades, but bright shades will need decolorisation. On the other hand, dyebaths containing those dyes that are chemically changed during dyeing will have to be decolorised. Based upon the above discussion, dyebath reuse techniques can be divided into two classes as discussed below.

Dyebath reconstitution techniques

This method is popular in the case of exhaust dyeing processes using basic, acid, or disperse dyes in the jet, winch, jigger, package or beam dyeing machines. There are two options for reusing exhaust dyebaths. In one option, after completion of the dyeing process, the spent dyebath is transferred to a holding tank and in the same machine the batch of fabric is washed with fresh water. After removing the cloth from the machine following washing, the washing effluent is discharged and the machine is refilled with effluent stored in the holding tank following dyeing. Then the bath is reconstituted after dyebath analysis and replenished with fresh dye, dyebath additives and fresh water to compensate for water loss through evaporation. Spent dyebaths are spectrophotometrically analysed to measure residual dyestuff concentrations. Commercial computer software is then used to calculate the quantities of fresh dyestuffs that need to be added to the residual quantities in order to achieve a particular shade in the next dyeing cycle.

As direct, basic and acid dyes are water soluble, they can be directly measured for residual dyes. In the case of water-insoluble disperse dyes, they are solvent extracted with a suitable solvent (such as toluene) and are then measured spectrophotometrically. The main advantage of this method is that there is no need to remove the fabric from the machine for washing following dyeing, but extra space is needed for the holding tank. A calibration curve can be prepared for a particular dye at its wavelength of maximum absorption at different concentration levels and the residual dye can be quantified from the calibration curve. At Georgia Tech in the USA, Tincher *et al.*[145–146] developed an automated batch dyeing process based on the above-mentioned spectrophotometric analysis method.

In the other option, after completion of dyeing, the yarn or fabric is removed from the machine and transferred to a different machine for washing to remove unfixed dyes from the dyed substrate. The exhaust bath left in the machine is replenished with fresh dye, additives for dyeing and water. Usually, in the case of basic and acid dyes, the dyebath is discharged at 60 °C after completion of dyeing. There is therefore no need to increase the temperature from cool to 60 °C for the next dyeing cycle as the bath is already at 60 °C, thereby reducing energy consumption. In this method, water loss is more than in the previous method, as when the fabric is removed from the machine, a similar weight of water to that of the fabric is also taken with it.

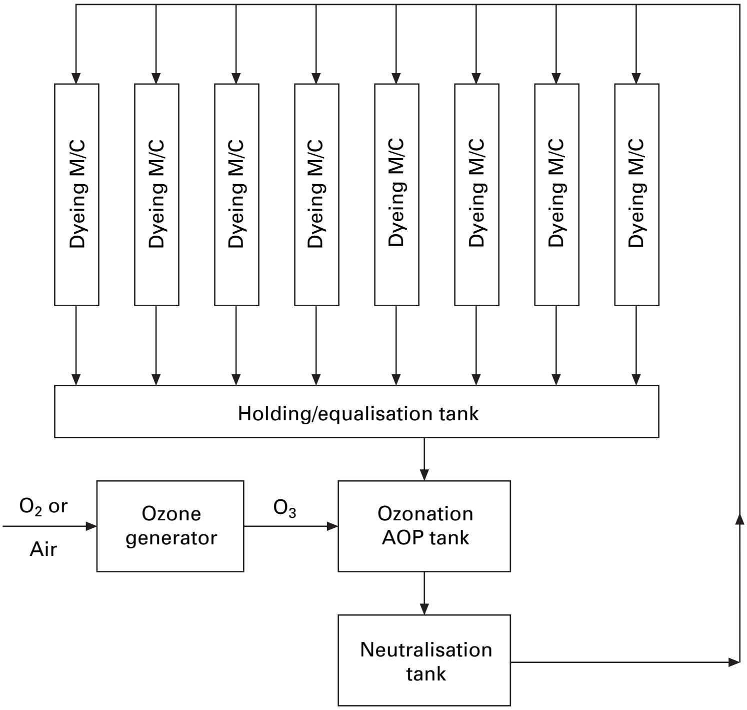
Two textile processing companies in the US have been reported to have reused and recycled spent dyebath.[147] One of them has realised savings of more than one million US$ per year and has reduced salt discharge to a nearby river by more than four tons per day. The other company at their two mills in North Carolina has observed a decrease in water usage of 35%, equivalent to a cost savings of four cents per kilogram of production.

Dyebath reuse through decolorisation techniques

This is a more expensive route for dyebath reuse compared with the previous route mentioned earlier. In this method, only water and a few dyebath additives (those that are not chemically changed during the decolorisation process, such as salt) can be reused. This method is suitable for dyes that are chemically changed during dyeing such as reactive, sulphur, azoic and vat dyes. In practice, rapid decolorisation of the spent bath is necessary.

Methods based on biological, photochemical, electrochemical oxidation, radiation or Fenton's reagent are therefore not suitable as they either require a long time or leave residual oxidant in the bath. In this respect, ozonation or catalytic ozonation are best as the reaction is very rapid, just a few seconds, and ozone decomposes to O_2 within minutes, leaving no by products. However, in the case of catalytic ozonation, metal load in the treated effluent may increase through dissolution of metallic catalysts.

The ozonation process is shown in block diagram form in Fig. 7.13. In this process, spent dyebaths from different dyeing machines are collected in a holding tank and are equalised for pH and dyestuff concentrations. Then, this effluent is pumped to the ozonation reaction chamber where, if catalytic



7.13 Set-up for reuse of spent dyebath through decolorisation by ozonation or catalytic ozonation.

ozonation is used, a suitable catalyst is added to the ozonation reactor. The acidic ozonated effluent is neutralised with diluted alkali and again sent to the dyeing machines. Reactive dyebaths are usually alkaline and ozonation can be carried out at alkaline pH without any pH adjustment. Most catalytic ozonation systems work under acidic conditions and, therefore, if the catalytic route is followed, the pH of the effluent collected at the holding tank should be adjusted to the required pH before pumping it to the ozonation reactor.

7.4.4 The effect of residual components

Spent reactive dyebath reuse is possible through decolorisation with ozone with little modification of existing processes. Ozonation of effluent leaves large quantities of salt, decomposition products of dyes (such as oxalic, glyoxalic acid and carbonic acid) and dyebath additives (e.g. wetting agent and surfactant) and alkali. If reactive dyebath is ozonated, the initial effluent will have had a large amount of added Na_2CO_3 used for the fixation of dye and will have to be neutralised with H_2SO_4 before ozonation. If this treated effluent is reused for dyeing with reactive dyes, the Na_2CO_3, H_2SO_4 and carboxylic acids form a strong buffered system and prevent the pH from increasing by consuming the alkali added during the later fixation stage. It is, therefore, necessary to check the fixation pH a few minutes after alkali addition and, if found low, more alkali should be added, as the optimum pH for most reactive dyes is between 10.5 and 11. Otherwise, if standard recipes are used, there will be insufficient alkali for fixation of the dye, resulting in low colour yields. However, if treated effluent is reused for dyeing with acid, disperse, or basic dyes, no buffering agent needs to be used, as adjusting with addition of acid will be enough to control the pH.

In our laboratory, we have successfully reused ozonated reactive dyebath not only for dyeing with reactive dyes, but also with disperse and direct dyes without any problem.[148] Spent dyebath of a trichromatic mixture of reactive dyes was collected from a jigger dyeing machine after alkali fixation and just before dropping the bath. Table 7.1 shows the results obtained when spent dyebath reuse was attempted for up to four cycles for dyeing with reactive, disperse and direct dyes. Renovated reactive dyebath can be reused for different dye classes and NaCl present in the effluent did not show any adverse effects on dye exhaustion in the case of dyeing polyester with disperse dyes. Ozonated dyebath can be reused for bleaching of cotton fabric and even for whitening of fabric provided the effluent is thoroughly decolorised.

7.5 Future trends

Dyebath reuse is an increasing trend, especially in western countries and reuse through reconstitution is becoming more popular in USA in the carpet

Table 7.1 Reuse of spent dyebath for dyeing with, reactive, disperse and direct dyestuffs

Effluent	Dye class	Dyes[a]	Control (dyed using normal water)	Sample (dyed using treated effluent)	ΔE
First reuse	Disperse	Terasil Pink 3G (2%)	11.5	11.3	0.2
		Foron Turquoise Blue S-BGL (2%) +	17.1	17.0	0.3
		Intrasil Brilliant Blue L-3RL (2%)	17.7	17.3	0.8
Direct		Direct Pink 3B (2%)	5.1	5.0	0.3
		Direct Pink 3B (4%)	7.1	7.2	0.8
Reactive		Levafix Turquoise Blue E-BA (2%) + Levafix Brilliant Red E-6B (2%)	15.2	15.3	0
		Levafix Turquoise Blue E-BA (4%)	15.1	14.1	0.3
		Procion Navy Blue HE4R (1.0%)	6.0	5.9	0.6[b]
		Procion Navy Blue HE4R (5.0%)	19.2	19.2	0.4[b]
Second reuse	Reactive	Evercion Green H-4BD (2.0%)	9.9	10.1	0.3
		Evercion Green H-4BD (4.0%)	19.2	19.5	0.2
Third reuse	Reactive	Levafix Torquoise Blue E-BA (2.0%) + Levafix Brilliant Red E-6B (2.0%)	15.2	15.3	0.1
		Levafix Turquoise Blue E-BA (1.0%) + Levafix Brilliant Red E-6B (3.0%)	15.7	15.5	0.2
Fourth reuse	Reactive	Procion Crimson H-EXL (2.0%)	6.0	6.0	0
		Procion Crimson H-EXL (4.0%)	11.4	11.4	0

[a] Values in parenthesis = depth of shade.
[b] 30% extra sodium chloride was used compared with control.

industry for dyeing polyamide with acid dyes. More research is going on concerning automation of dyebath reuse to minimise human error, reliability and shade variation.[145–146] Despite the fact that cotton retains its popularity in garments and these are most commonly dyed with reactive dyes, the problem of low fixation remains. This results in coloured effluent, which also contains high levels of salt and alkali. Recently, dye manufacturers have investigated ways of making reactive dyeing more efficient and less polluting. Fixation levels have been improved by introducing double or triple anchor points and by using different reactive groups in the same dye molecule. However, there will always be a certain percentage of dye that reacts with water and not the fibre, and so 100% fixation is impossible. Ozonation of effluent is therefore sometimes resorted to despite its expense and more than 250 textile mills in the USA use the treatment for their effluent. Some of these companies then recycle the decolorised effluent.

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8

Chemical treatment of textile dye effluent

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8.1 Introduction

The presence of highly visible colour in aquatic waste occurs in a number of industrial settings. Prominent among these are the pulp and paper, food processing and textile wet processing industries. In the case of the last of these, the colour in the waste water is dye that is not fixed in the dyeing of the fibre, yarn, fabric or garments being processed. The degree to which colour in waste water may be a problem can depend on the class of dye being used, the type of stream being discharged into, the degree to which the textile effluent contributes to the flow of the receiving body, the geographic location of the plant, and even the political environment that the plant operates in.

The amount of dye used each year in the textile industries of the world has been variously estimated, but it is undoubtedly more than 700 000 tons per year. Depending on the particular dye class in use, the percentage of dye that remains unfixed to the fibre during the dyeing process, and finds its way into the effluent, can range from 5–50%. This can present a very serious problem for the textile manufacturer who finds himself needing to meet effluent standards that include the colour in that water stream, as well as all the other standards dealing with such measures as pH, dissolved solids, chemical oxygen demand (COD), biological oxygen demand (BOD) and total organic carbon (TOC).

8.2 Colour

Colour is an intriguing part of our everyday lives. An intense red colour in the fabric of the garment that we wear may be highly satisfying, but that same red colour in the stream that flows through our grassy park is completely objectionable. It is not the colour *per se* that offends, but colour that is out of place, that does not belong. Dyes, the molecules that produce the colour on fabrics, have very high tinctorial power, absorbing intensely in the part of the electromagnetic spectrum that our eyes use to translate into images. The wavelengths of the visible spectrum are only a small part of the entire electromagnetic spectrum[1] (see Fig. 8.1), and are roughly in the range of 400 to 700 nanometers (10^{-9} m), the deep violet to dull red of human perception.

8.3 Dyes

Almost all of the dye compounds commonly used for dyeing textile fibres have the following characteristics. They:

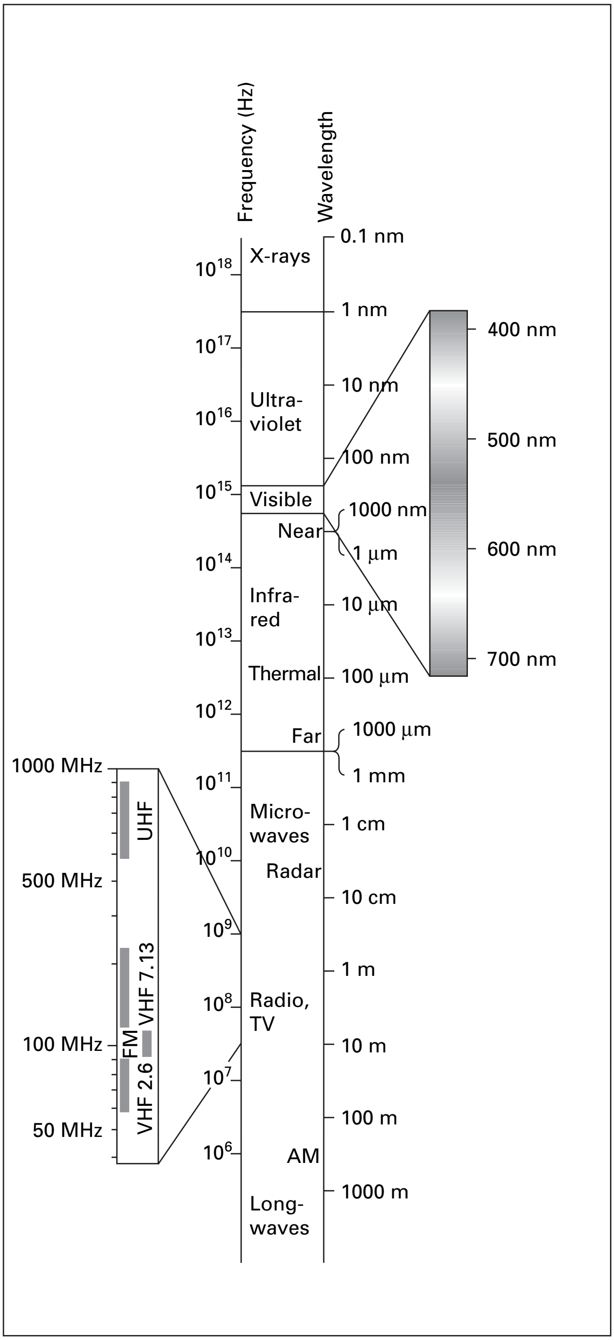
- absorb very strongly at wavelengths in the visible spectrum
- are composed of polyaromatic compounds
- are water soluble in their applied form, except for disperse dyes, vat dyes and pigments
- are substantive to certain fibres
- are resistant to biological degradation.

The last property means that dyes passed out in textile effluents are little affected by conventional biological waste treatments. In addition to recalcitrance to the usual purification processes, textile dye wastes are almost always a complex mixture containing starch, oils, high concentrations of chlorides, sulfates and carbonates, even higher sodium concentrations, and any number of different surfactants and biocides.

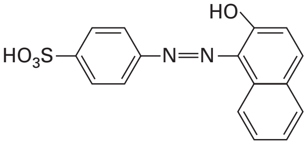
8.4 Classes of dye

Dyes are usually referred to by their Colour Index (CI) designation. The Colour Index system was developed by the Society of Dyers and Colourists.[2] The CI designation includes the name of the dye class, its hue, and a number. An example would be C.I. Disperse Red 1, the first red dye in the disperse class. Dyes for textiles are usually classified either by their method of application (basic, acid, direct), the type of interaction they have with fibres (reactive), their structural characteristic (azoic, sulfur), or a historical characteristic (vat). Most dyes are characterized chemically by either a major azo linkage or an anthraquinone unit.

Azo dyes have one or more double-bonded nitrogen units linking aromatic units. A typical example is shown in Fig. 8.2. These types of dyes account for 65–75% of all the dyes produced. Questions sometimes arise about these dyes because a small percentage have been implicated in assessments of environmental and health risks. This issue involves the possibility of formation of certain aromatic amines (notably benzidine) in their breakdown in the environment. Consumer goods that contain benzidine-based dyes have been banned for these reasons in Germany and some other European countries.[3]



8.1 Visible wavelengths within the electromagnetic spectrum.[1]



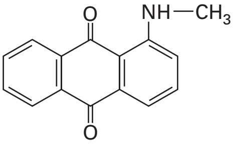
8.2 C.I. Orange II.

Another major chemical structure for dyes is that based on anthraquinone. Figure 8.3 gives an example of such a dye, C.I. Disperse Red 1. Vat and disperse dyes often are based on the anthraquinone structure. Both of these dye classes are characterized by the insolubility of their coloured form. Among the dye classes, basic dyes (cationic) are characterized by having amino groups attached to the larger aromatic structures. These dyes have amino groups that are positively charged. This gives them both water solubility and affinity for fibres such as nylon and acrylic that contain significant numbers of negatively charged groups. Acid dyes usually have sulfonic acid groups that give them a negative charge. Under acid conditions the amino groups in protein or polyamide fibres become protonated and have a positive charge, thus attracting the negative dye anions.

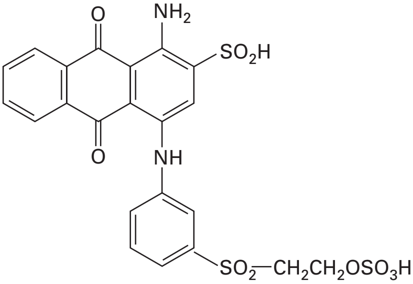
Reactive dyes are so-named because the groups that are attached to chromophores allow covalent bonds to be formed with cellulosic and protein fibres. Characteristic reactive groups attached to chromophores include vinyl sulfone (see Fig. 8.4) and triaziryl (see Fig. 8.5). Reactive dyes represent more difficult colour removal problems than most other dye classes. In the first place, their fixation rate is lower because of their propensity to react with water rather than the hydroxyl in the cellulose of the cotton fibre. This creates hydrolysed dye that has little affinity for the fibre. Secondly, reactive dyes are not absorbed onto biomass to any great degree. Pierce[4] cites figures of 30% as a maximum and 10% as an average. The fixation rate of the reactive dyes on the fibre may range from 50–70%. This contrasts to other dye classes which have fixation rates of 80% as an average and some much higher.

Disperse dyes, originally developed for acetate fibres, find most of their use in dyeing polyester fibres. They are characterized by their low water solubility which leads to their ability to colour fibres that have very high hydrophobicity. They are applied in an aqueous dispersion where there is a three-way equilibrium between the dye in dispersion, the small amount of dye soluble in water and the dye in the fibre.

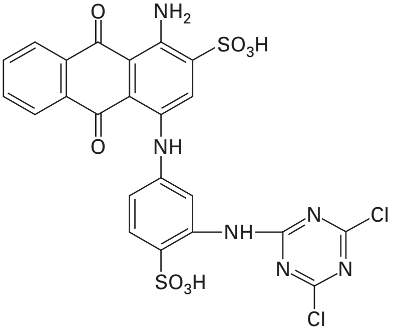
Vat dyes are so-named because of the historical method of application, in large vats that allowed the insoluble coloured form of the dye to be reduced to a soluble non-coloured form. It is the latter form, the 'leuco' form, that is applied to the cellulosic fibre, and then oxidized back to the coloured form and entrapped within the fibre. Figure 8.6 illustrates the most famous of vat dyes, indigo.



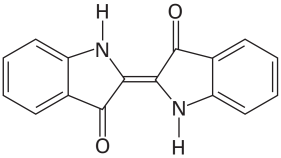
8.3 C.I. Disperse Red 1.



8.4 C.I. Reactive Blue 19.



8.5 C.I. Reactive Blue 4.



8.6 Indigo.

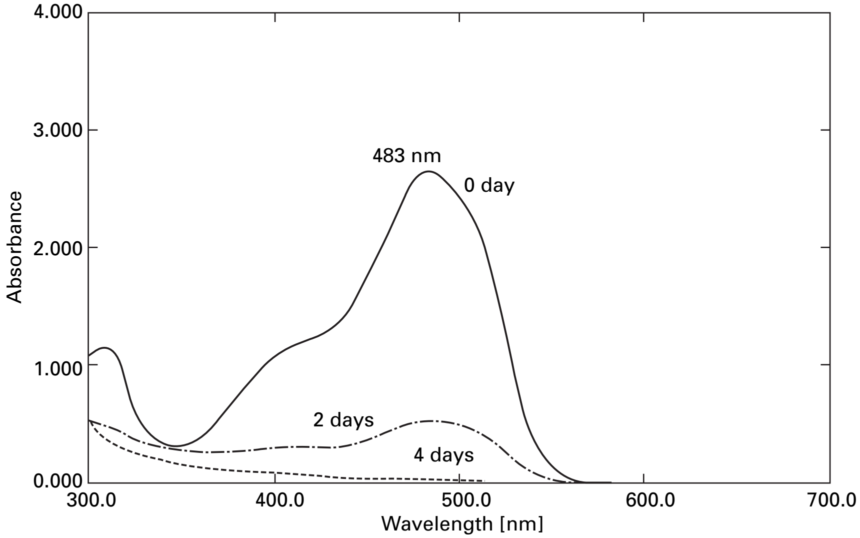
8.5 Measurement of colour removal

The removal of colour from textile effluent can be characterized as simply the disappearance of colour. This can be assessed visually, or monitored by visible spectrophotometry, using either the dominant wavelength if a single dye is involved, or by measuring the total area under the visible absorption curve for either a single dye or a mixture. In Fig. 8.7 the colour is being removed (in this case by enzymatic decolorization). The decrease in the area under the curve between 400 and 700 nm is a measure of the decolorization of the dyebath.

Disappearance of colour can occur if the coloured dye molecule is precipitated and falls out of solution (coagulation). Colour in the effluent also disappears if the molecule is cleaved such that the conjugated structure that absorbs visible wavelengths, and thereby creates colour, is broken up. Oxidation or reduction of the azo bond can cause this. Not visible are the further degradations of the dye molecule into fragments. If this progresses to the point that the dye molecule is changed into carbon dioxide, water and ammonia, then it is referred to as 'mineralization'. These then are the three basic ways in which chemical decolorization works.

8.6 Other measures of dye molecule fate

The measures that deal with the breakdown of coloured molecules after they are no longer visible are total organic carbon (TOC), chemical oxygen demand (COD) and biological oxygen demand (BOD). Total organic carbon in a sample is measured by the amount of CO_2 formed when organic carbon is oxidized through Pt-catalyzed combustion or a UV/persulfate reactor, and when the inorganic carbon is acidified. Chemical oxygen demand measurement uses potassium dichromate to oxidize the organic carbon in the sample. In the process, the dichromate is reduced to Cr^{+3}, which is then an indirect



8.7 Decolorization of Orange II.

measure of organic content. Biological oxygen demand measures the concentration of biodegradable organic matter. It monitors the rate of uptake of oxygen by micro-organisms at a fixed temperature over a given period of time. The ratio of BOD/COD is an indicator of the likelihood that the biological waste treatment alone will break down the organic molecules in the waste stream.

8.7 Chemical methods for colour removal

A variety of approaches have been used to remove dyes from textile waste effluent streams. In other chapters, the use of adsorbants, treatment of spent dyebaths with ozone, and biotechnological treatments have been discussed. In this chapter, chemical treatments will be discussed, though, in some cases, the chemical treatment is combined with adsorption and filtration using membranes. The treatments that will be discussed are:

Physico-chemical coagulation	with either calcium, iron or aluminum salts, by polymers with multiple charged sites, or by combinations of these agents.
Electro-coagulation	where the coagulating medium is generated by sacrificing the anode with the generation of ions that coagulate, flocculate, and either precipitate or float the agglomerated dye molecules.
Electrochemical	where a current is applied directly across electrodes, directly breaking bonds in the dye molecule and in the fragments created.
Oxidation	namely the application of oxidizing agents, and catalysts to boost their performance.
Other processes	for example, ion exchange.

8.7.1 Physico-chemical coagulation processes

Physico-coagulation, otherwise known simply as coagulation, has been used widely in treating textile waste water to remove colour. Very often coagulation can remove colour and meet the standards established by law or a consent agreement. The technology is simple and a wide variety of products are on the market to accomplish this purpose. Coagulation methods are useful in reducing the amount of colour in textile waste, but give only partial colour removal and reduction in COD.

At least three major difficulties present themselves for coagulation. The first is that the process can be expensive. The user is paying for chemicals whose only purpose is to be thrown away. The solids created add to the solid waste burden of the textile plant or to the municipal waste treatment facility. Secondly, dyes with high water solubility resist coagulation and larger additions of the coagulant may be required in order to achieve reasonable removal of colour from the effluent. Naturally, this increases the cost and solid waste load, as well as sometimes having a detrimental effect on oxidation of ammonia to nitrite and nitrates (nitrification) in the biological treatment plant.

Thirdly, the solid waste production requires that a suitable means of removing and disposing of coagulated dye waste must be added to what other solid waste is generated by the textile dyeing and finishing operation. Increasingly, the pressure from environmental regulators is to decrease solid waste load, and any process that adds to solid waste load will cause additional headaches for the environmental manager of the textile plant. The review article by Hao *et al.*[5] in 1999 discussed a wide range of colour removal methods, including coagulation. As was pointed out, the coagulation process is often used in conjunction with other processes because of the inability to completely remove some classes of dyes. For example, coagulation may be combined with oxidation by either using Fenton's reagent, or by pretreating with ozone.

Over the last decade, the research reported on coagulation for colour removal has continued unabated. Gao *et al.*[6] evaluated an aluminum silicate polymer composite as a coagulant for water treatment. Depending on how the composite was produced, the results were better coagulation but less stability at longer storage times. Sanghi and Bhattacharya[7] used a combination of powdered activated carbon and bentonite clay, along with polyaluminum chloride (PALC) as a coagulant to decolorize dye solutions of direct, mordant and basic dyes. The PALC not only increased dye removal, but formed a quick-settling sludge that could also be used for dye removal.

A comparison of the removal of disperse and reactive dyes by chemical coagulation with that of Fenton oxidation was done by Kim and Park.[8] Their work showed that disperse dyes, because of their lower solubility and lower soluble chemical oxygen demand (SCOD)/total chemical oxygen demand (TCOD) ratios, were more easily decolorized by chemical coagulation than were reactive dyes. The dyes in the reactive class have high solubility and are more resistant to removal from solution. Conversely, they are therefore more available to be broken down by the oxidative methods.

Papic *et al.*[9] examined the removal of reactive dyes from synthetic wastewater by a combination of Al(III) coagulation combined with carbon adsorption. The dyes were C.I. Reactive Red 45 and C.I. Reactive Green 8. The combination of treatments gave almost total elimination of both dyes from the solutions. A secondary benefit was that minimal amounts of sludge were formed, cutting down on both the initial cost and the cost of solid waste removal. Gao and Yue[10] evaluated the coagulation efficiency of a series of polyaluminum silicate chlorides (PACS) which had different OH/Al and

Al/Si ratios. These were prepared by copolymerization and composite techniques. The results were compared against polyaluminum chloride (PAC). The PACS prepared by copolymerization had the best results in coagulating and in lower residual aluminum in the wastewater. Another report by the same group focused on the PACS particle distribution and zeta potential and their effect on the coagulation performance. Two other papers by Gao's group dealt with aluminum species formed by different methods.[11,12]

Lee and Choi[13] evaluated a combination of adsorption and coagulation on removal of two reactive dyes, Orange 16 and Black 5. The adsorbent was coconut-based powdered activated carbon, and aluminium chloride was used as the coagulant. Coagulation followed by adsorption was found to be more efficient than the reverse. Their conclusion was that the combined process could reduce coagulation and adsorption amounts and thus produce less sludge. Joo, *et al.*[14] decolorized a high concentration reactive dye wastewater using a combination of polymer flocculant and inorganic coagulant. The four model reactive dyes used were Black 5, Blue 2, Red 2 and Yellow 2. The polymer was synthesized from cyanoguanidine and formaldehyde and applied with alum or ferric salt. Inorganic salt alone was not effective but as polymer was added the combination treatments gave colour removal efficiencies as high as 60%.

Lee *et al.*[15] evaluated a submerged hollow fibre microfiltration membrane coupled with combinations of coagulation and adsorption by activated carbon in removal of the reactive dyes, Orange 16 and Black 5. Under optimal conditions they were able to achieve removal of 99% for Black 5 and 80% for Orange 16. The hybrid process was judged to be far superior to the individual processes in removing both dyes. They concluded that this process would allow reduction in the use of coagulant and adsorbent. Petzoid and Schwarz[16] investigated the removal of dye by flocculation for two types of sludge and for pure dyes using polyelectrolytes and polyelectrolyte–surfactant complexes. The dyes examined included Acid Yellow 3 and Acid Blue 74.

They concluded that new particle forming flocculants can be 'tailored' so that colour can be completely removed over a wide concentration range. Saraso *et al.*[17] followed an ozonation treatment of industrial wastewater with treatment by $Ca(OH)_2$ to effect almost total elimination of compounds that were left over after the ozone application. However, aniline and chloroanilines were formed after the coagulation step, probably caused by the strong basic medium.

In summary, the coagulation method by inorganic salts alone probably will continue to be used. However, given the constraints on sludge disposal and the amounts of these materials needed for removing highly soluble dyes, either unique polyelectrolytes or various combinations of coagulation with oxidation techniques would seem to be the inevitable physico-chemical treatments to be employed, at least in those countries or US states with tight environmental standards to meet.

8.7.2 Electro-coagulation processes

Electro-coagulation processes have been used in several industries for removal of colour from waste effluent. These include pulp and paper, leather treatments, and textiles. The processes utilize an electric current that passes through sacrificial electrodes creating chemical reactions that then produce the desired effect with the dye molecules in solution. The results can be coagulation, flotation, reduction or oxidation. The cathodes and anodes involved can vary but the most common reactions are ones where the anode is a metal that becomes solubilized with the metal ions created serving as coagulating agents. If hydrogen is liberated in the process, the gas bubbles serve to carry the particles created to the surface where they are easily skimmed off. Precipitation can also occur if other ions are created and/or the pH of the solution is increased.[18]

In removing colour from waste streams, regular coagulation has the disadvantage of over-feeding of chemicals to the waste stream, with the result that the excess of chemicals added may add to the chemical pollution in the decolorized effluent. This excessive addition of coagulants can be avoided by the use of electro-coagulation. The coagulant is generated as needed rather than dosed without real knowledge of just how much is required. The coagulant is generated by electro-oxidation of a sacrificial anode. Electro-coagulation uses simple equipment, has an operation that is easy to control, and usually results in less sludge than conventional coagulation creates.[19–21]

As Hao *et al.*[5] pointed out, a number of factors affect the efficiency of electrochemical coagulation. These include the intensity of the current (which factors into the comparative cost of the process), the engineering design of the equipment used, the types of electrodes used as well as their physical characteristics, the pH and temperature of the process, the solution characteristics and, not least, the properties of the dyes in the mixtures being treated themselves.

McClung and Lemley[22] used an iron electrode to treat three acid dyes, after which they identified the by products of the process by HPLC. They indicated that there was probably a combination of adsorption and dye degradation. Chen *et al.*[23] created a novel electrode system for electroflotation treatment of wastewater. An IrO_x–$Sb_2O_5SnO_2$ coating was applied to titanium. The service life of the electrode was predicted to be about 20 years. It was claimed that the small inter-electrode gap that is possible with the system results in a significant energy savings with easy maintenance.

Yang and McGarrahan[24] examined the colour removal of three dyes, reactive, disperse and acid, with aluminium and ferric anodes as coagulant generators.

Both processes were successful in removal of colour from the dyebaths. The control of pH was deemed to be essential, particularly for the aluminium coagulation process. Kobya *et al.*[25] used an aluminium sacrificial anode to treat a Levafix orange dye solution. Over 95% decolorization was obtained. Kim *et al.*[26] decolorized disperse and reactive dyes by electrocoagulation. Their study concentrated on examining the operating parameters such as current density, electrode number, electrolyte concentration, electrode gap, dyestuff concentration, and pH of the solution on the decolorization rates and efficiencies.

8.7.3 Electrochemical processes

Electrochemical colour removal has some advantages over the coagulation methods. It does not involve consumption of added chemicals, does not produce sludge, and seems to break down the dye molecules to the point that there may not be a problem with creation of other more hazardous ('polluting') molecules. However, this last factor will depend upon the efficiency of the treatment. One factor to consider in evaluating electrochemical processes is that, like other 'colour removal' processes, the disappearance of colour, in itself, does not give much indication of how far the degradation of the dye molecules themselves has proceeded. The first process in oxidation or reduction, for example, is likely to be the breaking of the azo link and the creation of large fragments. These fragments are not coloured, but may well actually increase the pollutant load.

Vlyssides *et al.* treated effluent from a reactive dyeing process using a Ti/Pt anode and stainless steel as the cathode.[27] and found that the organic pollutants were oxidized to carbon dioxide and water. Measures of effectiveness of the process were reduction of ADMI units by 100%, COD by 86%, and BOD by 71%. Szpyrkowicz *et al.*[28] used a similar system on a synthetic textile wastewater containing partially soluble disperse dyes. Under conditions of free pH evolution, 39% removal of COD was obtained and when pH was kept at 4.5 a 90% removal of colour resulted.

One such study dealing with this[29] did show that with a carbon-fibre electrode a removal of 90% of the colour was accompanied by a much lesser extent of carbon oxygen demand (COD) removal. Just how far the process may then go ultimately to provide complete mineralization has seldom been investigated.

Recent advances in electrochemical processes include the work by Szpyrkowicz *et al.*[30] who did a comparative study on oxidation of disperse dyes by chemical methods to that obtained by electro-oxidation in a synthetic wastewater. This was done in an electrochemical undivided cell reactor using seven different anode materials with 0.1 M NaCl as the supporting electrolyte. The Ti/Pt/Ir anode showed the best performance. Under free pH conditions, 39% of the COD was removed after 40 min. At pH 4.5, 90% of the colour was removed.

Bechtold and Turcanu[31] applied direct cathodic reduction to dyes with azo groups in the treatment of nanofiltrated textile effluents from printing. The addition of a redox mediator caused a measurable increase in the decolorization rate, but the chemical consumption per kilogram of waste was significantly increased. The decolorization of printing pastes containing reactive dyes was achieved on a laboratory scale to 60–80%. Carneiro *et al.*[32] evaluated oxidation by a $Ti/SnO_2/SbO_x/RuO_2$ electrode. They achieved 100% decolorization and 60% total carbon removal in 0.2M Na_2SO_4 at pH 2.2

Vaghela *et al.*[33] used a thin electrochemical reactor under single-pass conditions with a stable catalytic anode and a stainless-steel cathode to treat textile effluents containing reactive azo dyes. Decolorization and COD reduction were measured at various current densities, flow rates and dilutions. The same group later did a series of detailed laboratory experiments on reactive dyes under single-pass conditions. Decolorization of 85–99% was achieved at low flow rates (5 ml min^{-1}) and 50–88% at high flow rates (10–15 ml min^{-1}). They also carried out field studies with a pilot scale unit at industrial plants.[34] Decolorization of about 94–97% was achieved.

Golder *et al.*[35] treated two industrial dyes, methylene blue and eosin yellow, using mild steel electrodes with NaCl as electrolyte. Energy consumption was measured in some detail. Sakalis *et al.*[36] created a novel electrochemical pilot plant for azo dye removal. Batch experiments were done for a single electrochemical cell and continuous flow experiments were done for a cascade serial electrolytic cell apparatus. Both synthetic and real wastewater samples were used. Under optimal conditions, the industrial wastewater yielded more than 94% colour reduction with significant COD reduction.

Electrochemical treatment shows promise for further development. Success and utility will depend on demonstration of almost complete mineralization, the magnitude of the flow rates that can be achieved, and the cost of electricity at the plant site.

8.7.4 Oxidation processes

Oxidation processes can include oxidation through biological organisms, ozone, sodium hypochlorite, hydrogen peroxide, and even acids. The first two are discussed in other chapters of this book. The oxidative process will produce smaller molecules as the dyes are broken down. These will be colourless molecules. However, if the oxidation is only partial and does not go to mineralization, then questions may arise as to possible toxicity of the smaller molecules produced from the larger dye molecules, which are not by themselves toxic. References to ‘advanced oxidation processes’, AOPs, can mean processes that involve the hydroxyl radical which may be produced by a variety of reactions. Such AOPs can be useful as pretreatments to textile wastewater to increase the subsequent biodegradation in conventional systems.[37] For the purposes of this review, AOPs are processes that utilize a catalyst of some kind to increase the speed of the reaction.

Chlorination

Chlorination usually means the use of sodium hypochlorite (NaOCl) for decolorizing waste. This compound is commonly used in homes for bleaching clothes, and is readily available in large quantities. Sodium hypochlorite is a powerful oxidizing agent and will readily break down most dye molecules to smaller fragments. If a dye is somewhat resistant to biological degradation, then pre-treatment with hypochlorite can improve the total mineralization. As with other processes the solubility of the dye enters the equation of effectiveness, and disperse dyes are not decolorized effectively.[38] A major reason for not using sodium hypochlorite is the concern about producing chlorinated organic compounds, generally a much undesired scenario. One study identified a number of chlorinated aromatics created when a factory had treated its waste by chlorination before returning it to a river. The compounds identified included chloroanilines, chlorobenzamines, chlorophenols, chloronitrobenzenes, chloroacetic acid and several compounds on the US EPA priority pollutant list.[17] In recent years, the emphasis on the elimination of chlorinated compounds from waste effluents has increased,[39] and it is unlikely that the risk of creating more toxic compounds would be deemed worth the effectiveness that chlorination represents.

Hydrogen peroxide

Hydrogen peroxide by itself can be used for decolorization. It is readily available, easily mixed with water, and is not expensive. It can be used to decolorize dyes and will generally lower the COD. Because it does not persist, it does not have a negative effect on any bacterial process. The disadvantages of using hydrogen peroxide include the long reaction time needed for effectiveness and the cost of equipment needed for storage. Without activation, it is not a viable choice.

Catalyzed or advanced oxidation methods

Catalyzed oxidation methods generate highly reactive radical species that then quickly react with dye molecules to break them up into smaller colourless fragments. The most common reactive species is the hydroxyl radical, which has a higher oxidation potential than other common oxidizing agents. The oxidation potentials for common agents are:[39]

$$O_2 + 4H^+ + 2e^- \rightarrow 2H_2O \qquad E_0 = 0.123\ \text{V}$$

$$H_2O_2 + 2H^+ \rightarrow 2H_2O \qquad E_0 = 1.78\ \text{V}$$

$$O_3 + 2H^+ \rightarrow H_2O_2 + {}^1/_2\, O_2 \qquad E_0 = 2.07\ \text{V}$$

$$^\bullet OH + H^+ \rightarrow H_2O \qquad E_0 = 2.28\ \text{V}$$

Possible oxidizing agents include Fenton's reagent (discussed in the next section in this chapter), ultraviolet light, UV with added catalyst such as titanium dioxide, hydrogen peroxide and ozone.[40] Excluding Fenton's reagent utilization, the majority of research and development work reported in the literature recently on catalyzed oxidation treatment of dye waste used TiO_2 photoactivation. In general, the photodegradability of azo dyes relates to the complexity of the dye.[41] For example, work by Reutergardh showed that monoazo dyes are easier to break down than triazo dyes.[42]

The overall process is also very sensitive to the conditions in which the oxidation is done. For example, Arslan *et al.*[43] created two simulated dyehouse effluents and treated them with novel TiO_2 photocatalysts. The treatment efficiency was very sensitive to pH in the range of 4–9. The best overall TOC removal was about 30% for one simulated effluent at pH7, and 37% for the other at pH4. No correlation was observed between the adsorptive qualities of the TiO_2 and their corresponding reaction rates. Large amounts of organic halogens were created, probably as a consequence of the high chloride content of the synthetic wastewater.

Wang[44] investigated the photocatalytic degradation of eight commercial dyes in TiO_2 suspensions. He showed that the process was feasible and that all dyes were degraded to varying extents. The comparison of chloride and sulfate ions production rates indicated the dye molecules degradation patterns and pathways. The research on Orange II by Fernandez *et al.*[45] was a factorial design methodology on three critical variables affecting dye decolorization, the concentration of the dye, the pH and the concentration of TiO_2. The modeling of the reactions took into account the interactive nature of the system. The correlation between experimental and predicted values for decolorization was better than 95%.

Titanium dioxide was immobilized on glass rings in the work by Fernandez *et al.* The catalysis of H_2O_2 provided decolorization and mineralization of Orange II, which was monitored by spectrophotometric analysis and total organic carbon measurement.[46] In the research by Mu *et al.*[47] Orange II was degraded in aqueous dispersions of TiO_2 using UV light irradiation. Manganese in the solution reduced the degradation efficiency, primarily because it absorbed onto the surface of the TiO_2. Two dye derivatives, chromotrope 2B and amido black 10B were investigated by Qamar *et al.*[48] These dye derivatives were studied in aqueous suspensions of TiO_2 subjected to UV radiation. A number of by products were created and these were studied by varying different parameters such as TiO_2, pH, substrate concentration and various electron receptors. This same group investigated an azo dye derivative, chrysoidine Y in suspensions of titanium dioxide and zinc oxide.[49] The change in substrate concentration was monitored using UV spectroscopic analysis and decrease in total organic carbon content as a function of irradiation time under a variety of conditions.

Instead of TiO_2 particles, Kuo[50] used a titanium dioxide film with solar light rather than UV to catalyze decolorization of methylene blue and two reactive dyes. The film gave the advantage of not having to separate TiO_2 particles from the purified water after reaction with the dyes. They concluded that the films gave potential for using natural light rather than an artificial source for wastewater decolorization.

Fenton's reagent

Although there are many metals that can improve the activity of hydrogen peroxide, iron is very common and can generate highly active hydroxyl radicals. Fenton's reagent was invented in 1894 by its namesake, but did not come into use to treat industrial wastes until the 1930s. The reagent is a solution of hydrogen peroxide and iron salts. The ferrous ion is oxidized to ferric ion with production of a hydroxyl radical and a hydroxyl anion, as illustrated in equation (1). The iron (III) is then reduced to iron (II) by hydrogen peroxide with creation of a peroxide radical and a hydrogen anion. The iron (acting as a catalyst) is conserved and hydroxide radicals are produced. The generated radicals then proceed to attack any available organic compounds, such as dyes. With the destruction of the chromophore the wastewater becomes decolorized. The general scheme is:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^{\bullet} + OH^{-} \qquad [8.1]$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + OOH^{\bullet} + H^{+} \qquad [8.2]$$

The reagent is inhibited by various iron chelators such as phosphates, bis carboxylic acids such as oxalic and citric, EDTA and phosphates, and the possibility of inactivation in this way has to be taken into account in using the reagent on industrial wastewaters. Although the method is not new, research continues on its application to colour removal in textile dye wastewater.

In a study by Kuo,[51] five different types of simulated dye wastewater were treated with Fenton's reagent. He found that decolorization was greatly affected by pH, the type of dye treated, the auxiliaries present in the wastewater, the temperature and the specific structure of the dyes themselves. Kim *et al.*,[52] compared disperse and reactive dye removals by chemical coagulation and Fenton oxidation. Fenton oxidation gave 90% reduction in COD and 99% dye removal. The disperse dye solutions were better decolorized by chemical coagulation but the reactive dye solutions were more effectively treated by the Fenton's reagent. This was due to the reactive dyes' higher solubility, lower suspended solids and higher soluble COD (SCOD) to total COD (TOD) ratio.

Szpyrkowicz *et al.*[53] compared the oxidation of disperse dyes by ozone, hypochlorite, and Fenton's Reagent to that by electrochemical oxidation. The results by hypochlorite were not impressive, but ozone reduced colour by 90%, though the COD after ozone treatment was still quite high. This probably meant that the azo bond was broken (thus breaking up the chromophoric system) but with little further effect. Electrochemical oxidation with a Ti/Pt–Ir electrode gave 40% and 79% COD reduction. The best results were from the Fenton's Reagent, with complete colour destruction and very low residual COD. Dutta *et al.*[54] studied the oxidation of methylene blue using Fenton's Reagent and controlled conditions. More than 98% colour removal was achieved with an 81% reduction in COD.

Neyens and Baeyen's review paper on Fenton oxidation[55] covers the various Fenton reagent reactions with all the possible side reactions. Though the paper does not focus on degradation of dyes, it is useful in understanding the complexity of the reagent. Malik and Saha[56] studied the use of Fenton's reagent on decolorization of two direct dyes, Blue 2B and Red 12B. Their results showed that the dyes decomposed in a two-stage reaction. The degradation rate was strongly dependent on initial concentrations of the dye, Fe^{2+} and H_2O_2. At their optimal concentrations, 97% decolorization was obtained in 30 min, while 70% removal of initial COD was achieved after 60 min. Swaminathan *et al.*[57] investigated the Fenton reaction applied to two commercial dyes, Red M5 and Blue MR, as well as H-acid, an intermediate used for synthesis of direct, reactive and azo dyes. Release of chloride and sulfate from the red dye and sulfate from H-acid and the blue dye indicated that the dye degradation proceeded through cleavage of the substituent group.

Nam *et al.*[58] examined the effects of substituents on azo dye oxidation by a Fe^{+3}–EDTA–H_2O_2 system. The dyes examined were 4-(4′-sulfophenylazo) phenol and 2-(4′-sulfophenylazo)phenol with methyl, methoxy and halide substituents on the phenolic ring. Orange I and Orange II naphthol dyes were also examined. All of the dyes tested were decolorized, but the degree of colour removal varied by a factor of ten. Dyes with halogen substituents oxidized more thoroughly than those with methyl or methoxy substitution. It was postulated that the halogen substituents made the phenolate anion more acidic and thus more easily attacked by the OH radical. This is supported by the observed correlation between the charge density of the phenolate anion and the degree of decolorization.

Szpyrkowicz *et al.*[59] compared removal of disperse dyes from water by four oxidation methods – hypochlorite, ozone, electrochemical and Fenton's reagent. Since disperse dyes are highly insoluble, hypochlorite was the least effective of the methods. Ozone gave good colour removal (up to 90%) but low (10%) COD removal. Electrochemical oxidation was more efficient, particularly with the COD decrease (79%). Of the methods, the most satisfactory response was obtained with the Fenton process, where the effluent was turned colourless and the COD was decreased substantially.

The study by Neamtu *et al.*[60] compared the decolorization of Disperse Red 354 by ozonation, Fenton's dark, UV/H_2O_2 and 'photo-Fenton'. After 30 min, the results showed that photo-Fenton was more effective and cost effective than the other methods as a pre-treatment for decolorization and detoxification of the effluent.

8.7.5 Other processes

Ion exchange

A unique approach to catalysis was the work by Neamtu *et al.*[61] who prepared a catalyst by ion-exchange, starting with a commercially available ultrastable zeolite. This was used with hydrogen peroxide to catalyze the degradation of a reactive dye. After only ten minutes at 50 °C, the colour removal was as high as 97% at pH3 and 53% at pH5. There was about 76% removal of the initial COD and 37% removal of the initial TOC. Tests showed that there was very little activity caused by leaching out of iron ions. Their conclusions were that, with this catalyst, it was possible to extend the range of values for Fenton-type oxidation, without sludge formation. Another study by the same group used these iron-exchanged zeolites to degrade C.I. Reactive Yellow 84.[62] The results were again very effective in removing colour, as well as most of the COD and about one-third of the TOC. Again, there was no leaching of the iron ions into the solution, thereby showing that the ion-exchange catalysts could be used without creating iron hydroxide sludges.

In another approach using an inorganic base, Wang *et al.*[63] exchanged Ca montmorillonite with titanium cations. This ion-exchanged product was used to adsorb C.I. Basic Green 5 and C.I. Basic Violet 10 into the pore structure of the montmorillonite. The decrease in the BET surface area was measured and used to determine the surface screening effect, as well as changes in the pore sizes before and after the adsorption of the basic dyes. The base for ion-exchange used by Dhodapkar and Rao[64] was that of a biodegradable polymeric absorbent. They studied a series of basic dyes using a jalshakti, a starch-based complex carbohydrate derivative. Infrared spectroscopy and potassium ion release showed that the basic dyes were selectively removed through an adsorption and ion-exchange mechanism.

8.8 Conclusions

Although biological decolorization of wastewater is a very active area of investigation, chemical approaches are still being used widely, and research in these areas continues to be active and innovative. An on-line search of ‘decolorization of textile wastewater’ turned up 174 articles published since 2002. A combination of the terms ‘colour removal’ and dyes resulted in 100 research articles since 2004, and the term ‘dye removal’ gave 100 articles since 2003. For ‘chemical approaches’, the areas of electrochemical oxidation and catalytic enhanced oxidation have the most activity. It is probably not a coincidence that both of these approaches do not require large amounts of chemical to be added nor do they result in creation of solid waste.

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9

Biotechnological treatment of textile dye effluent

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9.1 Introduction

Pollution of communal water bodies by waste dyestuff released from textile plants and dyehouses represents a major environmental concern. Although presently a wide range of physical and chemical methods is available to decolorize dye-contaminated effluents (Hao *et al.*, 2000), alternative processes based on biotechnological principles are attracting increasing interest (Kandelbauer and Gübitz, 2005) since they often avoid consumption of high quantities of additional chemicals and energy. In this chapter, a short overview is given of such biotechnological approaches. Their advantages and disadvantages and hence their range of applicability are outlined.

In Section 9.2.1, there is a discussion of biological treatment processes based on living and proliferating cell populations. These may consist either of well-defined species of special micro-organisms or of various kinds of different micro-organisms that have established an ecosystem suitable for dye elimination. One major advantage of such systems is the complete mineralization often achieved due to synergistic action of different organisms (Stolz, 2001). However, the actual biodegradation is always a stepwise chemical transformation consecutively catalyzed by different enzymes. Therefore, enzymes may be used as such for the treatment process in some cases. Some key information on enzyme remediation is given in Section 9.2.2.

Finally, some conclusions are drawn about potential future applications of bioremediation techniques in the treatment of textile effluent and partial process streams contaminated with residual dyestuff.

9.2 Biotechnology and dye effluent treatment

9.2.1 Microbial processes

General aspects

Most biotreatment systems are based on living micro-organisms. The common method for the treatment of wastewater in the textile finishing industry is physicochemical flocculation in combination with subsequent biological treatment (Krull *et al.*, 1998). Like most organic materials of animal and vegetable origin, dyes can be degraded into simpler compounds and are finally mineralized to water and carbon dioxide by a wide variety of aerobic or anaerobic organisms (Binkley and Kandelbauer, 2003; McMullan *et al.*, 2001). Biodegradation can take place in the presence of oxygen (aerobic degradation) or in the absence of oxygen (anaerobic degradation).

Biological treatment can be carried out directly at the site of an industrial plant or in a communal sewage treatment plant. In both cases, living whole cell systems are typically used in mixed cultures of various types of micro-organisms. Mixed populations are much more commonly applied than isolated cultures of single organisms because of their relative robustness and versatility against xenobiotic compounds. They are more resistant towards unexpected or sudden changes in environmental conditions. They are self-establishing little ecosystems and adapt continuously via natural selection. In particular, industrial on-site effluent plants develop very specialized micro-organism populations that are very powerful in the degradation of the specific waste produced at the plant. Usually the plants simply benefits from their presence.

However, studies have been published where such naturally evolved strains have been isolated and optimized further under chemostat conditions in the laboratory in order to create even more powerful species (Zimmermann *et al.*, 1984, Nigam *et al.*, 1996). The complete mineralization of specific xenobiotic compounds upon action of single organisms has been reported (Blümel *et al.*, 1998) but this is, however, not a typical result and thus is of limited use. Furthermore, by conventional methods this is very time-consuming and may take up to a year or more. By applying genetic methods, however, such super strains may be developed much faster in future and may be returned to the mixed culture again as a boosting inoculum assisting the overall biotreatment system.

In order to yield successful biotreatment, some requirements must be met. The micro-organisms must be kept healthy and active. It is important to keep type and concentration of potentially toxic substances at a level that does not cause any serious damage to the micro-organism population. Since dye degradation is attributed to secondary metabolic pathways, appropriate growth conditions have to be accomplished by addition of a nutritional supply. Sufficient amounts of nitrogen- and phosphorus-containing nutrients must be present in the effluent. Typical conditions necessary to ensure reliable performance of a biological mixed culture system are pH between 6.5 and 9, temperature at around 35 °C (or higher in the case of anaerobic systems), ratio of the biological oxygen demand (BOD) to nitrogen and BOD to phosphorus of approximately 17:1 and 100:1, respectively (Binkley and

Kandelbauer, 2003). At sewage treatment plants where domestic effluent is mixed with industrial effluents, C, N and P sources typically appear in quantities high enough to maintain the micro-organism population. Industrial on-site treatment plants on the other hand are limited to effluents containing the rather small range of solutes corresponding to the product range. It may thus be necessary to add supplemental N and P sources to a dye house on-site facility. This leads to additional loads of the effluent with chemicals.

The effect of structural parameters of the dye on bioelimination is generally linked to the mechanism of the treatment process. For example, in adsorption processes, where biomass – dead or alive – is basically used as a filter material, a large molecular size is typically of advantage for satisfactory decolorization (Cooper, 1993). Since, in this case, poor solubility is of advantage, functional groups that confer high water solubility, such as, for example, sulfonic acid groups, are unfavourable. On the other hand, for biodegradation processes involving bacteria where intracellular digestion takes place, solubility and suitable polarity seem to be of advantage. Furthermore, it is important that the dye molecule is able to penetrate the cell wall and thus it should be of relatively smaller size. Large functional groups such as, for example, sulfonic acid groups may again prove unfavourable if too many are present. In general, sufficient bioavailability must be guaranteed in order to efficiently eliminate dye molecules.

Aerobic treatment

Activated sludge

Aerobic treatment is carried out in stabilization ponds, aerated lagoons, activated sludge or percolating filters. In aerobic treatment, micro-organisms in the activated sludge utilize dissolved oxygen to convert the wastes into more biomass and carbon dioxide. Organic matter is partially oxidized and some of the energy produced is used for generating new living cells under the formation of flocs. The flocs are allowed to settle and are then removed as sludge. A proportion of the sludge removed is recycled back to the aeration tank to maintain the micro-organism population. The remainder of the sludge can be fed back in a subsequent anaerobic treatment. Combinations of anaerobic/aerobic pilot plant for the treatment of coloured textile effluents are very powerful (for instance, Sarsour *et al.,* 2001), especially for the elimination of azo dyes (Stolz, 2001).

Aerobic bacteria have been described that oxidatively decolorize many dyes from several classes, among which azo dyes always turned out to be the most recalcitrant compounds (Kandelbauer and Gübitz, 2005). The ease of elimination of a dye is strongly related to its solubility. The more sulfonic acid groups are present in the dye structure, the more soluble and, therefore, the less responsive to treatment is the dye to the activated sludge process.

Insoluble vat and disperse dyes can be removed in quite high proportions by primary settlement. Basic and direct dyes respond well to treatment in the activated sludge process. However, reactive dyes and some acid dyes seem to cause more of a problem. It is generally considered that the activated sludge process removes only low levels of these dyes.

If only aerobic treatment is performed, the sludge can be disposed of in landfill or by drying and incineration. Disposal through agricultural use as a fertilizer is mostly prohibited by law in many countries because of the presence of heavy metals from dye residues.

Fungi

In nature, the class of white-rot fungi is able to degrade complex substrates like lignin via oxidative radical pathways. They can also degrade textile dyes due to the unspecific nature of their lignin degrading enzymatic system. The enzymes responsible for this action are peroxidases and laccases. The enzymes show broad substrate specificities (see Section 9.2.2) and are excreted by the fungi. Since extracellular digestion of dyestuff takes place, physical separation of living organism and toxic waste can be accomplished. This makes fungi especially interesting for bioremediation. One drawback with fungal cultures is that they require rather long growth phases before actually producing high amounts of active enzymes.

A huge number of scientific papers show the versatility of white-rot fungi for decolorization (Fu and Viraraghavan, 2001) and consequently, much is known about their potential in treating dye contaminated (model) waste water and their resistance towards dye toxicity under more or less native conditions. The list of white-rot fungi known to degrade the various types of dyes is long: amongst others, various *Trametes* sp. (Abadulla *et al.*, 2000, Campos *et al.*, 2001, Kandelbauer *et al.* 2004a, b, and 2006, Shin and Kim, 1998b), *Trametes versicolor* (Swamy and Ramsey, 1999a,b), *Irpex lacteus* (Novotny *et al.*, 2001), *Pleurotus ostreatus* (Shin and Kim, 1998a), *Pycnoporus sanguineus* (Pointing and Vrijmoed, 2000), *Pycnoporus cinnabarinus* (Schliephake *et al.*, 2000), *Phlebia tremellosa* (Kirby *et al.*, 2000), *Geotrichum candidum* (Kim *et al.*, 1995), or *Neurospora crassa* (Corso *et al.*, 1981), and *Phanerochaete chrysosporium* (Martins *et al.*, 2001; Tatarko and Bumpus, 1998) seem to be the most extensively investigated fungi for dye decolorization working on dyes of all classes. The genus of *Penicillium* has been shown to degrade various polymeric dyes (Zheng *et al.*, 1999). *Trametes versicolor, Pleurotus ostreatus, Phanerochaete chrysosporium, Piptoporus betulinus, Laetiporus sulphureus* and several *Cyathus* species) have been described in literature to degrade triphenylmethane dyes (Azmi *et al.*, 1998). For an informative compendium of recent literature describing fungi able to decolorize dyes, see Fu and Viraraghavan (2001).

Living fungi can decolorize dye solutions by means of real biodegradation (Chagas and Durrant, 2001; Swamy and Ramsay, 1999b). Typically, dyestuff is added to either a more or less purified enzyme solution, culture filtrate or fermentation broth, which may still contain the living organism. The cultivation can be optimized with respect to dye decolorization by stimulation with inducing substances, which induce increased formation of active enzymes (Robinson *et al.*, 2001; Tekere *et al.*, 2001; Bakshi *et al.*, 1999).

Various types of reactor systems based on fungi have been described (Fu and Viraraghavan, 2001; Nicolella *et al.*, 2000) such as static biofilms on rotating discs (Kapdan and Kargi, 2002) and drum reactors (Dominguez *et al.*, 2001), biological aerated filter cascades (Basibuyuk and Forster, 1997), packed-bed bioreactors (Schliephake *et al.*, 1996), or fed-batch and continuous fluidized bed reactors (Zhang *et al.*, 1999).

Many methods use the adsorption of dye contaminants on biomass which is commonly referred to as biosorption. Such processes take place, for example, in the course of activated sludge treatment (see Section 9.2.1 General aspects). Cells of white-rot fungi are preferably used for biosorption on both growing cells and on dead biomass (Fu and Viraraghavan, 2001). Decolorization without any transformation readily takes place only physically via adsorption onto their mycelia (Assadi and Jahangiri, 2001; Robinson *et al.*, 2001). With living fungi, adsorption may be accompanied by concomitant biodegradation (Aretxaga *et al.*, 2001, Sumathi and Manju, 2000). Pellets consisting of activated carbon and mycelium of *Trametes versicolor* were used for effective textile dye decolorization (Zhang and Yu, 2000). Azo dyes have been shown to quickly bind onto the mycelium of active *Aspergillus niger* resulting in extensive colour removal higher than 95% (Sumathi and Manju, 2000). Evidently, decolorization with active biomass is highly effective. High decolorization rates were also achieved with a combination of biodegradation by bacteria and adsorption using carbon black as a carrier material (Walker and Weatherly, 1999).

Coloured substances may be adsorbed onto many materials like sawdust (Khattri and Singh, 1999), charcoals, activated carbon, clays, soils, diatomaceous earth, activated sludge, compost, living plant communities, synthetic polymers, or inorganic salt coagulants (Slokar and Marechal, 1998). When biodegradable materials which provide good growth substrates for white rot fungi such as agricultural residues are used for biosorption, the physical adsorption can be used to rapidly decolorize the effluent and preconcentrate the dye stuff in a first step. Subsequently, for complete mineralization of dyes solid state fermentation can be performed on the dried adsorbent using white rot fungi. (Robinson *et al.*, 2001, Nigam *et al.*, 2000).

The removal of acid dyes by biosorption onto the biomass rather than biodegradation was found to be related not to the number of sulfonic groups (and thereby the solubility), but to the size of the molecule. It is thought that the greater the molecular size, the greater the degree of adsorption (Cooper, 1993).

Anaerobic treatment

Anaerobic treatment occurs in sealed tanks and converts the waste into methane and carbon dioxide. Where nitrogenous and sulfide-containing pollutants are present, ammoniacal substances and hydrogen sulfide are produced. At some municipal sewage treatment plants, the sludge formed by the aerobic treatment process passes into tanks for anaerobic treatment. Considerable heat is produced from anaerobic treatment. By using heat exchangers to extract the heat, the bioenergy can be utilized to heat buildings. The methane produced is collected, compressed and then used in generators to produce electricity. The electricity produced can power site processes and the surplus is sold to the national grid. The production of this power not only reduces the running costs of the treatment plant but also provides a welcome income, thus reducing the costs further.

Under anaerobic conditions, the decolorization of many azo dyes via reduction of the azo bond has long been shown for anaerobic (e.g. *Bacteroides* sp., *Eubacterium* sp., and *Clostridium* sp.) and facultative anaerobic (e.g. *Proteus vulgaris* and *Streptococcus faecalis*) bacteria (Bragger *et al.*, 1997; Rafii *et al.*, 1990; Wuhrmann *et al.*, 1980; Gingell *et al.*, 1971). The main interest in this field has been focused on bacteria from the human intestine that are involved in the metabolism of azo dyes ingested as food additives (Chung *et al.*, 1992). The fecal enzyme activity of azoreductase is commonly considered a marker for procarcinogenic activity (Haberer *et al.*, 2003). The nonspecificity of the azoreductase reaction is demonstrated by many reports on the decolorization of azo dyes by sewage sludge under anaerobic conditions (Carliell *et al.*, 1994; Pagga and Brown, 1986). It seems that almost all azo compounds tested are biologically reduced under anaerobic conditions, although there are some indications that metal-ion-containing dyes sometimes have reduced decolorization rates (Chung and Stevens, 1993).

The conventional treatment of coloured effluents produces a lot of sludge, but does not remove all dyes, thus preventing recycling of the treated wastewater. In activated sludge treatments, dyeing effluents, e.g. reactive azo dyes and naphthalene-sulfonic acids as well as aromatic amino derivatives, represent an extensive nonbiodegradable class of compounds (Krull *et al.*, 1998) and can even inhibit activated sludge organisms. Such dyes often will respond better to anaerobic conditions than aerobic conditions. Many dyes are not biodegraded but only adsorbed under aerobic conditions. Studies have found that many azo dyes can be degraded under anaerobic conditions by reductive cleavage of the N=N double bond yielding the corresponding aromatic amines. Some of these amines are carcinogenic and thus pose a considerable potential health risk when released into the environment. However, as shown already, aromatic amines are most likely to be further degraded under anaerobic conditions (Laing, 1991). Specialized strains of micro-organisms can be conditioned to fully degrade azo dyes (Razo-Flores *et al.*, 1997a, b).

9.2.2 Enzymic processes

General aspects

The concept of using isolated and partly purified enzyme preparations has several advantages over whole cell approaches. The expression of the enzymes involved in dye degradation is not constant with time but dependent on the growth phase of the population when living organisms are used. This can be circumvented by using isolated enzymes. Instead of maintaining living cultures of micro-organisms at the site of pollution, the production, downstreaming and preparation of stabilized biocatalysts or enzyme cocktails is provided off-site by specialized production technologies. Enzymes are easier to handle than living organisms and can be regarded more as speciality chemicals. Enzymes can be produced on a large scale and may already be applied in crude form (Moreira *et al.*, 1998; Linko, 1988; Fahreus and Reinhammar, 1967) in order to keep the costs considerably low. For industrial applications, immobilization of enzymes allows the reuse of the enzyme and thus further reduces the cost for such a process.

Tailor-made enzymes can be optimized independently by exploring induction reagents or using genetic engineering methods. This results in specialized biocatalysts, which may be superior to their naturally evolved counterparts. Efficiency may be increased upon combination with suitable additives and stabilizers and their application in much higher concentrations and in clearly defined quantities is possible unlike with naturally grown systems, which are much more susceptible towards variations. Thus, constant performance may be easier achieved.

Since isolated enzymes are protein molecules, they do not metabolize dyes like living whole cell organisms do. They only catalyze a specific type of transformation. Mineralization of dyes can therefore never be achieved by only using enzymes. However, enzymatic modification of dyes may often be sufficient at a certain stage in the process. Decolorization may be readily achieved by enzymatic destruction of the chromophoric centre of the dye. Detoxification may already be achieved after enzyme treatment by the transformation of the functional group conferring toxicity.

The major potential for enzyme reactors lies in special treatments of specific partial process streams of relatively constant and known composition.

In such cases, biological processes other than defined enzymatic systems may not be applicable at all. For example, the selective biological removal of hydrogen peroxide at high pHs and temperatures from partial process streams within the plant is only possible by using an immobilized catalase enzyme system specifically designed for this purpose. Such a reactor system has already been successfully tested in industry (Paar *et al.*, 2001).

Although the enzymes used for dye remediation display broad substrate specificities and practically all the different structural patterns such as the triphenylmethane, anthraquinonoid, indigoid, and azodyes can be degraded, the molecular structure of the waste dyestuff plays a considerable role on the rate and extent of transformation. Dyes are generally designed to exhibit high stability. They must resist irradiation with UV light, they must survive numerous washing processes and, of course, they have to resist microbial attack while in use on a textile fabric.

Various structural parameters of the dye molecule are to be taken into consideration when its potential degradation in bioremediation processes is discussed. No single model is currently available that would describe all the observations of structural effects on biodegradability since too many different aspects are to be taken into consideration. With redox active enzymes, the redox potential of the dye plays a central role (Xu, 1996; Xu and Salmon, 1999). While electron-withdrawing substituents enhance the reductive biodegradation of azo dyes (Maier *et al.*, 2004), the opposite trend was observed for the oxidative pathway (Kandelbauer *et al.*, 2004a, b and 2006). The redox potentials of textile dyes were successfully used for the quantitative prediction of the biodegradability of a wide structural variety of different textile dyes (Zille *et al.*, 2004). For a more detailed discussion of substrate specifities and various observations on structural effects with dyes of very different molecular structure, see, for instance, Kandelbauer *et al.* (2004a, b, and 2006) Knackmus (1996) and the references given therein.

Oxidative enzyme remediation

In general, there are two kinds of classes of oxido-reductases that are involved in dye degradation: electron transferring enzymes and hydroxy-group inserting enzymes. Peroxidases and laccases act via electron transfer and yield an oxidized dye species. They are the most important types of enzymes involved in enzymatic dye degradation. Both are secreted by lignolytic fungi (Mester and Tien, 2000; Duran and Esposito, 2000).

The second type of oxido-reductive enzymes is the oxygenases. They insert hydroxy-groups into a substrate. Depending on the number of hydroxy-groups transferred by the enzymes they are classified as mono- or dioxygenases. Oxygenases rely on complicated organic cofactors such FAD(H), NAD(P)(H) or cytochrome P450. For efficient regeneration of the catalytic system, living organisms are needed and, thus they are not used for enzyme reactors as such. Oxygenases are not only present in whole cell systems and mixed cultures used for dye degradation, but are ubiquitously found within the cell walls of every living organism. They play a vital role in the breakdown of aromatic ring systems. Upon hydroxylation, the subsequent cleavage of the aromatic ring yields carboxylic acids, which are further metabolized.

Laccases (benzenediol:oxygen oxidoreductase, EC 1.10.3.2) catalyze the removal of one hydrogen atom from the hydroxyl group of *ortho*- and *para*-substituted mono- and polyphenolic substances and from aromatic amines by one-electron abstraction. Thereby, free radicals are formed which are capable of undergoing further degradation or coupling reactions, demethylation or quinone formation (Thurston 1994, Yaropolov *et al.*, 1994). In contrast to other types of enzymes, such as hydrolytic enzymes like cellulases or lipases, laccases exhibit very broad substrate specificities. By using additional low molecular compounds such as ABTS, HBT and TEMPO which act as redox mediators (Fabbrini *et al.*, 2002; Almansa *et al.*, 2004), polyoxometalates (Tavares *et al.*, 2004) or osmium-based redox polymers, their substrate specificity can further be expanded. Redox mediating compounds are also secreted by lignolytic fungi in order to assist the extracellular digestion process (Eggert *et al.*, 1996; Johannes and Majcherczyk, 2000a, b). Laccases contain active copper centres. Hence, traces of copper may be introduced into the effluent upon excessive addition of laccase.

Peroxidases (e.g. EC 1.11.1.9) are enzymes that catalyze the transfer of two electrons from a donor molecule to hydogen peroxide or organic peroxides. The oxidized substrate may be a textile dye. Peroxidases are a much more diverse group of enzymes than laccases and the structure of the electron donor may limit the choice of peroxidases. Most commonly, manganese peroxidases and lignin peroxidases from ligninolytic fungi are employed in the degradation of textile dyes (Mester and Tien, 2000). The presence of low molecular substances may enhance the performance of peroxidases as well. Thus, the addition of veratryl alcohol was shown to positively influence decolorization of azo and anthraquinone dyes catalyzed by lignin peroxidase. However, this effect may either be attributed to the protection of the enzyme against being inactivated by hydrogen peroxide or to the completion of the oxidation-reduction cycle of the lignin peroxidase rather than to redox-mediation (Young and Yu, 1997).

Laccases and peroxidases may exhibit different substrate specificities. For example, the laccase treatment of the three different triphenylmethane dyes malachite green, crystal violet and bromophenol blue resulted in overall decolorizations of 100, 20, and 98%, respectively (Pointing and Vrijmoed, 2000). In contrast, an analogous experiment using the same dyes in a treatment with a peroxidase yielded a different ratio of reactivities of 46, 74, and 98%, respectively (Shin and Kim, 1998a).

The major advantage in using laccases lies in that they just require molecular oxygen as a co-substrate. Such treatment systems therefore only require sufficient aeration of the system and are therefore relatively simple. Peroxidases require hydrogen peroxide as a co-substrate in order to oxidize the dye molecules and catalyze degradation. Thus, here additional chemical load is required in order to gain catalytic transformation. Consequently, in the past decade, the focus on designing enzyme reactors for dye decolorization has been on laccase systems.

Laccases decolorize a wide range of industrial dyes (Rodriguez *et al.*, 1999; Reyes *et al.*, 1999; Campos *et al.*, 2001; Kandelbauer *et al.*, 2004 a, b). In the presence of redox mediators, this range was extended (Reyes *et al.*, 1999; Soares *et al.*, 2001a, b; Almansa *et al.*, 2004) or the extent of decolorization of degradable dyes was significantly enhanced (Abadulla *et al.*, 2000). The presence of low molecular weight compounds like 2,2′-azino-*bis*-(3-ethylbenzothiazoline-6-sulfonic acid) (ABTS) was in some cases necessary to initiate the actual electron transfer steps of laccases (Wong and Yu, 1999). Dye degradation intermediates may have an enhancing effect on decolorization due to redox mediation. Anthraquinonoid dyes act as redox mediators (Kandelbauer *et al.*, 2004) and they may assist in the laccase catalyzed remediation of dye mixtures.

For technical applications, enzymes are immobilized. Various applications of laccases immobilized on different types of supports have been reviewed recently (Duran *et al.*, 2002). Immobilization of fungal laccases on various carrier materials such as activated carbon (Davis and Burns, 1992), sepharose (Milstein *et al.*, 1993), or porosity glass (Rogalski *et al.*, 1995 and 1999) has been shown to increase stabilities of the enzyme at higher pH and tolerance to elevated temperatures and to make the enzyme less vulnerable to inhibitors such as Cu chelators. Membrane enzyme reactors containing laccases from *Neurospora crassa* (Luke and Burton, 2001) or *Pyricularia oryzae* (Lante *et al.*, 2000) have been employed for the bioremediation of phenols. Laccase bound to Eupergit (Hublik and Schinner, 2000; D'Annibale *et al.*, 2000) has also been used for this purpose. Reyes *et al.* (1999) reported the application of a bioreactor based on *Coriolopsis gallica* laccase immobilized on activated agarose. A laccase from *Lentinula edodes* was immobilized on a chitosan solid support (D'Annibale *et al.*, 1999).

An important issue for the industrial application is the long-term stability of biocatalytic systems. The application of *Trametes hirsuta* laccase upon covalent immobilisation to a γ-Al_2O_3-carrier was described for the efficient use in the detoxification and degradation of structurally diverse dyes. Reactors containing such laccase preparations were run in ten repeated batch decolorizations for about 15 h while still retaining 85% of their initial activity (Abadulla *et al.*, 2000). Model dye house effluents containing a wide variety of structurally different textile dyes such as triphenyl methane dyes, heterocyclic azo dyes, anthraquinonoid dyes and Indigo Carmine were successfully decolorized by using a similarly immobilized enzyme reactor based on a laccase from *Trametes modesta* (Kandelbauer *et al.,* 2003 and 2004b). Here, the simulated effluent was pumped continuously through a reaction cell and dye loads were added in regular intervals yielding dye concentrations of 50 mg l^{-1} and more. Mainly due to mechanical abrasion of the enzyme from the support, the reactor had lost 50% of its activity after 10 h and within five decolorization cycles. Other experiments with an authentic textile effluent caused a loss in laccase activity resulting in 14% retained activity (Reyes *et al.*, 1999). The authors investigated all known components of the effluent like salts, soap, and dispersant and their mixtures for laccase inactivation but none of them was identified as detrimental to the enzyme.

Thus, one major problem with enzyme reactors is currently their limited lifetime under harsh conditions. Especially when real-life effluent streams are approached, enzyme reactors seem currently no useful solution for end of pipe operations. Here, whole cell populations with mixed cultures will always perform much more reliably.

However, within partial process streams at more defined loads and reaction conditions, promising results have been presented with enzymes. After treatment with immobilized enzyme, decolorized dyeing water was recycled within the dyeing process (Abadulla *et al.*, 2000). This is not possible with effluents treated with micro-organisms since they require additional components to support growth, which cause substantial changes in the process water composition. Both nutrients added to the effluent and metabolites secreted by micro-organisms can cause problems in the recycling of effluents (Abadulla *et al.*, 2000).

The lifetime and resistance of enzyme reactors can possibly significantly be enhanced by applying enzymes from other sources. Currently, practically all laccases used for dye remediation are derived from white-rot fungi. Despite promising efficiency in dye decolorization in general, with these enzymes, one is typically restricted to reaction conditions which correspond to the natural environment of the fungi in which they are formed. Thus, no decolorization activities at all are observed at values higher than 7 and temperatures well above 45 °C (e.g. Kandelbauer *et al.*, 2004b and 2006).

A very potent candidate for future high-performance enzyme sources is therefore the class of extremophilic micro-organisms. Since they live under extreme heat and pH conditions such as on the sea bottom or in hot sulfate-containing springs, their enzymatic systems are more likely to withstand extreme environmental conditions. Consequently, screening for suitable enzymes expressed by thermo-alkalophilic organisms is of special interest with respect to their potential applicability at elevated temperatures and pHs. Organisms of this kind are impossible to cultivate using conventional fermentation protocols. However, this is not required. The enzymes of interest could be cloned, genetically transferred and expressed by organisms for which efficient standard production methods are already well established (Kruus *et al.*, 2001).

However, it might not even be necessary to go for extremophiles in the first place. The universally present class of bacteria might still hold unexplored potential that is more readily available. One example for the extension of the range of reaction conditions is the bacterial laccase from a *Bacillus* species (Held *et al.*, 2004 and 2005).

In contrast to fungal laccases, which have been known for many years, laccase activity in bacteria was only discovered in 1993 for *Azospirillum lipoferum* and was only recently characterized in more detail (Diamantidis *et al.*, 2000). Interestingly, the spore coat protein CotA of *Bacillus subtilis* was identified as a laccase (Hullo *et al.*, 2001). Bacterial laccases seem to be involved in pigment formation with some bacterial spores (Solano *et al.*, 2001) and, in this function, they are assumed to be widespread among that class of bacteria (Alexandre and Zhulin, 2000). Since spores serve micro-organisms to survive drastic conditions, spore coat enzymes are likely also to withstand high temperatures or extreme pH values, which would be advantageous for industrial applications.

When using preparations of bacterial laccase immobilized on spores for the treatment of 50 mg l^{-1} of Indigo Carmine, Diamond Black PV 200 or Diamond Fast Brown (Held *et al.*, 2005), complete decolorization was achieved at pH 9 within two hours. While with fungal laccases, the optimum temperature for dye decolorization was never above 40 °C, the best results with bacterial laccase were found at 60 °C. Within a pH range of 5.0–7.0 the half-life was more than 120 h, compared with a half-life of 13 h under similar conditions as previously measured for a laccase from *Trametes hirsuta* (Abadulla, 2000); this is a ten-fold increase in stability.

Most studies in the past decade have been focused on the laccase-catalysed degradation of dye molecules. However, since laccases are primarily involved in the initial formation of reactive radicals, the same enzymes could also advantageously be used to increase the molecular weight of waste dyestuff.

In a recent study, it was found that, upon laccase catalysis, the acid dye Indigo Carmine was either completely degraded or transformed to another product of higher molecular weight. Which pathway the reaction followed depended strongly on the reaction conditions, especially on the pH: at higher pHs (pH 5–6), the predominant product formed was that of higher molecular weight (Kandelbauer *et al.*, 2006).

In an earlier study using a peroxidase in the Indigo Carmine transformation, the observation of an unidentified by-product in small quantities was reported that might also have been formed by an polymerization pathway as well (Podgorny *et al.*, 2001). This might indicate that the strategy of increasing the molecular weight is not limited only to laccase reactors. And it is certainly not limited to indigoid dyes. By-products of higher molecular weight than the starting material were observed in the laccase-catalyzed transformation of the azo dye Diamond Black PV 200 and various structurally related azo dyes (Kandelbauer *et al.*, 2004a). *Trametes villosa* laccase in solution was used for the degradation of azodyes over a period of 72 h of oxidative conditions, demonstrating not only degradation of the dyes but also polymerization to some degree (Zille *et al.*, 2005).

The consequent application of this idea would lead to a strategy opposite to the one pursued so far. Instead of aiming at biodegradation, polymerized dye stuff of high enough molecular weight could be produced and subsequently readily removed from the effluent by filtration. Thereby, the chance of producing potentially toxic residual by products as in the degradation process would be minimized.

Laccases are already used industrially in hair dyeing formulations, as described in various patents for the dyeing of keratinous fibres (Lang and Cotteret, 2002; Onuki *et al.*, 2000; Aaslyng *et al.*, 1999) and a number of publications have been published on laccase-catalyzed coupling reactions meaning that much useful knowledge may be already available from other research fields.

Reductive enzymes

Unlike the oxidative enzymes laccase and peroxidase, the application of reductases or oxidases requires cofactors like NAD(H), NADP(H), or FAD(H), which are extremely expensive compounds. Enzyme remediation systems based upon such enzymes is therefore economically not feasible and industrially very difficult to implement. Most decolorizations in connection with reductive enzymes usually take place in whole cell applications. Bacterial degradation of azo dyes may be attributed to unspecific reduction of dyes (Yoo, 2002; Nam and Renganathan, 2000) or the action of azoreductase activity (Ramalho *et al.*, 2005; Maier *et al.*, 2004; Zimmermann *et al.*, 1984).

9.3 Future trends

Although enzyme remediation of dyestuff successfully removes its colour, a potentially harmful organic load may remain in the process waters. Thus, an interesting future perspective in the application of laccases for the treatment of process waters containing waste dyestuffs is the coupling of phenolic dye fragments rather than their oxidative breakdown. If such polymerized fragments were of sufficiently increased molecular weight, they could readily be removed by a subsequent filtration step (laccase-assisted dye precipitation). Consequently, future research activities should focus on optimization of the reaction conditions in order to achieve maximum oxidative coupling of primarily formed dye fragments.

Exploring the potential of different or newly discovered organisms such as various species of extremophiles or bacteria will lead to more powerful organismic and enzymatic treatment systems. Genetic methods will be of increasing interest in designing and tailoring new super-enzymes with expanded potential not only in effluent treatment but in all fields of industrial microbiology. They will also help to optimize fermentation technology in order to further reduce the costs and increase availability of enzymes.

Application of the present knowledge about the relationships between the chemical structure and its influence on biodegradability could possibly lead to the design of novel dyes that are perfectly stable while in use on the textile but that provide sufficient affinity towards bioremediation systems to be completely biodegradable.

Intelligent combination of different treatment techniques will provide more powerful integrated tools. For instance, the adsorption of dyestuff on living material paired with subsequent enzymatic degradation is not new, but is a very good illustration of the concept for using the advantages and avoiding the disadvantages of two different methods. Another example is the combination of laccase systems with ultrasound (Rehorek *et al.,* in press) in order to enhance the biodegradation process. The use of peroxidases depends on the availability of hydrogen peroxide as a second substrate. Here, a combination of enzyme remediation with conventional chemical regeneration processes relying on a combination of UV and hydrogen peroxide could prove beneficial in the future. In both cases, the enzymes have to be protected against too high an energy input since they easily may be destroyed. Therefore, sequential application of the different techniques may provide an industrially feasible solution. Physicochemical pretreatment of waste loads in order to facilitate subsequent biological treatments is presently well established.

9.4 References

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