

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.

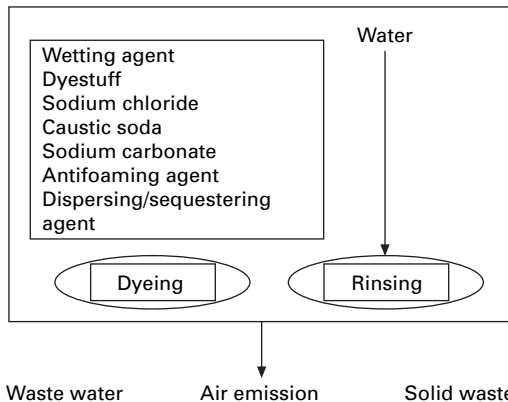
The components generally present in a textile dye bath are the dyestuff (colorant), solubilising chemicals, buffer system/pH controller, electrolyte (common salt or Glauber's salt), specialty dyeing assistants (such as retarder/accelerant, levelling agent, lubricant, defoamer, surfactant/dispersant, 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 cellulose, 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 Wimbush² 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.

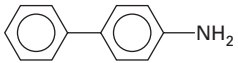
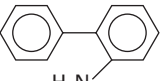
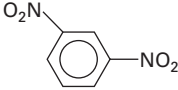
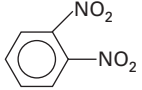
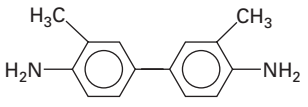
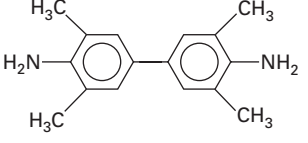
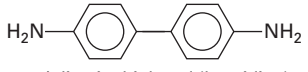
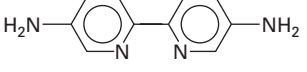
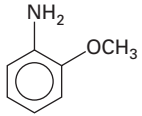
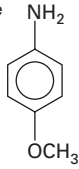
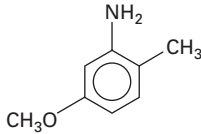
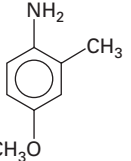
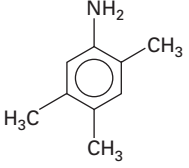
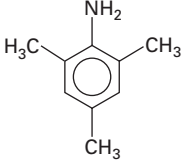
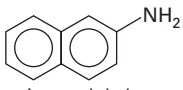
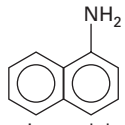

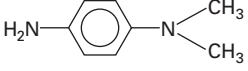
In recent decades, several environmental agencies¹⁵ and activist groups have advocated a ban on chlorine and chlorinated chemicals as essential to protect the environment. The dioxin reassessment began in 1991. Greenpeace activity demands that chlorine should be banned in incinerators, paper and plastic 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

Mutagenic	Non-mutagenic
 <p>4-aminobiphenyl</p>	 <p>2-aminobiphenyl</p>
 <p>1,3-dinitrobenzene</p>	 <p>1,2-dinitrobenzene</p>
 <p>3,3'-dimethylbenzidine (o-toluidine)</p>	 <p>3,3', 5,5'-tetramethylbenzidine (o-toluidine)</p>
 <p>4,4'-diaminobiphenyl (benzidine)</p>	 <p>2,2'-bipyridine-4,4'-diamine</p>
 <p>2-methoxyaniline (o-anisidine)</p>	 <p>4-methoxyaniline (p-anisidine)</p>
 <p>5-methoxy-2-methylaniline</p>	 <p>4-methoxy-2-methylaniline</p>
 <p>2,4,5-trimethylaniline</p>	 <p>2,4,6-trimethylaniline</p>
 <p>2-amino naphthalene</p>	 <p>1-amino naphthalene</p>
 <p>1,4-phenylenediamine</p>	 <p>N,N-dimethyl 1,4-phenylenediamine</p>

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 100000 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 Gupta²² have reported that the dried aqueous extract of banana flower petaloid can be used as a mordant for dyeing of wool. Shukla²³ 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 LC₅₀ 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.

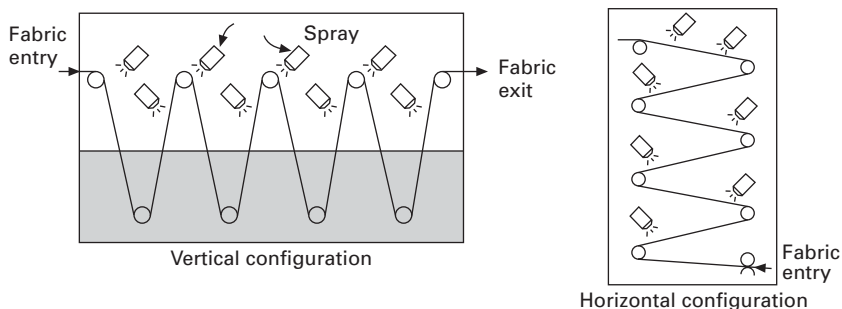
A report on water consumption for a typical continuous bleach range found that consumption at washing stages accounted for 90% of the total. The application of properly regulated counter current flows reduces the water use. A process modification such as a combined one-stage bleach and scour also would 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 exhausted 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

Wastewater characteristics	Effect of wastewater characteristic on			
	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 necessary 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 equipments⁴³

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 classes⁴⁵

Dye class	Typical <i>K</i>	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, insolubilisation 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 wherever 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: $(owf) \times (\text{bath ratio}) = (owm)$. For example, at a 5:1 liquor to fabric ratio, 50 g l⁻¹ of salt is 25% owm, but at 40:1 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 CO₂ 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} Polyester⁵³ 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 Liposomes⁶⁰ 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 0H3, 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 (P²AD) 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

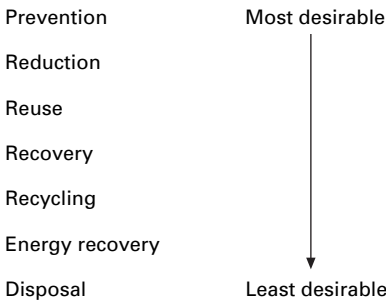
On a priority basis, pollution should be dealt with as depicted in Fig. 6.4. Pre-screening of chemicals can be done using the product's MSDS. Quality control and pre-screening before use of the incoming raw material, practices for pollution prevention, include a comprehensive programme to pre-screen

Table 6.10 Maximum levels for the indirect discharge of effluents⁷²

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-labelling⁷

	Criteria/norms stipulated (ppm)					
	MST*	OTN 100	Clean Fashion	Steilmann	COMITEXTIL **	Indian eco-levels
<i>Formaldehyde</i>						
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
<i>Toxic pesticides</i>	1	5	1	1	0.1 – 1	1
<i>Pentachloro-phenol</i>	0.5	–	0.5	Ban	0.05–0.5	0.5
<i>Heavy metals</i>						
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			
<i>Azo dyes containing carcinogenic amines</i>	Ban	Ban	Ban	Ban	Ban	50
<i>Halogen carrier</i>	Ban	–	–	Ban	Ban	200
<i>Chlorine bleaching</i>	–	–	–	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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