

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

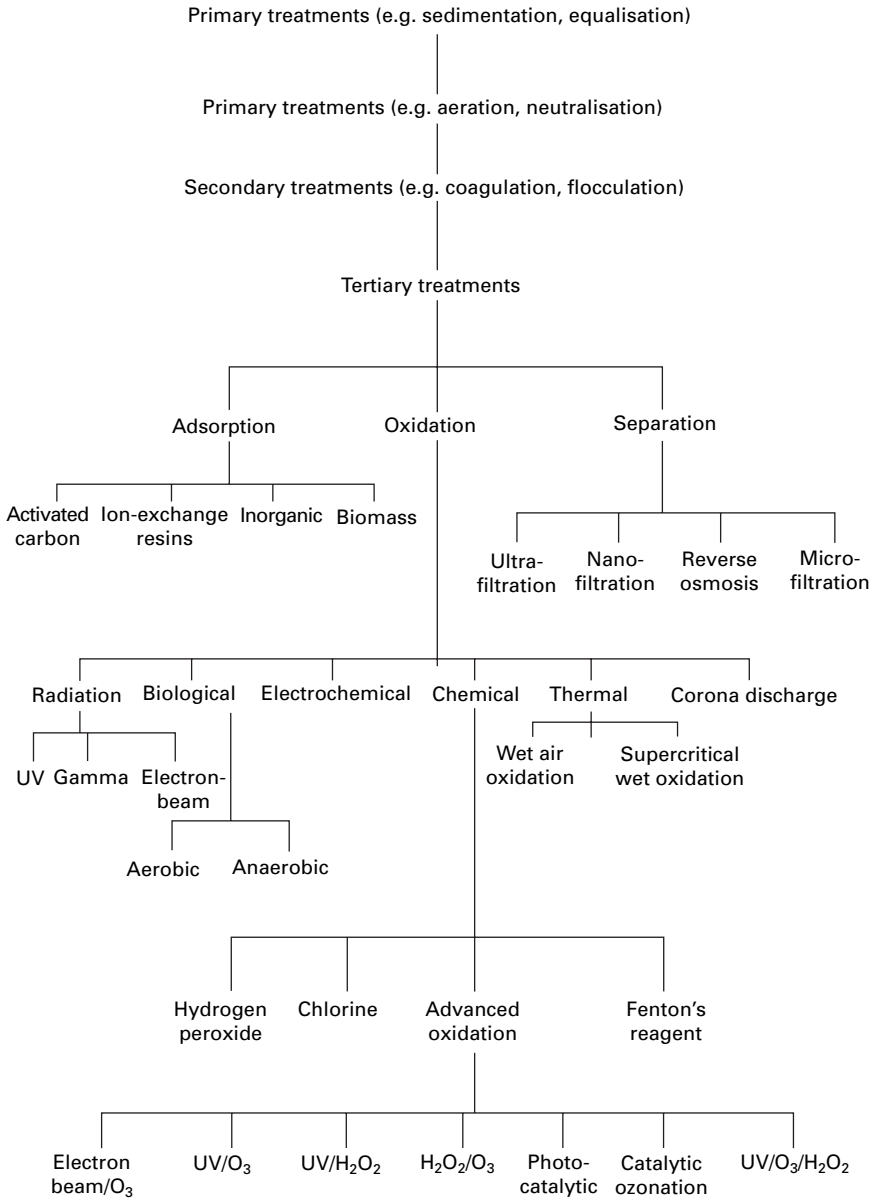
M. M. H A S S A N, AgResearch Ltd, New Zealand and
C. J. H A W K Y A R D, University of Manchester, UK

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, *Rhizopus 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-workers⁸ 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 Taeger⁹ 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} , $80 \text{ mg l}^{-1} \text{ Ca}^{2+}$ 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 adsorbents, 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 investigated¹⁴ and found to be effective for their removal. Malik and Taneja¹⁵ 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 ($\text{UV}/\text{H}_2\text{O}_2$ and $\text{H}_2\text{O}_2/\text{O}_3$) 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 $\text{H}_2\text{O}_2/\text{O}_3$ 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 Sivakumar¹⁷ 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 investigated¹⁹ 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.

McKay²⁶ carried out a detailed study on colour removal by chitin, which is a by-product of the shellfish industry. Chitin contains —OH and —NH₂ 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 Coste³⁹ 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

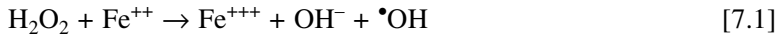
Chlorine in the form of sodium hypochlorite has long been used for bleaching of textile materials. Water-soluble dyes such as reactive, acid, direct and metal complex dyes are decolorised readily by hypochlorite, but water-insoluble disperse and vat dyes are resistant to decolorisation in this process.⁴⁰⁻⁴¹ 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 ($\bullet\text{OH}$) in the presence of ferrous ions in the following way.⁴⁴



In this scheme, RH is any organic compound.

The $\bullet\text{OH}$ 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's⁴⁷ 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 $\bullet\text{OH}$ 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/oxidase

Hydrogen peroxide can also be activated by peroxidase enzyme. Klibanov and co-workers⁵⁰ 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):



At the cathode (reduction):



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.



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 $\bullet\text{OH}$ chemistry, which is the major reactive intermediate responsible for organic substrate oxidation.

H₂O₂/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 $\bullet\text{OH}$ radicals.



The important factors that influence colour removal in the H₂O₂/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/H₂O₂ 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

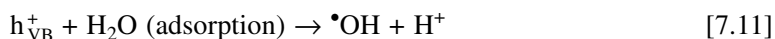
effective for chlorotriazine-based azo reactive dye decolorisation. Colonna *et al.*⁵⁹ studied decolorisation of five acid dyes and one reactive dye by ultraviolet radiation in the presence of hydrogen peroxide and all of them completely decolorised and mineralised in a relatively short time. TOC decreased 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 Fe³⁺-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 TiO₂, ZnO, CdS, WO₃ and SnO₂, can be used in the photocatalytic process. The basic mechanism of the process has been described by several researchers.⁶³⁻⁶⁵ When TiO₂ particles are irradiated by UV photons, photon energy exceeding the band gap energy excites an electron on the TiO₂ 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 H₂O molecules are available, then the photo-generated 'hole' extracts electrons from them, generating •OH radicals and superoxide ions according to the following equations:



The superoxide ions produce hydrogen peroxide through disproportionation as follows:



Then the $\bullet\text{OH}$ 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.

O₃-based AOPs

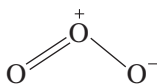
O_3 -based AOPs such as ozonation in combination with γ -radiation was found to be effective for decolorisation of wastewater.⁶⁹ It was reported that the use of hydrogen peroxide with ozone for the decolorisation of metal-complex dyes could not improve colour removal efficiency and added cost.⁷⁰ The 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 $\bullet\text{OH}$ 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 $\text{O}_3/\text{H}_2\text{O}_2/\text{UV}$ 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 $127^\circ \pm 3^\circ$, 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 $\bullet\text{OH}$ radicals, which have an even higher oxidation potential than ozone. Ozone is highly selective in its reaction with organic compounds, but $\bullet\text{OH}$ 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. Horning⁷⁶ 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 unchanged⁸⁰ 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. Cooper⁸² 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 exist 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

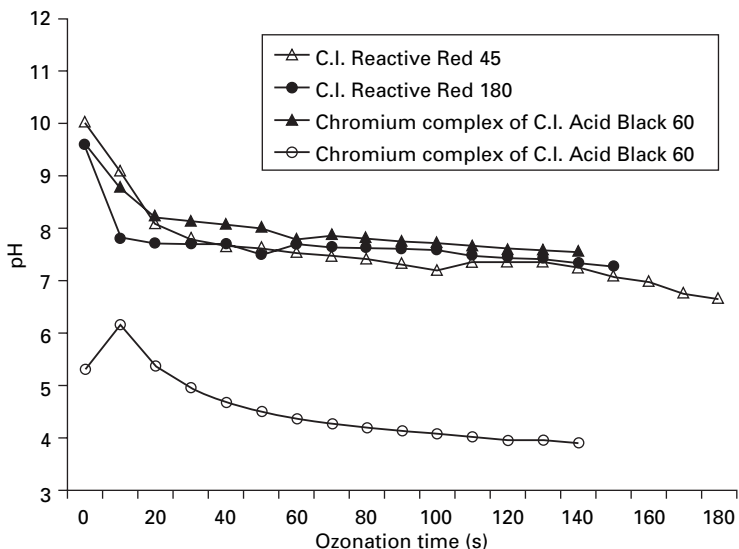
The study of the effect of pH on decolorisation by ozone is very important, as several researchers have found that the pH of water in single-phase ozonation affects O₃ decomposition; as the solution becomes more basic, the rate of ozone decomposition significantly increases.⁸⁵⁻⁸⁷ The decolorisation of dye should increase with increasing pH of the solution as higher fractions of ozone are decomposed to form •OH radicals at higher pH values⁸⁸ 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 H₂SO₄/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 l^{-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 $\cdot\text{OH}$ and $\cdot\text{O}_2^-$ 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 $\cdot\text{OH}$ 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

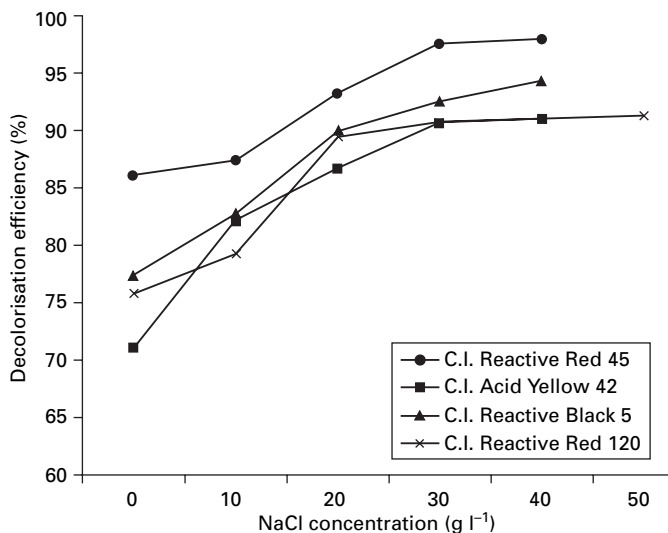
The admixtures present in dyehouse wastewater can greatly influence the efficiency of the decolorisation process, since they may also react with ozone, thereby increasing its consumption.

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.

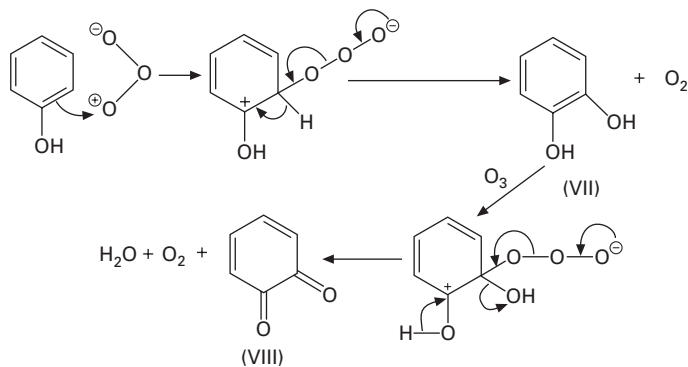


7.3 Effect of NaCl concentration on decolourisation of various reactive and acid dyes in the ozonation process.

7.2 Decolourisation 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 $\bullet\text{OH}$ 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 $\bullet\text{OH}$ 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



7.5 Ozone attack on phenol via electrophilic substitution.¹⁰⁹

Ozone can also attack molecular sites with an electron deficit (such as $-\text{COO}^-$) and, more frequently, at sites with carbon carrying electron-withdrawing groups (such as $-\text{NH}_3^+$, $-\text{NO}_2$, $-\text{CN}$, $-\text{SO}_3\text{H}$, etc).

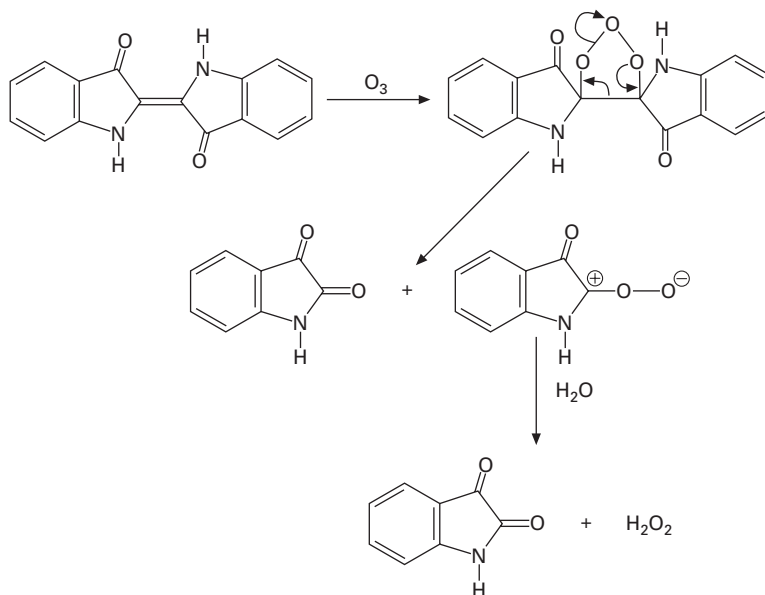
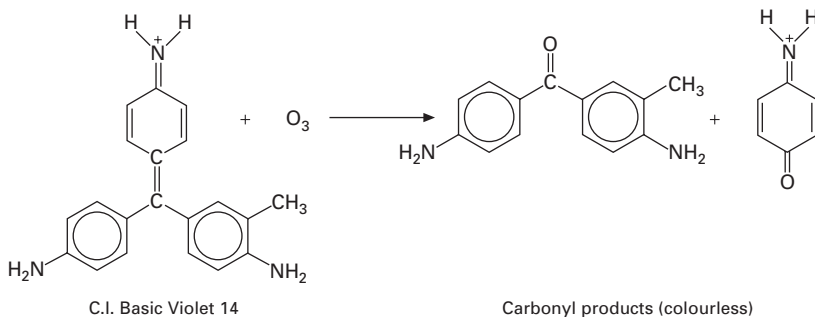
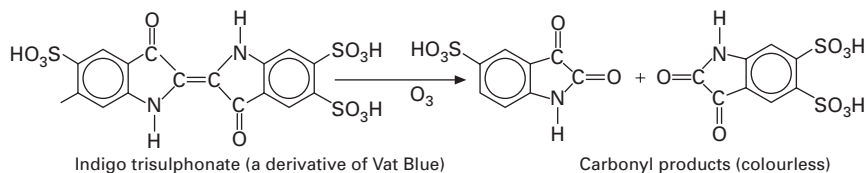
7.2.1 Reaction with dyestuffs

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 $>\text{C}=\text{C}<$ double bonds in dye molecules of C.I. Basic Violet 14 produces ($>\text{C}=\text{O}$) groups in the following way as shown in Fig. 7.7.¹¹⁴

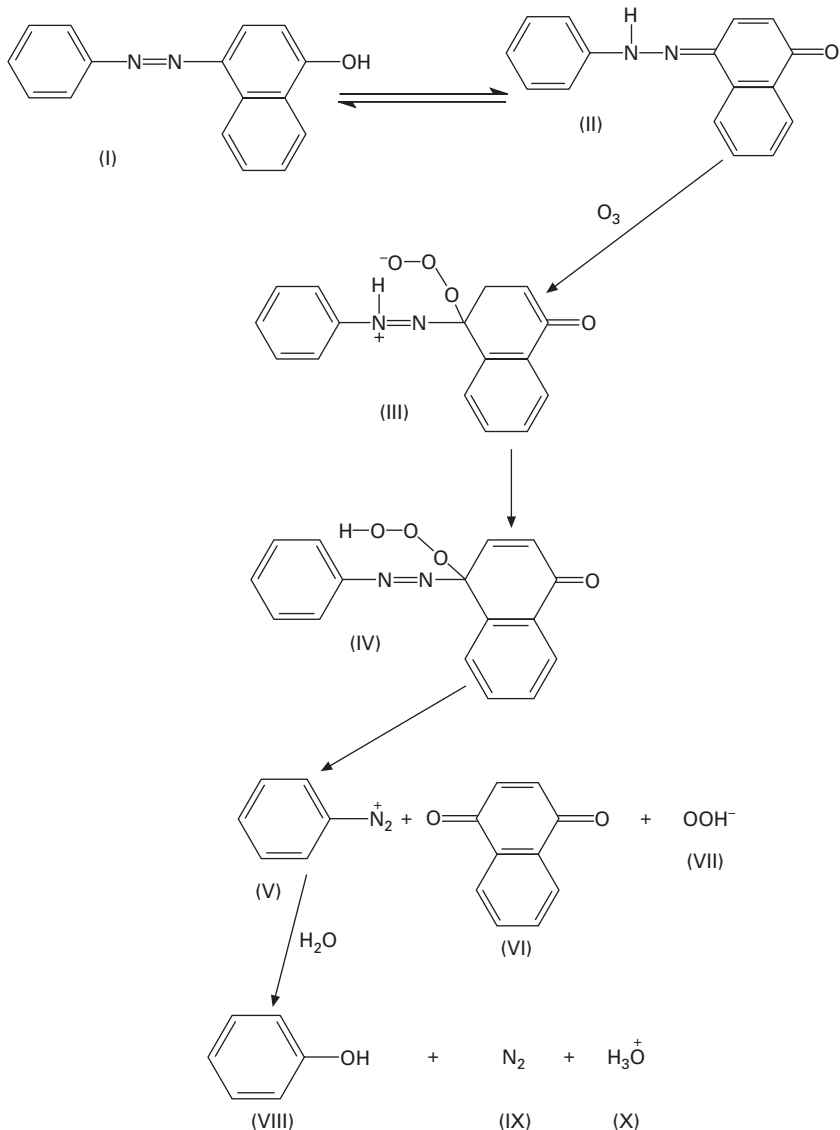
The mechanism of ozonation of 1-phenylazo-4-naphthol dye was described by Matsui^{112,115} as shown in Fig. 7.8. It is acknowledged that hydroxyazobenzene exists as azo-hydrazo tautomers in aqueous solutions and that equilibrium is established between them. Initially, the carbon atom in the 4 position 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.⁴¹7.7 Reaction of ozone with indigo trisulphonate and C.I. Basic Violet 14.¹¹⁴

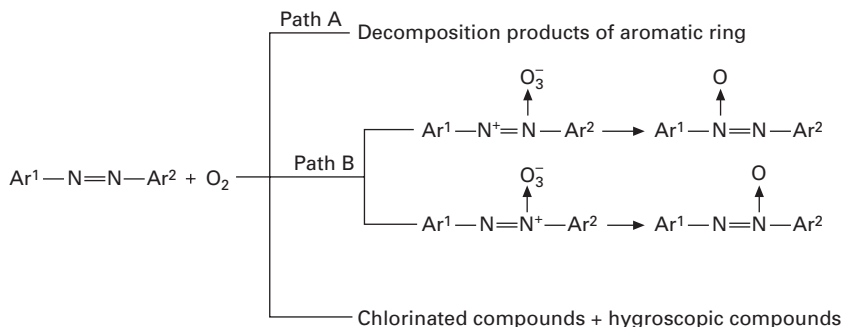
7.2.2 Hydroxyl radical generation in AOPs

To increase the concentration of hydroxyl radicals, ozone is activated with UV, H_2O_2 , and various catalysts such as activated carbon, alumina, Ferral, platinumised 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 $\bullet\text{OH}$ 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 $\bullet\text{OH}$ radicals.



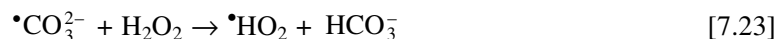
7.9 Reaction of ozone with aromatic azo compound.



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.



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



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

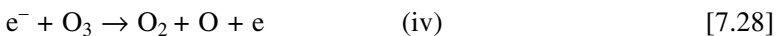
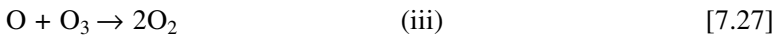
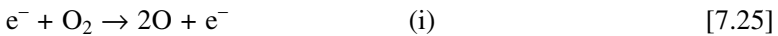
Increasingly, ozone is being used both for water purification and effluent decolorisation. This is partly due to environmental considerations but also to improvements in the design of ozone generators.

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.

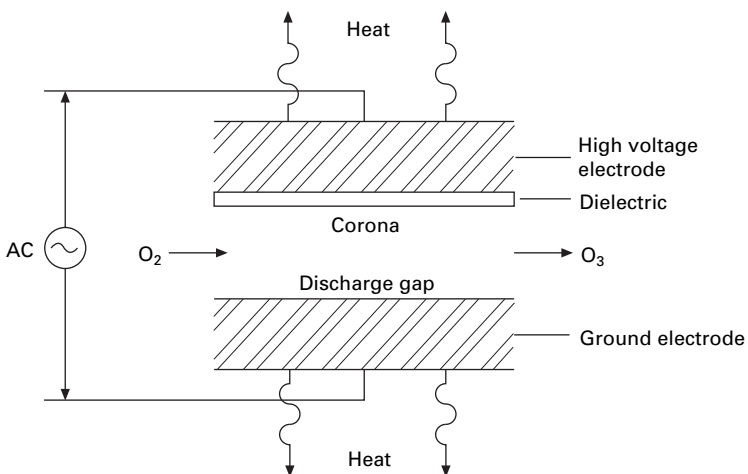
At very high voltages, the electrons in the discharge, having high kinetic energy, collide not only with each other, but also with oxygen molecules, and break the molecular bonds to generate free oxygen atoms. At the same time, ozone is formed from oxygen atoms formed by the dissociation of oxygen molecules 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.



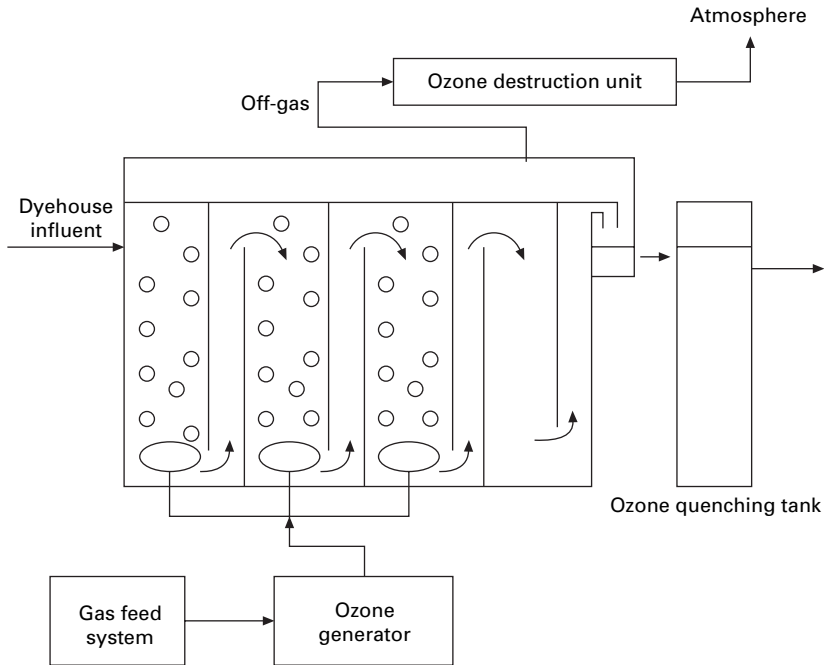
Since the half-life of O atoms is 10^5 times less than that of oxygen, the stationary conditions in the discharge according to the second equation above are quickly established even in the case of a relatively high flow velocity.

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 $-60\text{ }^{\circ}\text{C}$. 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

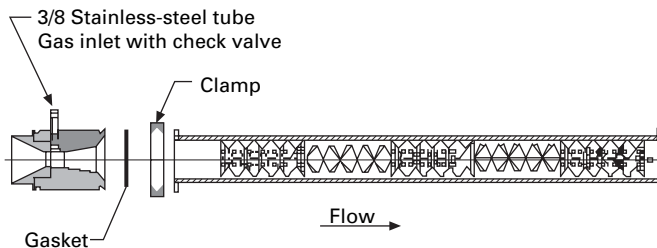
A typical industrial ozone generator uses oxygen as the feed gas rather than air, and converts it by means of corona discharge to ozone. Two different geometric configurations for the electrodes are used in commercial generators:

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 Pavlosthesis *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.

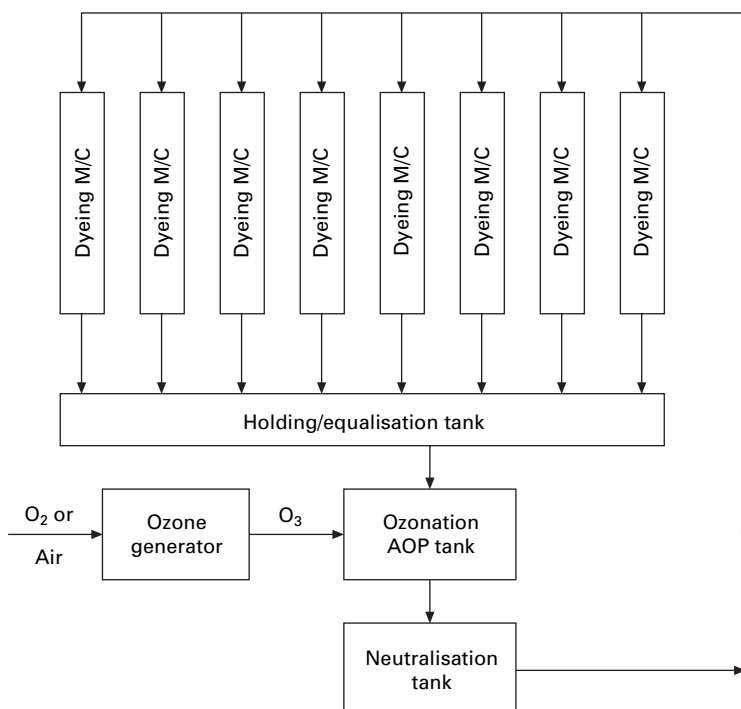
Two textile processing companies in the US have been reported to have reused and recycled spent dyebath.¹⁴⁷ One of them has realised savings of more than one million US\$ per year and has reduced salt discharge to a nearby river by more than four tons per day. The other company at their two mills in 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%) +	15.2	15.3	0
		Levafix Brilliant Red E-6B (2%)			
		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
Second reuse	Reactive	Procion Navy Blue HE4R (5.0%)	19.2	19.2	0.4 ^b
		Evercion Green H-4BD (2.0%)	9.9	10.1	0.3
Third reuse	Reactive	Evercion Green H-4BD (4.0%)	19.2	19.5	0.2
		Levafix Torquoise Blue E-BA (2.0%) +	15.2	15.3	0.1
Fourth reuse	Reactive	Levafix Brilliant Red E-6B (2.0%)			
		Levafix Turquoise Blue E-BA (1.0%) +	15.7	15.5	0.2
Fourth reuse	Reactive	Levafix Brilliant Red E-6B (3.0%)			
		Procion Crimson H-EXL (2.0%)	6.0	6.0	0
		Procion Crimson H-EXL (4.0%)	11.4	11.4	0

^aValues in parenthesis = depth of shade.

^b30% 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.

7.6 References

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