

8.1 Introduction

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

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

8.2 Colour

Colour is an intriguing part of our everyday lives. An intense red colour in the fabric of the garment that we wear may be highly satisfying, but that same red colour in the stream that flows through our grassy park is completely objectionable. It is not the colour *per se* that offends, but colour that is out of place, that does not belong. Dyes, the molecules that produce the colour on fabrics, have very high tinctorial power, absorbing intensely in the part of

the electromagnetic spectrum that our eyes use to translate into images. The wavelengths of the visible spectrum are only a small part of the entire electromagnetic spectrum¹ (see Fig. 8.1), and are roughly in the range of 400 to 700 nanometers (10^{-9} m), the deep violet to dull red of human perception.

8.3 Dyes

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

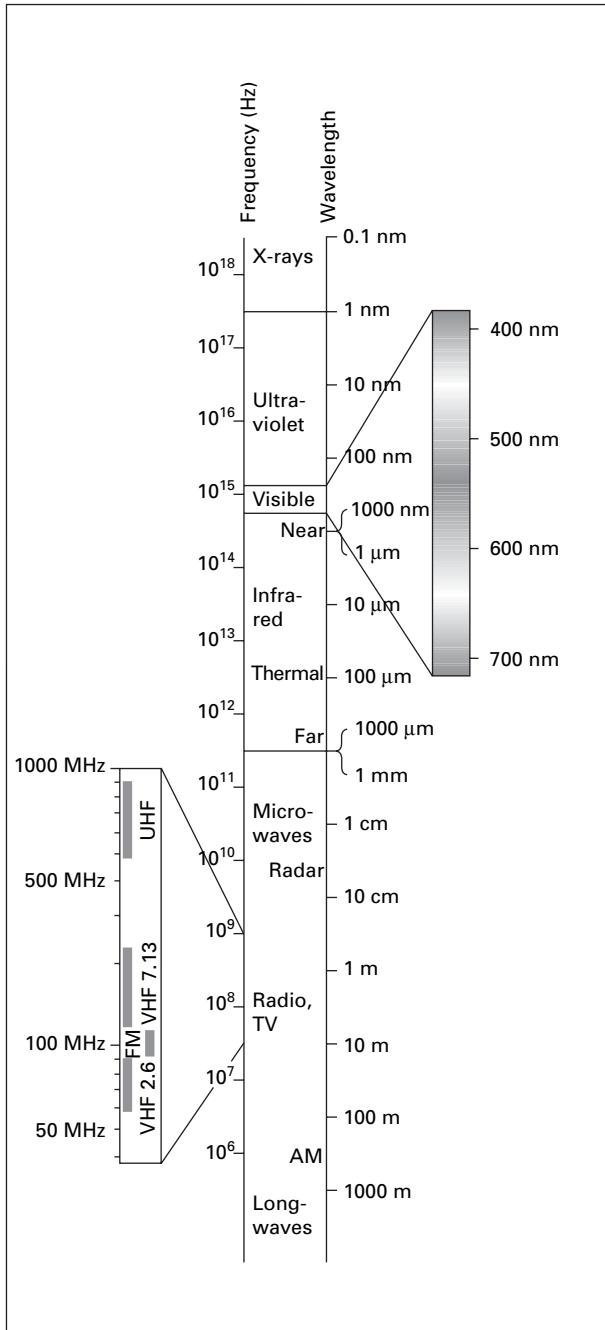
- absorb very strongly at wavelengths in the visible spectrum
- are composed of polyaromatic compounds
- are water soluble in their applied form, except for disperse dyes, vat dyes and pigments
- are substantive to certain fibres
- are resistant to biological degradation.

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

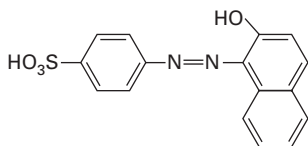
8.4 Classes of dye

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

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



8.1 Visible wavelengths within the electromagnetic spectrum.¹



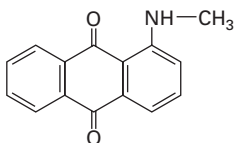
8.2 C.I. Orange II.

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

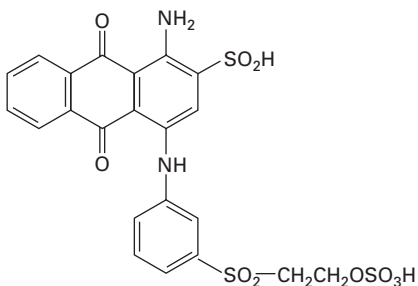
Reactive dyes are so-named because the groups that are attached to chromophores allow covalent bonds to be formed with cellulosic and protein fibres. Characteristic reactive groups attached to chromophores include vinyl sulfone (see Fig. 8.4) and triaziryl (see Fig. 8.5). Reactive dyes represent more difficult colour removal problems than most other dye classes. In the first place, their fixation rate is lower because of their propensity to react with water rather than the hydroxyl in the cellulose of the cotton fibre. This creates hydrolysed dye that has little affinity for the fibre. Secondly, reactive dyes are not absorbed onto biomass to any great degree. Pierce⁴ cites figures of 30% as a maximum and 10% as an average. The fixation rate of the reactive dyes on the fibre may range from 50–70%. This contrasts to other dye classes which have fixation rates of 80% as an average and some much higher.

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

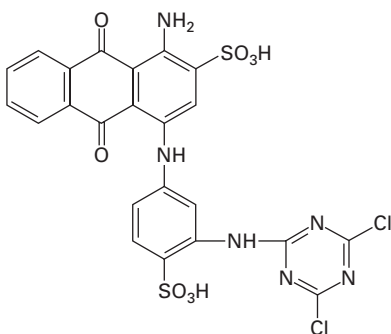
Vat dyes are so-named because of the historical method of application, in large vats that allowed the insoluble coloured form of the dye to be reduced to a soluble non-coloured form. It is the latter form, the 'leuco' form, that is applied to the cellulosic fibre, and then oxidized back to the coloured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



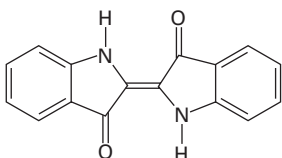
8.3 C.I. Disperse Red 1.



8.4 C.I. Reactive Blue 19.



8.5 C.I. Reactive Blue 4.



8.6 Indigo.

8.5 Measurement of colour removal

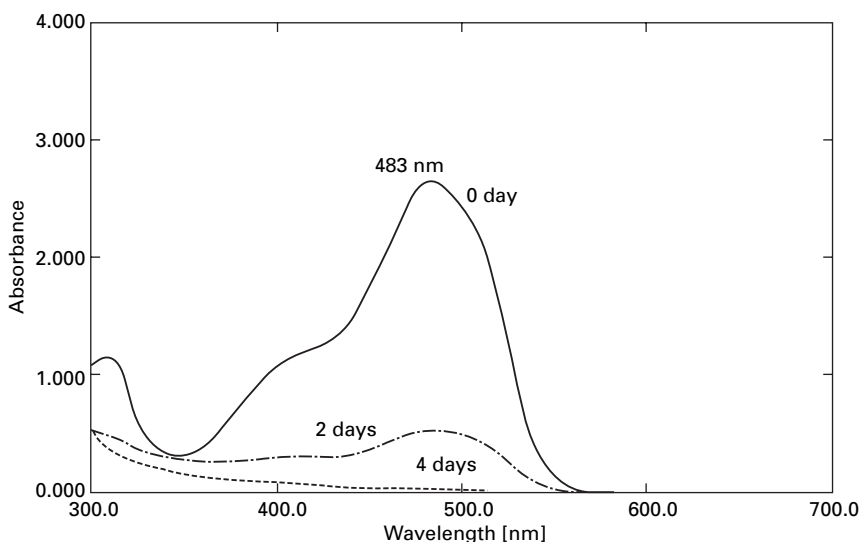
The removal of colour from textile effluent can be characterized as simply the disappearance of colour. This can be assessed visually, or monitored by visible spectrophotometry, using either the dominant wavelength if a single dye is involved, or by measuring the total area under the visible absorption

curve for either a single dye or a mixture. In Fig. 8.7 the colour is being removed (in this case by enzymatic decolorization). The decrease in the area under the curve between 400 and 700 nm is a measure of the decolorization of the dyebath.

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

8.6 Other measures of dye molecule fate

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



8.7 Decolorization of Orange II.

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

8.7 Chemical methods for colour removal

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

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

8.7.1 Physico-chemical coagulation processes

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

At least three major difficulties present themselves for coagulation. The first is that the process can be expensive. The user is paying for chemicals whose only purpose is to be thrown away. The solids created add to the solid

waste burden of the textile plant or to the municipal waste treatment facility. Secondly, dyes with high water solubility resist coagulation and larger additions of the coagulant may be required in order to achieve reasonable removal of colour from the effluent. Naturally, this increases the cost and solid waste load, as well as sometimes having a detrimental effect on oxidation of ammonia to nitrite and nitrates (nitrification) in the biological treatment plant.

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

Over the last decade, the research reported on coagulation for colour removal has continued unabated. Gao *et al.*⁶ evaluated an aluminum silicate polymer composite as a coagulant for water treatment. Depending on how the composite was produced, the results were better coagulation but less stability at longer storage times. Sanghi and Bhattacharya⁷ used a combination of powdered activated carbon and bentonite clay, along with polyaluminum chloride (PALC) as a coagulant to decolorize dye solutions of direct, mordant and basic dyes. The PALC not only increased dye removal, but formed a quick-settling sludge that could also be used for dye removal.

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

Papic *et al.*⁹ examined the removal of reactive dyes from synthetic wastewater by a combination of Al(III) coagulation combined with carbon adsorption. The dyes were C.I. Reactive Red 45 and C.I. Reactive Green 8. The combination of treatments gave almost total elimination of both dyes from the solutions. A secondary benefit was that minimal amounts of sludge were formed, cutting down on both the initial cost and the cost of solid waste removal. Gao and Yue¹⁰ evaluated the coagulation efficiency of a series of polyaluminum silicate chlorides (PACS) which had different OH/Al and

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

Lee and Choi¹³ evaluated a combination of adsorption and coagulation on removal of two reactive dyes, Orange 16 and Black 5. The adsorbent was coconut-based powdered activated carbon, and aluminium chloride was used as the coagulant. Coagulation followed by adsorption was found to be more efficient than the reverse. Their conclusion was that the combined process could reduce coagulation and adsorption amounts and thus produce less sludge. Joo, *et al.*¹⁴ decolorized a high concentration reactive dye wastewater using a combination of polymer flocculant and inorganic coagulant. The four model reactive dyes used were Black 5, Blue 2, Red 2 and Yellow 2. The polymer was synthesized from cyanoguanidine and formaldehyde and applied with alum or ferric salt. Inorganic salt alone was not effective but as polymer was added the combination treatments gave colour removal efficiencies as high as 60%.

Lee *et al.*¹⁵ evaluated a submerged hollow fibre microfiltration membrane coupled with combinations of coagulation and adsorption by activated carbon in removal of the reactive dyes, Orange 16 and Black 5. Under optimal conditions they were able to achieve removal of 99% for Black 5 and 80% for Orange 16. The hybrid process was judged to be far superior to the individual processes in removing both dyes. They concluded that this process would allow reduction in the use of coagulant and adsorbent. Petzold and Schwarz¹⁶ investigated the removal of dye by flocculation for two types of sludge and for pure dyes using polyelectrolytes and polyelectrolyte–surfactant complexes. The dyes examined included Acid Yellow 3 and Acid Blue 74.

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

In summary, the coagulation method by inorganic salts alone probably will continue to be used. However, given the constraints on sludge disposal and the amounts of these materials needed for removing highly soluble dyes, either unique polyelectrolytes or various combinations of coagulation with oxidation techniques would seem to be the inevitable physico-chemical

treatments to be employed, at least in those countries or US states with tight environmental standards to meet.

8.7.2 Electro-coagulation processes

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

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

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

McClung and Lemley²² used an iron electrode to treat three acid dyes, after which they identified the by products of the process by HPLC. They indicated that there was probably a combination of adsorption and dye degradation. Chen *et al.*²³ created a novel electrode system for electroflotation treatment of wastewater. An $\text{IrO}_x\text{-Sb}_2\text{O}_5\text{SnO}_2$ coating was applied to titanium. The service life of the electrode was predicted to be about 20 years. It was claimed that the small inter-electrode gap that is possible with the system results in a significant energy savings with easy maintenance.

Yang and McGarrah²⁴ examined the colour removal of three dyes, reactive, disperse and acid, with aluminium and ferric anodes as coagulant generators.

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

8.7.3 Electrochemical processes

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

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

One such study dealing with this²⁹ did show that with a carbon-fibre electrode a removal of 90% of the colour was accompanied by a much lesser extent of carbon oxygen demand (COD) removal. Just how far the process may then go ultimately to provide complete mineralization has seldom been investigated.

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

39% of the COD was removed after 40 min. At pH 4.5, 90% of the colour was removed.

Bechtold and Turcanu³¹ applied direct cathodic reduction to dyes with azo groups in the treatment of nanofiltrated textile effluents from printing. The addition of a redox mediator caused a measurable increase in the decolorization rate, but the chemical consumption per kilogram of waste was significantly increased. The decolorization of printing pastes containing reactive dyes was achieved on a laboratory scale to 60–80%. Carneiro *et al.*³² evaluated oxidation by a Ti/SnO₂/SbO_x/RuO₂ electrode. They achieved 100% decolorization and 60% total carbon removal in 0.2M Na₂SO₄ at pH 2.2

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

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

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

8.7.4 Oxidation processes

Oxidation processes can include oxidation through biological organisms, ozone, sodium hypochlorite, hydrogen peroxide, and even acids. The first two are discussed in other chapters of this book. The oxidative process will produce smaller molecules as the dyes are broken down. These will be colourless molecules. However, if the oxidation is only partial and does not go to mineralization, then questions may arise as to possible toxicity of the smaller molecules produced from the larger dye molecules, which are not by

themselves toxic. References to ‘advanced oxidation processes’, AOPs, can mean processes that involve the hydroxyl radical which may be produced by a variety of reactions. Such AOPs can be useful as pretreatments to textile wastewater to increase the subsequent biodegradation in conventional systems.³⁷ For the purposes of this review, AOPs are processes that utilize a catalyst of some kind to increase the speed of the reaction.

Chlorination

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

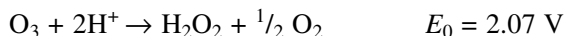
Hydrogen peroxide

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

Catalyzed or advanced oxidation methods

Catalyzed oxidation methods generate highly reactive radical species that then quickly react with dye molecules to break them up into smaller colourless fragments. The most common reactive species is the hydroxyl radical, which

has a higher oxidation potential than other common oxidizing agents. The oxidation potentials for common agents are:³⁹



Possible oxidizing agents include Fenton's reagent (discussed in the next section in this chapter), ultraviolet light, UV with added catalyst such as titanium dioxide, hydrogen peroxide and ozone.⁴⁰ Excluding Fenton's reagent utilization, the majority of research and development work reported in the literature recently on catalyzed oxidation treatment of dye waste used TiO₂ photoactivation. In general, the photodegradability of azo dyes relates to the complexity of the dye.⁴¹ For example, work by Reutergardh showed that monoazo dyes are easier to break down than triazo dyes.⁴²

The overall process is also very sensitive to the conditions in which the oxidation is done. For example, Arslan *et al.*⁴³ created two simulated dyehouse effluents and treated them with novel TiO₂ photocatalysts. The treatment efficiency was very sensitive to pH in the range of 4–9. The best overall TOC removal was about 30% for one simulated effluent at pH7, and 37% for the other at pH4. No correlation was observed between the adsorptive qualities of the TiO₂ and their corresponding reaction rates. Large amounts of organic halogens were created, probably as a consequence of the high chloride content of the synthetic wastewater.

Wang⁴⁴ investigated the photocatalytic degradation of eight commercial dyes in TiO₂ suspensions. He showed that the process was feasible and that all dyes were degraded to varying extents. The comparison of chloride and sulfate ions production rates indicated the dye molecules degradation patterns and pathways. The research on Orange II by Fernandez *et al.*⁴⁵ was a factorial design methodology on three critical variables affecting dye decolorization, the concentration of the dye, the pH and the concentration of TiO₂. The modeling of the reactions took into account the interactive nature of the system. The correlation between experimental and predicted values for decolorization was better than 95%.

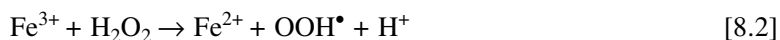
Titanium dioxide was immobilized on glass rings in the work by Fernandez *et al.* The catalysis of H₂O₂ provided decolorization and mineralization of Orange II, which was monitored by spectrophotometric analysis and total organic carbon measurement.⁴⁶ In the research by Mu *et al.*⁴⁷ Orange II was degraded in aqueous dispersions of TiO₂ using UV light irradiation. Manganese in the solution reduced the degradation efficiency, primarily because it absorbed onto the surface of the TiO₂. Two dye derivatives, chromotrope 2B and

amido black 10B were investigated by Qamar *et al.*⁴⁸ These dye derivatives were studied in aqueous suspensions of TiO₂ subjected to UV radiation. A number of by products were created and these were studied by varying different parameters such as TiO₂, pH, substrate concentration and various electron receptors. This same group investigated an azo dye derivative, chrysoidine Y in suspensions of titanium dioxide and zinc oxide.⁴⁹ The change in substrate concentration was monitored using UV spectroscopic analysis and decrease in total organic carbon content as a function of irradiation time under a variety of conditions.

Instead of TiO₂ particles, Kuo⁵⁰ used a titanium dioxide film with solar light rather than UV to catalyze decolorization of methylene blue and two reactive dyes. The film gave the advantage of not having to separate TiO₂ particles from the purified water after reaction with the dyes. They concluded that the films gave potential for using natural light rather than an artificial source for wastewater decolorization.

Fenton's reagent

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



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

In a study by Kuo,⁵¹ five different types of simulated dye wastewater were treated with Fenton's reagent. He found that decolorization was greatly affected by pH, the type of dye treated, the auxiliaries present in the wastewater, the temperature and the specific structure of the dyes themselves. Kim

et al.,⁵² compared disperse and reactive dye removals by chemical coagulation and Fenton oxidation. Fenton oxidation gave 90% reduction in COD and 99% dye removal. The disperse dye solutions were better decolorized by chemical coagulation but the reactive dye solutions were more effectively treated by the Fenton's reagent. This was due to the reactive dyes' higher solubility, lower suspended solids and higher soluble COD (SCOD) to total COD (TOD) ratio.

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

Neyens and Baeyen's review paper on Fenton oxidation⁵⁵ covers the various Fenton reagent reactions with all the possible side reactions. Though the paper does not focus on degradation of dyes, it is useful in understanding the complexity of the reagent. Malik and Saha⁵⁶ studied the use of Fenton's reagent on decolorization of two direct dyes, Blue 2B and Red 12B. Their results showed that the dyes decomposed in a two-stage reaction. The degradation rate was strongly dependent on initial concentrations of the dye, Fe^{2+} and H_2O_2 . At their optimal concentrations, 97% decolorization was obtained in 30 min, while 70% removal of initial COD was achieved after 60 min. Swaminathan *et al.*⁵⁷ investigated the Fenton reaction applied to two commercial dyes, Red M5 and Blue MR, as well as H-acid, an intermediate used for synthesis of direct, reactive and azo dyes. Release of chloride and sulfate from the red dye and sulfate from H-acid and the blue dye indicated that the dye degradation proceeded through cleavage of the substituent group.

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

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

The study by Neamtu *et al.*⁶⁰ compared the decolorization of Disperse Red 354 by ozonation, Fenton's dark, UV/H₂O₂ and 'photo-Fenton'. After 30 min, the results showed that photo-Fenton was more effective and cost effective than the other methods as a pre-treatment for decolorization and detoxification of the effluent.

8.7.5 Other processes

Ion exchange

A unique approach to catalysis was the work by Neamtu *et al.*⁶¹ who prepared a catalyst by ion-exchange, starting with a commercially available ultrastable zeolite. This was used with hydrogen peroxide to catalyze the degradation of a reactive dye. After only ten minutes at 50 °C, the colour removal was as high as 97% at pH3 and 53% at pH5. There was about 76% removal of the initial COD and 37% removal of the initial TOC. Tests showed that there was very little activity caused by leaching out of iron ions. Their conclusions were that, with this catalyst, it was possible to extend the range of values for Fenton-type oxidation, without sludge formation. Another study by the same group used these iron-exchanged zeolites to degrade C.I. Reactive Yellow 84.⁶² The results were again very effective in removing colour, as well as most of the COD and about one-third of the TOC. Again, there was no leaching of the iron ions into the solution, thereby showing that the ion-exchange catalysts could be used without creating iron hydroxide sludges.

In another approach using an inorganic base, Wang *et al.*⁶³ exchanged Ca montmorillonite with titanium cations. This ion-exchanged product was used to adsorb C.I. Basic Green 5 and C.I. Basic Violet 10 into the pore structure of the montmorillonite. The decrease in the BET surface area was measured and used to determine the surface screening effect, as well as changes in the pore sizes before and after the adsorption of the basic dyes. The base for ion-exchange used by Dhodapkar and Rao⁶⁴ was that of a biodegradable polymeric absorbent. They studied a series of basic dyes using a jalshakti, a starch-based complex carbohydrate derivative. Infrared spectroscopy and potassium ion release showed that the basic dyes were selectively removed through an adsorption and ion-exchange mechanism.

8.8 Conclusions

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

8.9 References

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