DYES, ENVIRONMENTAL CHEMISTRY

1. Introduction

The presence of residual color, high levels of electrolytes, toxic substances (eg metals and unreacted raw materials), and cancer-suspect agents in dye wastewater has led various regulatory agents to decide that certain dye manufacturing and dye application processes produce wastewaters that pose unacceptable environmental risks. In the case of textile dyeing operations, the concerns raised can arise from incomplete dyebath exhaustion and/or the presence of dyeing auxiliaries and metal ions that are toxic to aquatic life. With regard to dye manufacturing, unreacted raw materials used in the syntheses, worker exposures to genotoxic aromatic amines, and the use of toxic metals in the synthesis of certain dyes and their intermediates have raised concerns. As a consequence, companies involved in the manufacture and use of synthetic organic colorants have faced increasingly stringent domestic and international environmental regulations over the past decade. While these policies have led to the removal of certain products from commerce, they have also provided a stimulus for new research pertaining to the environmental chemistry of synthetic colorants. Whereas the initial studies involved the design and development of wastewater treatment methods, these methods provided time for both types of industries to pursue waste minimization source reduction approaches to their environmental “opportunities”.

With the abovementioned points in mind, this article provides an update to the one published in this Encyclopedia in 1993. In this regard, recent results from studies conducted in industrial, academic, and governmental research laboratories are presented. Specifically, this article covers five broad topics: (*1*) effluent treatment methods, (*2*) pollution prevention, (*3*) fate of dyes, (*4*) analytical methods, and (*5*) corporate programs, with emphasis placed on topics 1 and 2. With regard to effluent treatment methods, developments pertaining to the use of carbon adsorption, membrane filtration, and flotation-based separations to decolorize wastewater are summarized. Also covered in this section are reduction- and oxidation-based systems employing borohydride, zero-valent iron, and electrochemistry for the former type system, and ozone, Fenton’s reagent, and TiO_2 for the latter. A summary of biological methods for wastewater treatment concludes this section, which includes the PACT process because of its associated biodegradation pretreatment step. The pollution prevention section deals with studies aimed at reducing pollution through source reduction. Examples drawn from studies leading to potential alternatives to (a) dyes and pigments based on toxic metal ions, (b) genotoxic aromatic amines, (c) dyes requiring high electrolyte levels, and (d) the destruction of excess color following reactive dye application. Also presented are results from studies pertaining to process optimization, energy savings, and the recovery and reuse of water and salt. In the remaining three sections, brief summaries of commonly used analytical methods in this field, the fate of key dye types in aquatic environments, and industry initiatives aimed at establishing high standards for product stewardship are provided.

In an attempt to enhance the potential utility of this review to chemists, especially, but also engineers, a large number of specific dye–pigment structures germane to this field are given. It is anticipated that this will prove invaluable in the design of cost-effective new colorants and treatment methods that help insure the viability of the dye manufacturing and allied industries for many years.

2. Effluent Treatment Methods

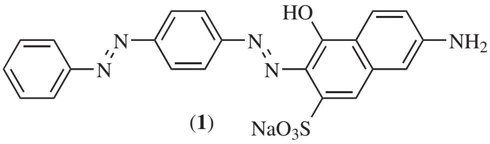
2.1. Physical Methods. *Adsorption.* Activated carbon adsorption has been widely studied as a waste treatment method for the removal of different classes of dyes from wastewater. Although this effluent treatment method is neither efficient nor economical when used alone, when used in tandem with polymer flocculation, chemical reduction, or biodegradation, it is a very useful polishing step for efficient dye removal.

Factors such as the choice of activated carbon, temperature, pH, contact time, and dosage must be taken into consideration for optimum removal of dyes from wastewater. Also, the molecular structure of a given dye has a significant effect on the extent to which the dye will be adsorbed, enhancing removal efficiency (1). Examples of dye removable by carbon adsorption are found among commercial disperse, basic, reactive, acid, and direct dyes.

Reverse Osmosis and Ultrafiltration. Specific industrial operations utilizing membrane filtration include the recovery of indigo following the dyeing of yarns for denim and the treatment of effluents from dyeing cotton with reactive dyes and dyestuff–chemical manufacturing (2).

Adsorptive Bubble Separation. Adsorptive bubble separation techniques such as ion flotation, solvent sublation, and adsorbing colloid flotation have been investigated as possible treatments for dye wastewater. The principles associated with separations using adsorptive bubble separation techniques are based on differences in surface activity. Surface-active material, which may be ionic, molecular, colloidal, or macroparticulate in nature, is selectively adsorbed at the surface of bubbles rising through the liquid. In this regard, 98–99.8% of Direct Blue 1 was removed from wastewater (3).

2.2. Chemical Methods. *Borohydride Reduction.* Sodium borohydride is one of the strongest water-soluble reducing agents commercially available, having an oxidation potential of 1.24 V. In this method, SO_2 is produced when borohydride is used in combination with bisulfite catalysis in the pH range of 5–8, which readily reduces azo dyes. In the overall process, bisulfite is regenerated rather than consumed. The utility of this method has been demonstrated in lab studies involving a variety of azo dyes (**1–6**), giving percent color reductions of 83–99% for acid, direct, and reactive dyes, and 74–99.9% for metallized direct and phthalocyanine dyes (**7–10**; Fig. 1). It has also been demonstrated that 93–99% color removal can be achieved by using bisulfite-catalyzed borohydride in the treatment of industrial dye manufacturing wastewater. This has led to the use of bisulfite-catalyzed borohydride reduction technology in tandem with polymer adsorption in dye manufacturing operations, to remove color and to stabilize the solids generated in wastewater and tank washes (4). In this



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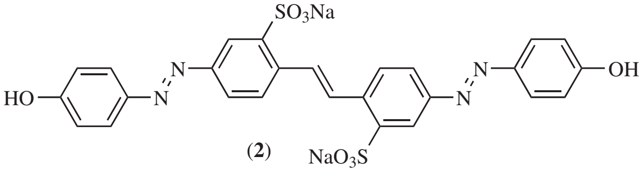

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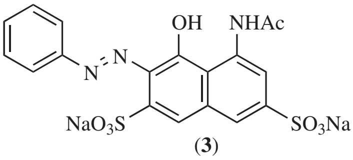

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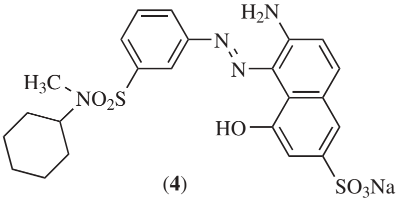

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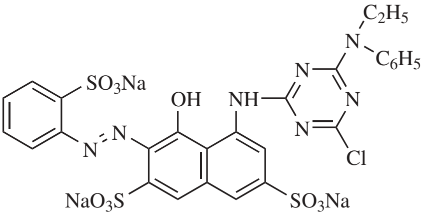

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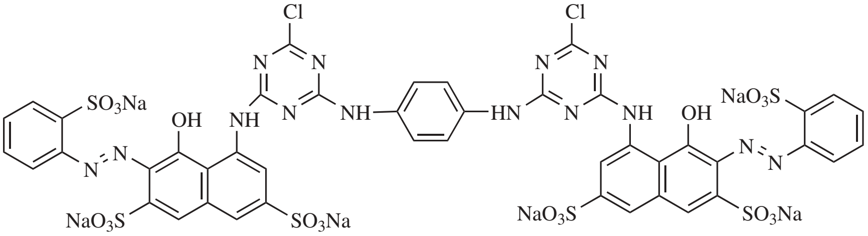
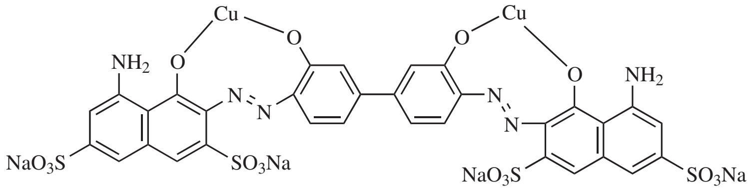


(**6**)

Fig. 1. Structures of dyes used in borohydride reduction studies: Direct Red 254 (**1**), Direct Yellow 4 (**2**), Acid Red 1 (**3**), Acid Red 361 (**4**), Reactive Red 24 (**5**), Reactive Red 120 (**6**), Direct Blue 218 (**7**), Direct Blue 189 (**8**), Direct Blue 86 (**9**), and Direct Blue 199 (**10**).



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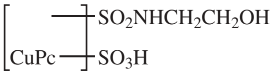
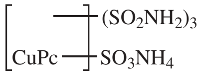


$$\left[\mathrm{CuPc}\right]\begin{matrix}-SO_2NHCH_2CH_2OH\\-SO_3H\end{matrix}$$

(**8**)

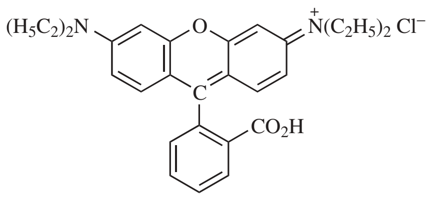
$[\mathrm{CuPc}]$—$(SO_3Na)_2$

(**9**)



$$\left[\mathrm{CuPc}\right]\begin{matrix}-(SO_2NH_2)_3\\-SO_3NH_4\end{matrix}$$

(**10**)



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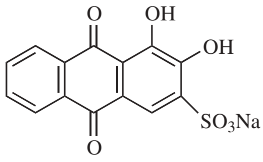


(**12**)

Fig. 1 (*Continued*)

regard, 0.01% aqueous solutions of each dye were treated with a mixture of 250–500 mg/L $Na_2S_2O_5$ and 17–50 mg/L $NaBH_4$, at room temperature and pH 5–6 for 15 min.

In the case of dyes **7–10**, 0.01–0.6% aqueous solutions were treated with a mixture of 250–800 mg/L $Na_2S_2O_5$ and 17–42 mg $NaBH_4$ at room temperature and pH 6 for 15 min. An anionic or cationic flocculant and a filtration step were employed in solutions containing the latter three dyes, reducing color by >99%. Subsequently, this method was extended to industrial wastewater containing either a mixture of azo disperse dyes or azo reactive black dyes. These solutions were treated with a mixture of 400–500 mg/L $Na_2S_2O_5$, 12–25 mg/L $NaBH_4$, and 0–200 mg cationic flocculant, reducing color by $93–99^{+}$%.

Zero-Valent Iron. An economical and innovative technology that has emerged in the last few years involves the use of zero-valent iron for contaminated groundwater remediation. Two types of treatment schemes are currently being pursued that utilize either *in situ* reactive barriers or above ground reactors. Results from a study by the (EPA) indicated that reductive transformation by zero-valent iron is a surface-mediated process. In laboratory experiments, 4-aminozobenzene and Disperse Blue 79 were reduced by zero-valent iron to the corresponding aromatic amines. It is believed that this technology can be used to decolorize industrial wastewater (5–7).

Electrochemical Oxidation. A 700-gal/min system has been developed for treating wastewater containing vat and direct dyes. After removing lint and other large particles, colored water was processed through an electrochemical cell to degrade dye. Subsequent pH adjustment, flocculation, and filtration produced treated water that was suitable for reuse. Although the initial system included a carbon adsorption effluent-polishing unit for the total flow, it was not needed for the recycled stream because of the high quality water produced by the electrochemical process. Operating costs were ~\$0.80/1000 gal, and solids were disposable as nonhazardous material (8).

Ozone-Based Oxidation (Ozonization). Although no practical commercial method for ozone treatment of dye wastewater has been reported so far, there have been interesting results from pilot plant studies. Examples include ozone treatment studies involving 120 dyehouses in Japan. In these studies, >95% of the wastewater generated consisted of dye effluent. Although the composition and amount of wastewater varied, its color was always blackish purple. The average volume of wastewater was about 100,000 tons/day and it was found that ozonization easily reduced the level of wastewater components absorbing at 580 nm. However, the 410 nm absorption was always observed, indicating that yellow organic components in the wastewater were not decomposed completely. Both TOC and COD levels were decreased from 30 to 20 ppm by ozone treatment, whereas BOD levels increased from 2 to 6 ppm. This suggested that the chemical substances in the wastewater had undergone biodegradation after ozone treatment, and it was concluded that ozone could be used for dye wastewater treatment if this process were cost effective. The cost of the ozone treatment process (calculated for 100,000 ton/day) accompanied by active sludge is ~\$1.57/ton, about twice that of the activated sludge process, which costs ~\$0.72/ton (9).

Recently, ozonization was successfully used to remove food dyes from wastewater generated at a pet food manufacturing facility before discharges into the city sewer, saving the manufacturer \$1000/day in effluent charges (10). Similarly, results from a study involving the use of ozonization to decolorize dyehouse wastewater immediately following the dyeing process indicated that the efficiency and economics of ozonization were increased. Though not effective for decolorizing vat dye solutions, ozonization did decolorize wastewater containing azoic, disperse, sulfur and reactive dyes (11).

Results from other studies suggested that the ozonization of spent dyebaths followed by conventional biological treatment decreased the toxicity of the resultant wastewater (12).

Fenton's Chemistry. Fenton's reagent (Fe^{2+}/H_2O_2) has been used commercially to oxidize and decolorize effluents containing a number of azo, anthraquinone, and reactive dyes (13–15). Dyes removed in these studies include reactive azo and anthraquinone dyes.

Titanium Dioxide (TiO_2). The cationic dye Rhodamine B, Basic Violet 10 (**11**; CI45170), and the anthraquinone mordant dye Alizarine Red (Mordant Red 3, **12**, CI58005) can be decomposed by TiO_2 in the presence of visible light. Degradation occurs via the interaction of dye with hydroxyl radicals (OH•). Two of the final degradation products are phthalic acid and carbon dioxide (16,17).

2.3. Biological Methods. *Powdered Activated Carbon Treatment (PACT).* This method employs a combined activated sludge–powdered activated sludge system. Consequently, it provides an improvement over the standard biological treatment system used for treating dilute solutions of dyes in municipal and industrial facilities. Two recent papers have provided extensive summaries pertaining to the history, technical process, comparisons with other physical, chemical, and biological environmental remediation methods, the removal of organics (including priority pollutants and volatile organic chemicals—VOCs) and metals, regeneration of carbon, ammonia removal, toxicity reduction, TOC and BOD removal using the PACT process. These reports include examples regarding the use of the PACT system for treating wastewater at several dye and textile plants (18,19). The PACT system is used to treat dye wastewater that is too dilute for oxidation methods and those that are too strong for treatment with granulated activated carbon alone (18).

Bioaugmentation and Bioremediation. These methods are currently used by the textile and dyestuff industries in Hong Kong to decolorize wastewater (20). In the present chapter, emphasis is placed on three more recent reports.

An emerging method in this area involves the decolorization of dye wastewater using enzymes (21). In this regard, enzymes such as laccases, lignin peroxidases, and manganese peroxidases have proved effective in cleaving aromatic rings, making these enzymes potential substrates for decoloring organic dyes. However, there are two downsides to using enzymes for wastewater decoloration. One involves the rate of reaction, which can be slow unless pH and temperature are optimal. The second and more significant downside is the difficulty associated with the commercial production of lignin peroxidase and manganese peroxidase enzymes, which are the types found most effective for dye degradation. While there are commercial products based on laccase, no lignin peroxidases or manganese peroxidases based products are commercially available.

A different approach, but one that takes advantage of the environmentally friendly action of enzymes, involves the use of whole microorganisms such as fungi to decolorize wastewater. In this regard, the decolorization of wastewater containing five dyes (**13–17**) was conducted using several species of white rot fungi (Fig. 2). The results of this study indicated that six strains of white rot fungi could be used to decolorize a variety of textile dyes (22).

After extensive studies involving a superfund site at a former dyestuff manufacturing plant, an on-site bioremediation system for approximately 145,000 yd^3 of contaminated soil was established (23). The types of colorants treated included anionic, cationic, and nonionic dyes.

Constructed Wetlands. It has been reported that constructed wetlands remove metal ions such as copper and zinc, organic substances, suspended solids, and color from textile wastewater, in addition to lowering chronic toxicity. Mechanisms by which wetlands remove pollutants from wastewater are believed to include adsorption on soil, precipitation, uptake by plants (phytoremediation), and aerobic and anaerobic degradation (24–28).

In a recent study, the use of a constructed wetland to treat wastewater from a textile plant engaged in mercerization, scouring, and dyeing of cotton with vat and reactive dyes led to little reduction of color and TOC. However,

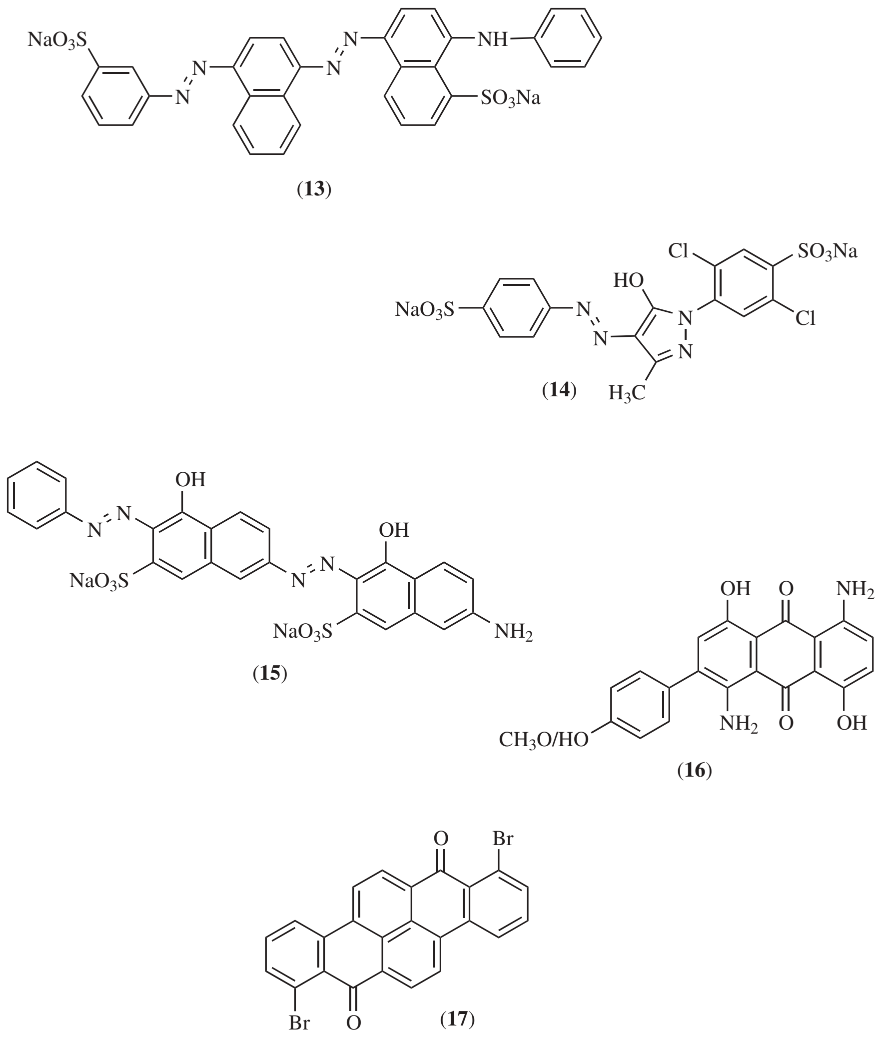
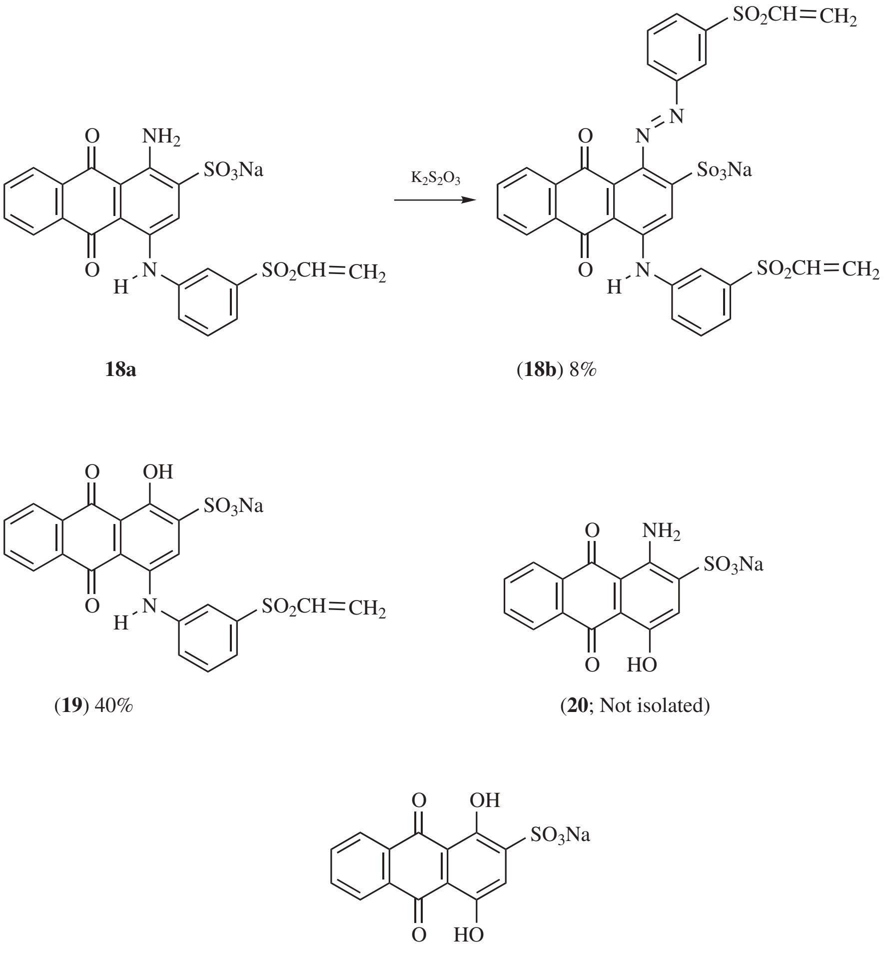


Fig. 2. Structures of dyes removed using biological treatments: Acid Blue 113 (**13**), Acid Yellow 17 (**14**), Direct Red 16 (**15**), Disperse Blue 73 (**16**), and Vat Golden Yellow RK (**17**).

total COD, copper content, and acute and chronic toxicity were appreciably lowered (29).

3. Fate of Dyes

It has been shown that the chemical reaction of Methyl Violet (CI 42535) and Indigo Sulfonate (CI 73015) with ozone leads to the formation of colorless carboxyl-containing products (11). In other studies, the interaction between the large volume reactive dye, Reactive Blue 19 (**18a**), and the strong oxidant



18a

(**18b**) 8%

(**19**) 40%

(**20**; Not isolated)

(**21**) 5%

Fig. 3. Major decomposition products from the degradation of Reactive Blue 19 (4mM) with peroxydisulfate ions (8 mM) at 65°C.

potassium peroxydisulfate via the process known as Direct Chemical Oxidation has been examined (30). This treatment process led to the formation of products arising from replacement of the amino ($-NH_2$) and anilino groups by $-OH$ groups (compounds **19–21**) and an unusual oxidative coupling, which is characterized by the introduction of an arylazo moiety in the 1-position (compound **18b**; Fig. 3). In this study, the structure of compound **20** was established by mass spectrometric analysis.

It has been reported that bioaugmentation and bioremediation treatments using white rot fungi can be used to degrade azo, anthraquinone and vat dyes (31). In the same study, the degradation of a sulfonated phthalocyanine dye (**22**) by white rot fungi and microbes was examined and is believed to follow the pathway outlined in Figure 4 (31). Studies such as this are of interest

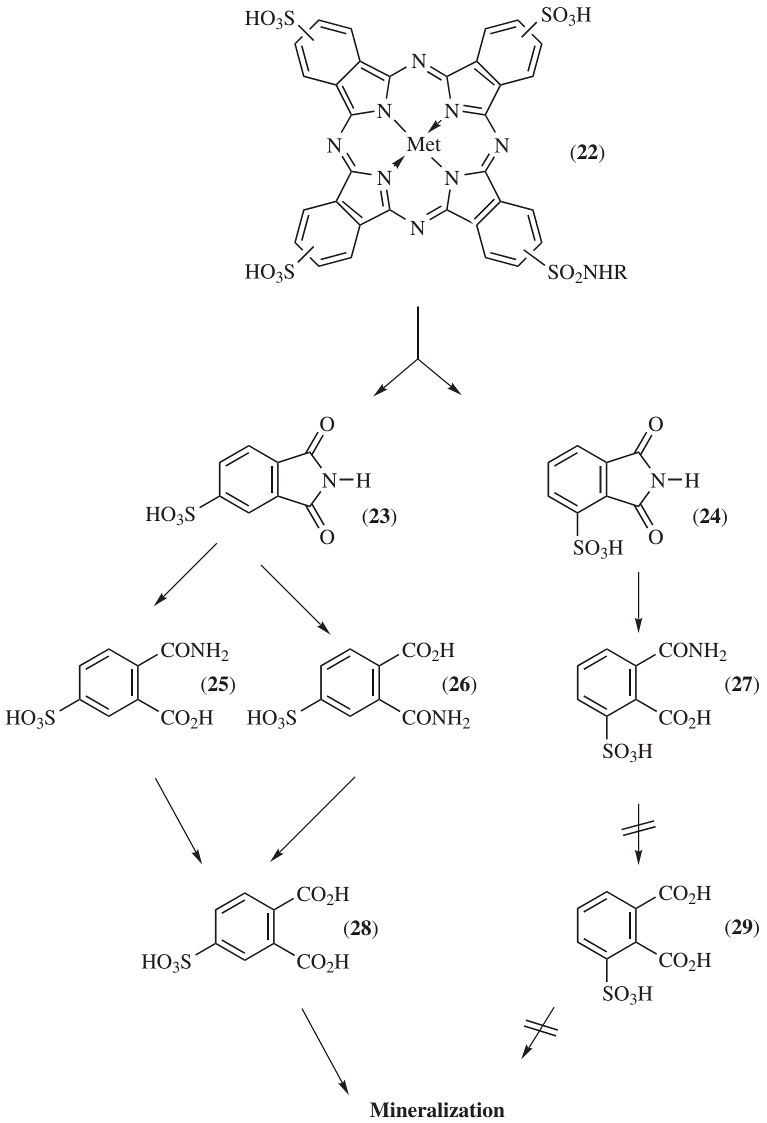


Fig. 4. Proposed degradation pathway for the decolorization of metal-phthalocyanine dyes with white rot fungi, where Met = metal (eg, Cu).

because of the potential for the release of toxic metal ions such as Cu^{2+} as a product of the biodegradation process. In this case, it seems that emphasis was placed on the organic compounds (**23–29**) produced.

A very detailed report on the fate of the high volume commercial dye Disperse Blue 79:1 (**30**) in anaerobic environments has been published, the results of which are summarized in Figures 5–7 (32). It can be seen in Figure 5, that the expected products arising from hydrosulfite-induced reductive-cleavage of the azo bond and nitro group reduction (**31–34**) were observed.

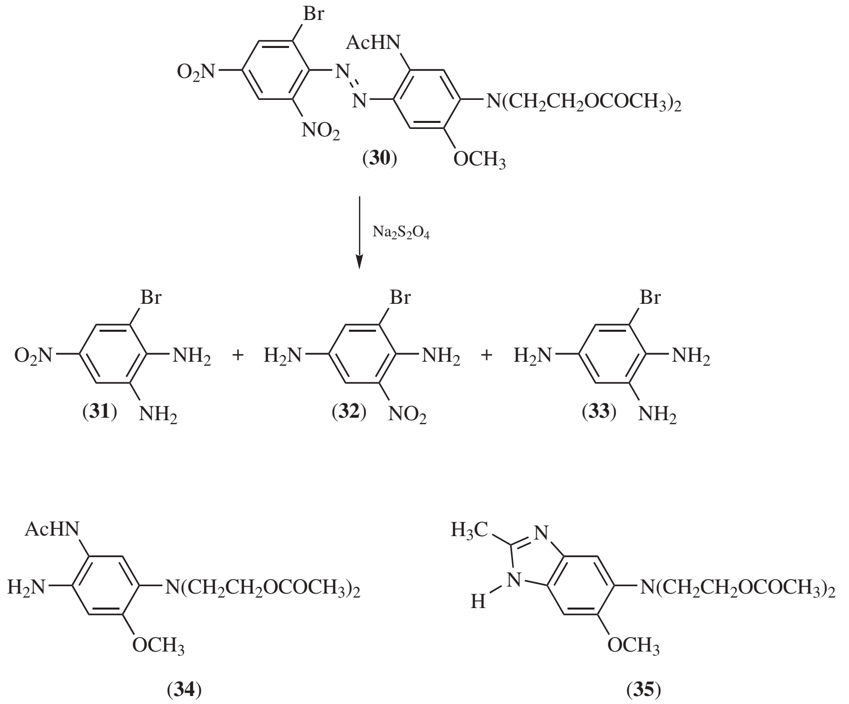


Fig. 5. Products identified following the hydrosulfite reduction of Disperse Blue 79:1.

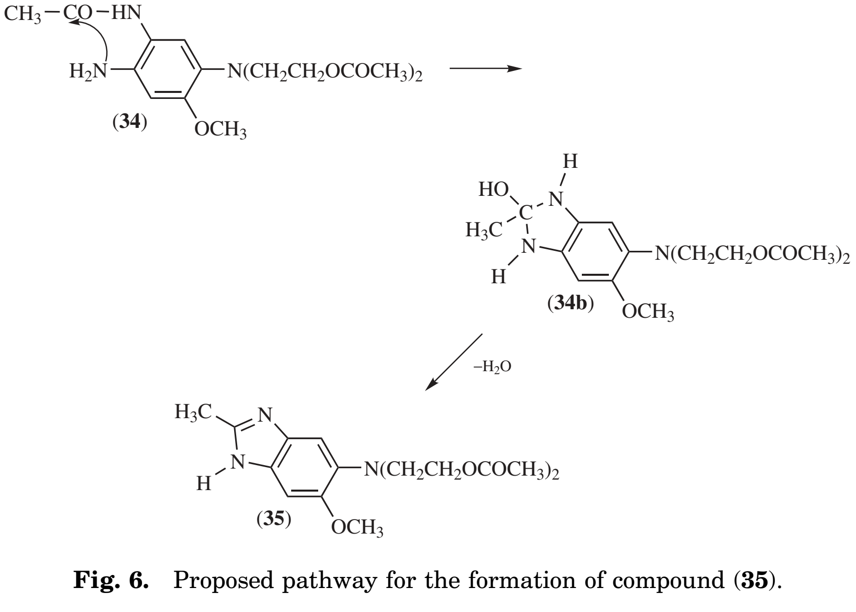


Fig. 6. Proposed pathway for the formation of compound (**35**).

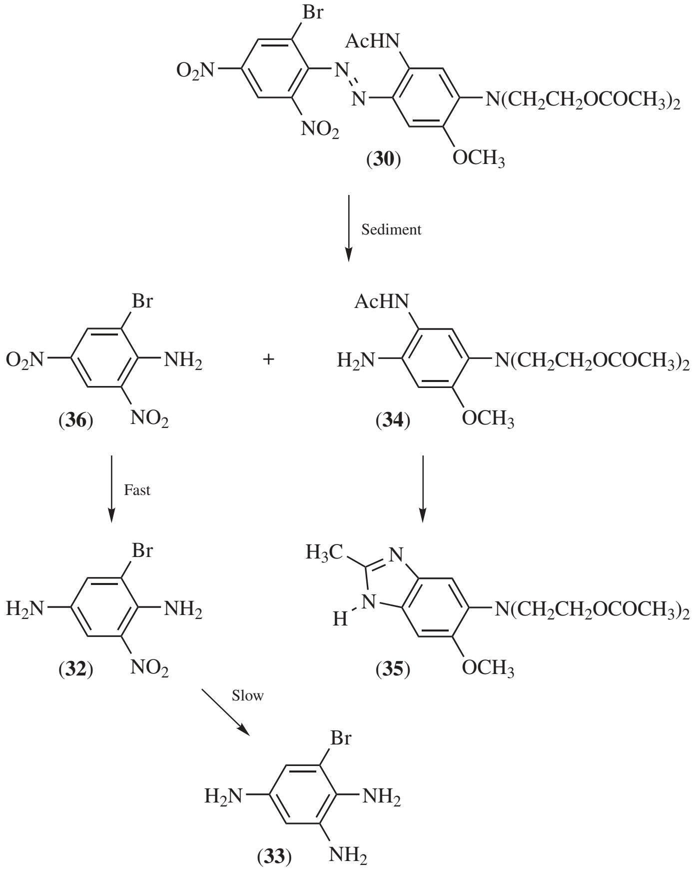


Fig. 7. Products identified following the sediment reduction of Disperse Blue 79:1.

While the formation of a substituted benzimidazole (**35**) was somewhat of a surprise, it could be accounted for by the pathway outlined in Figure 6. Step 1 involves an intramolecular cycloaddition reaction to give intermediate (**34b**), which undergoes dehydration to form compound (**35**).

Figure 7 depicts the fate of Disperse Blue 79:1 in the presence of a reducing sediment and it can seen that this milder agent led to the identification of 6-bromo-2,4-dinitroaniline (**36**), in addition to products isolated following hydrosulfite reduction. It was evident from these experiments that compound **36** quickly underwent reduction of the 2-nitro group, which accounts for its absence among the products from the more stringent conditions of the hydrosulfite reduction.

The fate of several anthraquinone disperse dyes in anoxic sediments has been studied and the reaction pathway shown in Figure 8 was proposed for the degradation of Disperse Red 11 [**37**; (33)]. The identified reaction products arise from *O*-dealkylation (cf. **38**) and an unusual and significantly slower deamination process (cf. **39–40**).

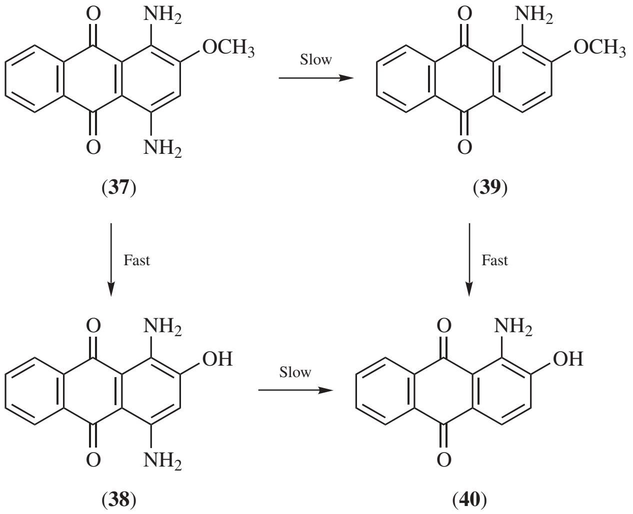


Fig. 8. Proposed reaction pathway for the sediment-induced degradation of Disperse Red 11.

4. Analytical Methods

The key to success in studies pertaining to the fate of dyes has been the development of suitable methods for characterizing products produced from the chemical and biological degradation methods. In this regard, the uniqueness of dyes, among the many classes of organic compounds, necessitated the development of specific analytical methods. This was especially important in the case of sulfonated structures, which are involatile and often insoluble in traditional nuclear magnetic resonance (nmr) solvents.

To facilitate studies in this area, an excellent paper has been published that pertains to the analysis of environmental samples of organic colorants by using various extraction, spectrophotometric, and chromatographic methods (34). The chromatographic methods include paper, thin-layer, gas and high performance liquid chromatography (HPLC). In addition, capillary electrophoresis and mass spectrometry (direct probe, fast-atom bombardment, electrospray, particle beam, field desorption, and laser desorption) were employed. Dye classes used in this comprehensive study included acid, basic, disperse, and vat dyes.

The analysis of basic, disperse and solvent dyes in wastewater using mass spectrometry has also been undertaken. In this regard, suitable methods for determining the structures of dyes present in textile effluents have been reported (35,36).

5. Pollution Prevention

In view of the tough regulations facing companies that manufacture and use inorganic and organic colorants, it was evident that the best way to address these safeguards responsibly would involve adopting pollution prevention through waste minimization and/or source reduction measures (37–39). This approach is the most effective mechanism because it provides a reduction in waste management and treatment costs, a lowering of raw material costs, enhanced public standing in the community, added protection for the health and safety of workers and consumers, and substantial reductions in the environmental management needs connected with manufacturing operations.

5.1. Process Optimization. In some cases, especially in dye manufacturing, components that must be removed from wastewater arise from reactions that do not go to completion. In the case of azo dyes, this leaves residual couplers, diazo components, or by-products in the liquors produced in the filtration step. When disperse dyes based on heteroaromatic amines are used, the presence of excess coupler provides a solvent for the dye produced, enhancing the amount of un-precipitated dye in the filtrates and giving deeply colored wastewater.

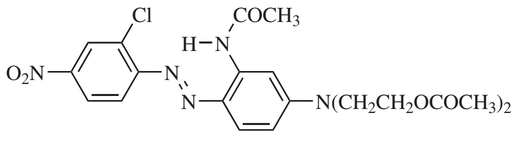
Effective measures in this area have involved developing ways to push reaction yields as close to the theoretical level (100%) as possible. In this regard, it has been possible to synthesize azo dyes and pigments such as Disperse Red 167:1 (**41**), Disperse Red 177 (**42**), Pigment Red 3 (**43**), Pigment Red 48 (**44**), Pigment Red 21 (**45**), Pigment Yellow 14 (**46**), and Pigment Yellow 1 (**47**) in yields of 97–100% (40–44). To achieve these yields, efficient diazotization and azo coupling steps were combined with a neutralization/heat stabilization step (38).

Process optimization in the textile industry has included the use of initiatives such as product substitution, process analysis, effluent reduction, chemical use reduction, and process modification, to reduce costs associated with effluent wastewater treatment and disposal. This in turn has improved profitability through savings on raw materials and energy, and increased productivity (45). In closely related work, the combined efforts of the POTW of Dalton, Georgia, the carpet capital of the world, the Pollution Prevention Assistance Division of the Georgia Department of Natural Resources, and the carpet manufacturers led to a reduction in COD loadings. This was achieved through the use of lower COD substitutes for many of the commonly used chemicals and through a reduction in the amounts of chemicals employed in wet processing.

Similarly, a reduction in water usage was achieved by implementing a closed-loop system that involved the reuse of vacuum pump cooling water rather than discharging it as wastewater after a single use. This change resulted in substantial production cost savings (46,47) (see Fig. 9).

The effectiveness and environmental impact of rinsing in reactive dye application have been studied. The results showed that a high temperature rinse without soap with limited neutralization did not adversely affect colorfastness but did lower the COD arising from organic pollutants in effluent wastewater (48).

5.2. Heavy Metals. Metals such as copper, chromium, mercury, nickel, and zinc have been designated as priority pollutants (56). This is an important point because a number of compounds containing these metals have long been used as catalysts and complexing agents in the synthesis of dyes and key intermediates. For instance, Acid Blue 25 (**48**) is synthesized using copper catalysis.



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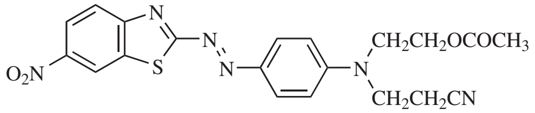

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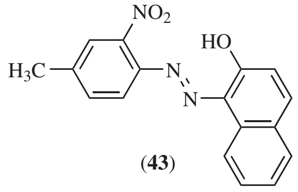

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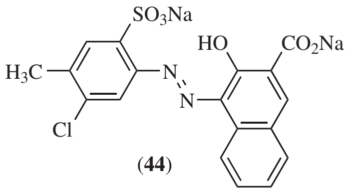

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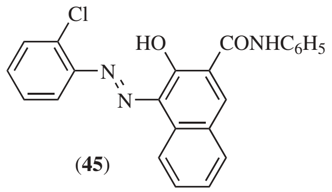

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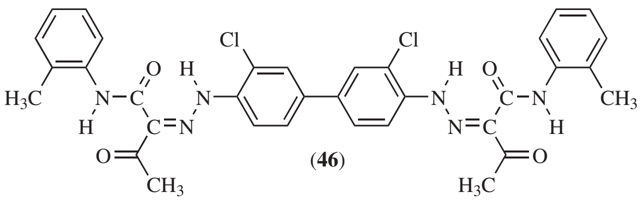

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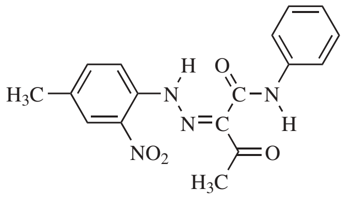
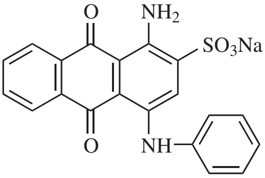


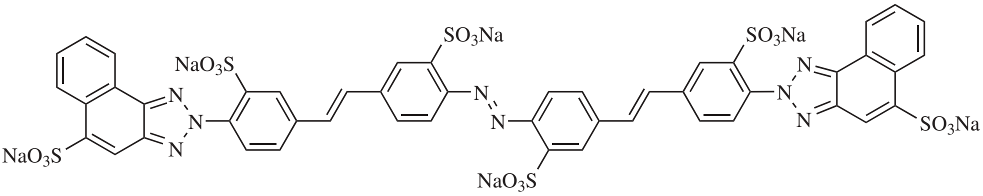
(**47**)

Fig. 9. Examples of azo dyes and pigments giving high reaction yields on a commercial scale.

In this regard, 1-amino-2-sulfonic-4-bromoanthraquinone is condensed with aniline in the presence of a Cu^{2+} salt, a process known as the Ullmann reaction (57). Another example involves the formation of the triazole ring of Direct Yellow 106 (**49**), using $CuSO_4$ as an oxidizing agent (58,59).



(**48**)



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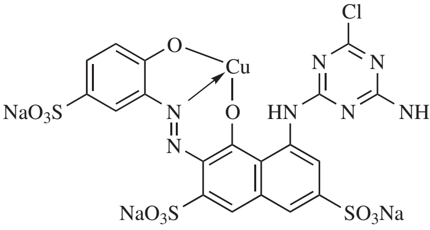
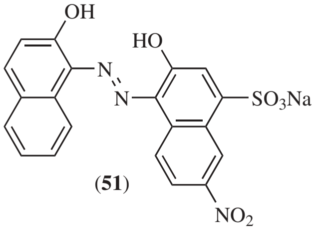
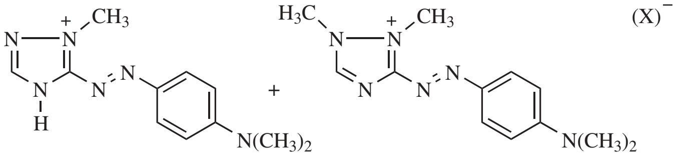


(**50**)



(**51**)



(**52**)

Metal ions are used to make dyes such as copper-complexed direct and reactive dyes for cotton and chromium-complexed acid dyes for nylon and wool. Examples are Direct Blue 218 (**7**) (97), Reactive Violet 2 (**50**) (61), and Acid Black 52 (**51**; 2:3 Cr complex) (62). Similarly, zinc is used to prepare the double salt of basic dyes, an example of which is Basic Red 22 (**52**; where X^- is a zinc salt) (63).

Since the aforementioned manufacturing processes led to residual toxic metal ions in the associated wastewater, a number of studies have been conducted that pertain to the removal of heavy metals from processing waters. The methods used involve coagulation (64–67), polymer adsorption (68), ultrafiltration (69,70), carbon adsorption (71–72), electrochemistry (73,74), incineration and land disposal (75), PACT (76,77), neutralization (78), and bisulfite-catalyzed borohydride reduction (4). In addition, the removal of heavy metals by methods involving ion exchange (79), sulfide precipitation (79), chelation with trimercaptotriazine (80), mercaptobenzothiazole (81), diethyldithiocarbonate (82), carbonotrithioic acid (83), adsorptive filtration (84), and carbon adsorption followed by stripping the metals with an acid regenerant and recovering them by electrolysis have been explored (85).

An emerging effective and inexpensive method for removing metals such as cobalt, chromium, and copper is phytoremediation. This natural process has been carried out by using vegetation for an *in situ* treatment of contaminated soils and sediments (86,87).

Reactive and acid dyes complexed with chromium, copper, and nickel have been decolorized by ozonation followed by treatment with chelating resins. This led to a 77–86% removal of the heavy metals (88).

Several studies have been conducted on the fate of copper in textile dyehouse wastewater. The results indicated that the use of biological solids in the wastewater afforded efficient sorption of copper containing direct and reactive phthalocyanine dyes. Therefore, little of the copper bound in dyes of these types would be discharged in the wastewater in soluble form. Biological solids and wastewater adsorbed a portion of copper-containing formazan and azo reactive dyes, although not nearly as efficiently as direct dyes. Also, it was concluded that sequestrants in wastewater would compete with biological solids for free and bound copper ions, thereby decreasing the tendency of copper to attach to the solid phase during wastewater treatment (89–91).

Questions about the toxicity of textile mill discharges to plant life in receiving waters led to an evaluation of the toxicity of 46 dyes to fresh water green algae. All except two of the dyes were anionic colorants, many of which were reactive and/or metal complexes. Only the two cationic dyes exhibited toxicity (92).

5.3. Metal Complexed Dyes.

One of the most serious environmental problems in the dye, textile, and leather industries is associated with the manufacture and use of metallized azo dyes that are complexed with chromium or cobalt to obtain desirable fastness properties (93). This issue arises because the superior lightfastness required for applications involving polyamide fibers can only be achieved by using metallized azo dyes in which the azo linkage is protected from light-induced degradation. Examples of these important dyes are metallized forms of the azo and formazan dyes shown in Figure 10.

Although metallized dyes can be removed from wastewater using various chemical, physical, and biological methods, such treatments can be expensive and may result in sludges that must be disposed by incineration or land filling. In view of an emphasis on pollution prevention instead of waste treatment (94), the merits of substituting iron (Fe) for chromium (Cr) and cobalt (Co) in a group of commercially important acid dyes has come to the forefront of studies in this area. Although Fe is innocuous, until relatively recently, little had been published about the utility of Fe-complexed dyes as environmentally friendly alternatives to widely used Cr and Co complexed acid dyes. This was the case despite the long-standing existence of Fe-complexed type **53** ligands (eg, Acid Brown 98) as colorants for leather.

Studies in this area have led to the synthesis of Fe complexed azo dyes for nylon and wool that possess good fastness properties. Examples are the Fe

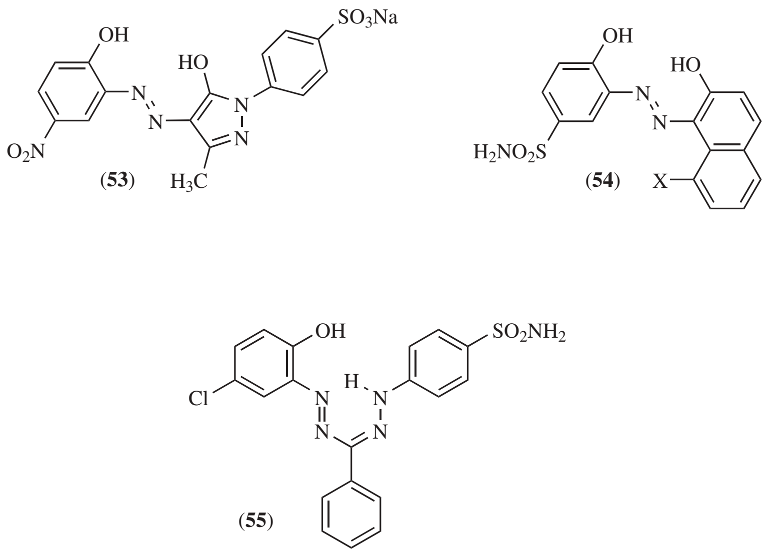


Fig. 10. Structures of some commercial metallized dyes include **53** (1:1 Fe complex), **54** (X = H, NHAc; 1:2 Co complex), and **55** (1:2 Co complex).

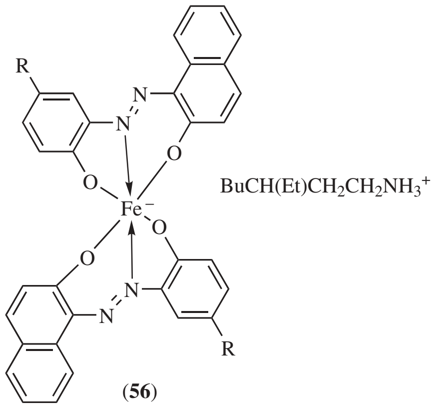
analogues of azo dyes such as **54** (49–51) and formazan dyes such as C.I. Acid Black 180 (**51**) (52,53). Interestingly, in all three cases the introduction of Fe into the commercial dyes led to photostable black dyes. In the case of Fe complexed formazan dyes, it was also possible to produce reddish-violet, violet, and blue colors, colors that had not been previously reported for Fe complexes (52–54).

In related studies, it has been shown that Fe(II) sulfate can be used as a metallizing agent to produce 1:2 iron complexes of azo dyes inside wool fibers by treating wool previously dyed with an unmetallized dye. The photostability of the resultant fibers was the same as that of fibers dyed with the premetallized dyes. This achievement helped address problems associated with the low water solubility of premetallized Fe complexes of type **54** dyes.

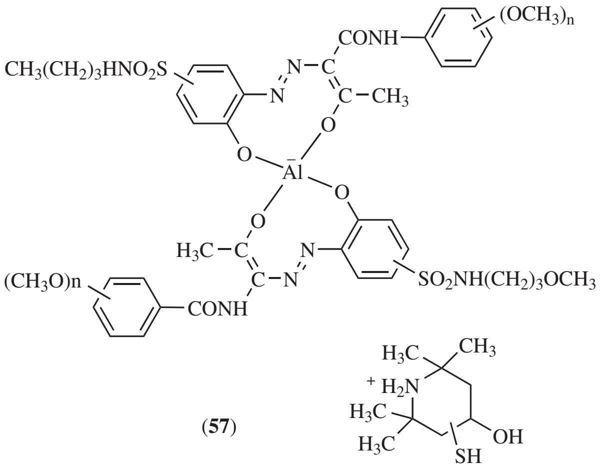
When mordant dyes were used as substrates for metallizations involving Fe(II) sulfate, it was found that dyes possessing an *ortho, ortho′*-bis-hydroxyazobenzene system readily gave a 1:2 Fe-dye complex, but the formation of a 1:2 Fe complex of mordant dyes containing an *ortho*-hydroxy, *ortho′*-carboxyazobenzene system could not be confirmed (94). Consequently, it was not surprising to find a correlation between photostability of the Fe-mordant dyes and the ease of forming the metal complex. Even though the colors of Fe complexed dyes were not as bright as the corresponding Cr and Co complexes, very good wash fastness was always observed.

Other studies have led to the patenting of 1:2 Fe-complexed solvent dyes such as **56** and 1:2 Al-complexed solvent dyes of type **57** (95,96). See Figure 11.

5.4. Dye Manufacturing. At least one major dyestuff manufacturer has developed a method for eliminating mercury as a catalyst in the sulfonation step employed in the synthesis of key intermediates for anthraquinone dyes (97).



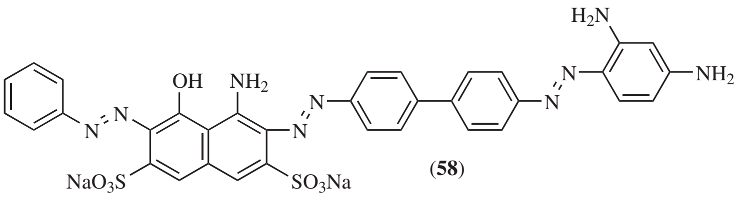
(**56**)



(**57**)

Fig. 11. Structures of recent metallized solvent dyes [$R = SO_2NH(CH_2)_3OCH_3$].

Similarly, one of the most important pollution prevention measures implemented to date has been the termination of the use of toxic and carcinogenic compounds historically associated with the production of certain azo dyes and pigments. Examples of such compounds were 2-naphthylamine and benzidine. In the case of benzidine, the termination of its use has curtailed the manufacture and sale of 67 dyes, including large volume products such as Direct Black 38 (**58**), Direct Blue 6 (**59**), and Direct Brown 95 (**60**) (37,98,99). This change has led to the use of nonbenzidine-based dyes such as C.I. Direct Black 80 (**61**).



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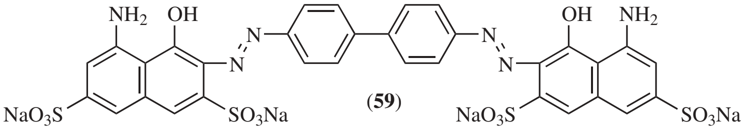

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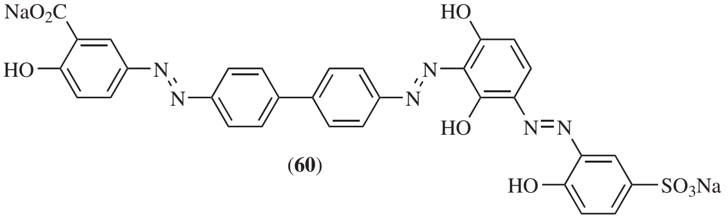

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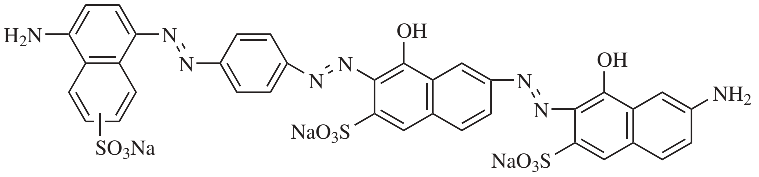

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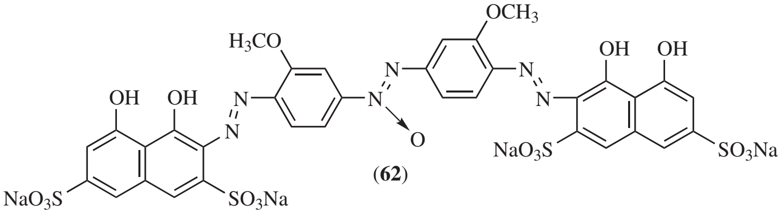
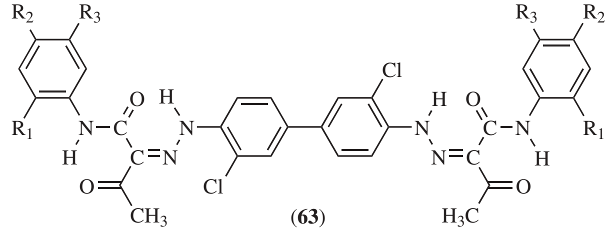


(**62**)



(**63**)

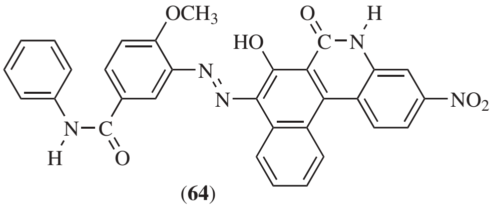
R^1	R^2	R^3	Pigment
H	H	H	Yellow 12
CH_3	CH_3	H	Yellow 13
OCH_3	H	H	Yellow 17
H	CH_3	H	Yellow 55
OCH_3	Cl	OCH_3	Yellow 83

No doubt the most stringent pollution prevention measure is one imposed by Germany. In this regard, the Consumer Goods Ordinance has barred the distribution of fabric containing azo dyes capable of forming an established carcinogenic aromatic amine, namely (*o*-amino-azotoluene, 4-aminobiphenyl, benzidine, *p*-chloroaniline, 4-chloro-*o*-toluidine, 3,3′-dichlorobenzidine, 3,3′-dimethoxy benzidine, 3,3′-dimethylbenzidine, 4-methoxy-*m*-phenylenediamine, 6-methoxy-*m*-toluidine, 4,4′-methylenebis (2-chloroaniline), 4,4′-methylenedianiline, 4,4′-methylenedi-*o*-toluidine, methyl-*m*-phenylenediamine, 2-naphthylamine, 5-nitro-*o*-toluidine, 4,4′-oxydianiline, 4,4′-thiodianiline, *o*-toluidine, and 2,4,5-trimethylaniline).

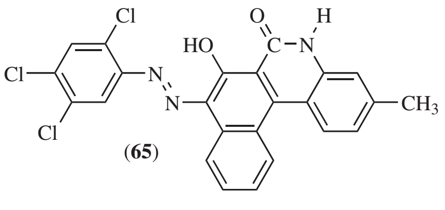
The presence of benzidine congeners such as 3,3′-dimethoxybenzidine (*o*-dianisidine), 3,3′-dimethylbenzidine (*o*-tolidine), and 3,3′-dichlorobenzidine on this list will impact the manufacture and use of important dyes such as Direct Blue 218 (**7**) and Direct Blue 281 (**62**), as well as large volume diarylide yellow pigments **63** (100).

5.5. Pigment Replacements. In the pigments area, naphthol AS pigments such as Pigment Red 31 (**64**) and 112 (**65**), high performance polycyclic pigments such as perylenes (Pigment Red 123, **66**) and quinacridones (Pigment Red 209, **67**) serve as nontoxic alternatives to certain barium lakes [eg, Pigment Red 48:1 (**68**) and 49:1 (**69**)] (101,102). Similarly, substitution of environmentally safe synthetic organic pigments such as Pigment Red 48:2 and Pigment Red 49:2 for toxic inorganic pigments containing cadmium, lead, nickel, or copper is also deemed prudent (103). The substitutes have included the corresponding Ca lakes of pigments **68** and **69**.

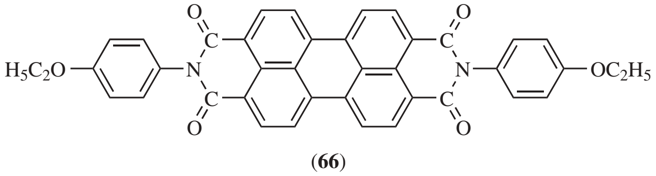
In 1996, the Office of Pollution Prevention and Toxics of the USEPA commended a U.S. pigment company for its development of a new yellow pigment to replace those based on a heavy metal and dichlorobenzidine (104). Initiatives of this type led to U.S. patents, which cite monoazo green shade yellow and red shade yellow pigments that employ pyrazolone-based coupling components (105,106). A third patent cites pigments that are Ca, Sr, Mn, or Zn lakes of sulfonated azo dyes (107).



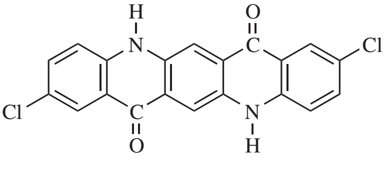
(**64**)



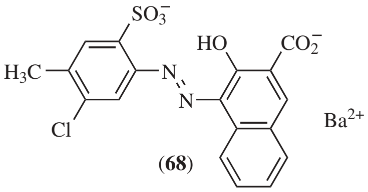
(**65**)



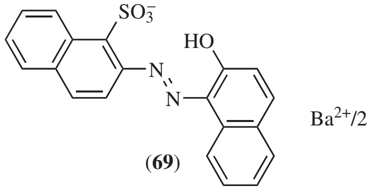
(**66**)



(**67**)

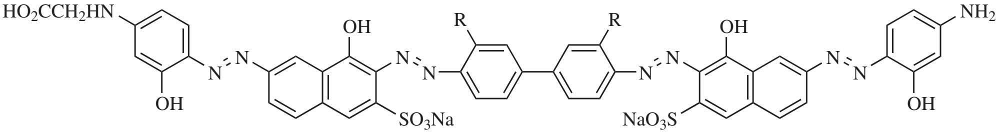


(**68**)

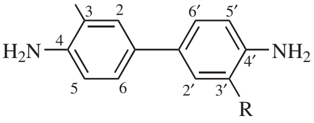


(**69**)

5.6. Aromatic Amines. Various research groups have conducted studies aimed at the development of nonmutagenic benzidine analogues for use in the synthesis of organic dyes and pigments. In the initial studies in the area, it was shown that the mutagenicity of benzidine could be removed by incorporating bulky alkyl or alkoxy groups *ortho* to the amino groups (**70**; Fig. 12). This work led to the design of nonmutagenic azo dyes (**71**; R = OC_3H_7, OC_4H_9) for ink-jet application (108). These dyes had good wet fastness but light fastness requires improvement.



(**71**)



(**70**)

R Group	Mutagenic Properties
H	Mutagenic
OCH_3	Mutagenic
OC_2H_5	Mutagenic
OC_3H_7	Nonmutagenic
OC_4H_9	Nonmutagenic
OCH_2CH_2OH	Nonmutagenic

Fig. 12. Effect of *n*-alkoxy groups on the mutagenicity of benzidine analogues.

In subsequent studies, 5,5′-dipropoxybenzidine and 2,2′-dimethyl-5,5′-dipropoxybenzidine were synthesized and coupled to a variety of aminohydroxynaphthalene couplers to produce orange to blue direct dyes (109). Similarly, 3,3′-dipropoxybenzidine, 3,3′-dibutoxybenzidine, 3,3′-dimethoxyethoxybenzidine, 2,2′-dimethyl-5,5′-dipropoxybenzidine, and 2,2′-dimethoxy-5,5′-dipropoxybenzidine were synthesized (110) and used to prepare environmentally safe pigments upon coupling to acetoacetanilides, pyrazolones, naphthols, benzimidazolones, and reacting with barbituric acid and pyrimidines (110–114).

5.7. Recovery and Reuse.

Hydrolyzed Reactive Dyes. Reactive dyes such as **50** are used to provide dyeings on cotton that possess high wet fastness. They are applied under alkaline conditions and form a covalent bond with hydroxyl groups on the cellulose chain (cf. **50a**). Unfortunately, dye-fiber bond formation is always accompanied by alkaline hydrolysis of the reactive group in the dyes employed and the resultant hydrolyzed dye (cf. **50b**) can no longer react with cotton (Fig. 13). In rare cases, as much as 20% hydrolysis occurs, producing a deeply colored dyebath containing “useless” dye. It is this color that must be removed in the waste treatment process.

An alternative to the destructive decolorization of dyebaths remaining following the application of reactive dyes to cotton has been explored. The approach developed involves using hydrolyzed reactive dyes as colorants for nylon and wool. In one study, the affinity of the hydrolyzed forms of C.I. Reactive Black 5 and C.I. Reactive Blue 19 was compared to the structurally analogous acid dyes, C.I. Acid Black 1 and C.I. Acid Blue 25 (115,116). This study utilized nylon 66, nylon 6, and wool, and the effects of temperature, pH, and electrolytes on dyeing with hydrolyzed reactive dyes were investigated. It was reported that the hydrolyzed dye remaining after dyeing cotton with reactive dyes could be used to dye nylon and wool and that the resultant fibers had similar wash fastness and light fastness to those dyed with acid dyes of similar structure.

In a second study, a group of 20 commercial vinylsulfone and chlorotriazine dyes was used: (a) to compare the exhaustion and affinity of reactive dyes on cotton, wool, and nylon, (b) to determine conditions for applying color remaining from dyeing cotton with reactive dyes (mainly hydrolyzed dyes) to wool and nylon, and (c) to determine possible relationships between dye structure and the utility of hydrolyzed reactive dyes as colorants for nylon and wool (117). In this study, a pH of 3–4 was found to give the highest percent exhaustion of hydrolyzed dyes on wool and nylon, and the fastness properties of the resultant dyeings were generally acceptable. Results from structure–performance assessments also suggested that the hydrolyzed form of polysulfonated reactive dyes had greater affinity for wool than nylon, while the mono- and disulfonated dyes showed greater affinity for nylon than wool.

Decolorized Dyebaths. In a study involving the reuse of ozone-decolorized dyebath water after the dyeing of cotton with a reactive dye, dyebaths containing 90% ozone-treated water and 10% fresh tap water gave excellent color reproducibility and required only 10% of the amount of salt used in the initial dyeing process (118,119). Similarly, a carpet mill has effectively used recycled treated wastewater to dye carpets (120). In addition, a textile plant was able

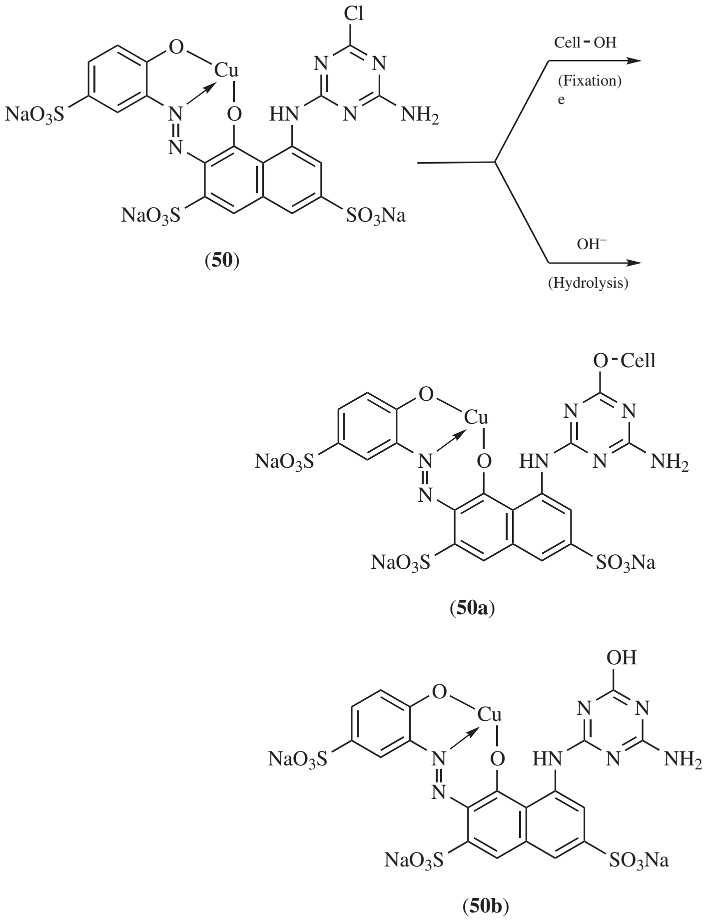
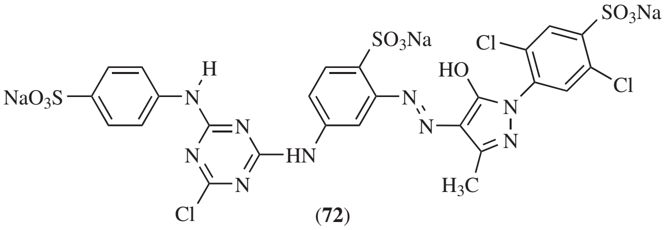


Fig. 13. Chemistry associated with the application of a reactive dye to cotton under alkaline conditions.

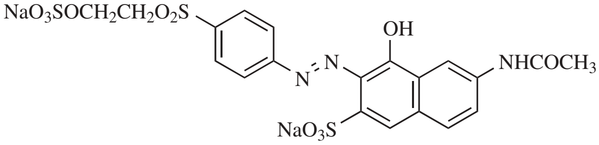
to recycle its wastewater by treating effluents containing hydrolyzed reactive dyes with sodium hydrosulfite stabilized with carbonates and sulfates along with flocculants and coagulants, resulting in a substantial cost savings (121).

Key Chemicals. In a study involving the use of fungi and bacteria to remove Reactive Black 5, Reactive Blue 19, and Leuco Sulfur Black 1 from wastewater effluents, it was found that the hydrolyzed reactive dyes could be desorbed from the microbial sludge and reused (122). In this case, the resultant dyes were also applied to nylon and wool fibers.

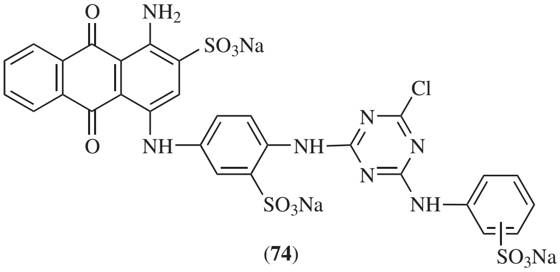
It has been demonstrated feasible to recover sodium sulfate from agricultural drainage salt and use it to help dye cotton fabrics with reactive dyes such as Reactive Yellow 2 (**72**), Reactive Orange 16 (**73**), and Reactive Blue 2 (**74**), Reactive Red 2 (**75**) (123).



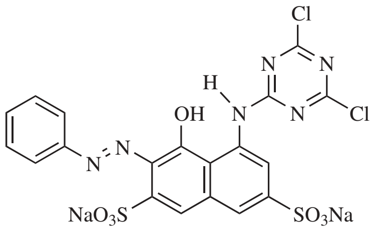
(**72**)



(**73**)

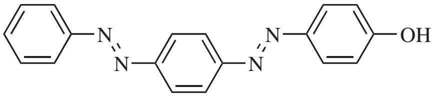


(**74**)



(**75**)

Although not yet widely carried out, priority pollutant waste intermediates such as aniline, phenol, and *p*-cresol can be converted to important commercial dyes in lieu of undergoing chemical or biological degradation (124). For instance, waste aniline and phenol can be used to prepare Disperse Yellow 23 (C.I. 26070, **76**), a high volume disperse dye for polyester and acetate fibers. The synthesis is a two-step process involving the conversion of aniline to *p*-aminoazobenzene and diazotization and coupling to phenol (a compound that also generates a high BOD). Similarly, waste *p*-cresol, a toxic compound that causes high BOD in a waste treatment facility, can be coupled with *p*-aminoacetanilide to prepare Disperse Yellow 3 (C.I. 11855, **77**)—a high volume disperse dye for nylon fabrics and carpets.



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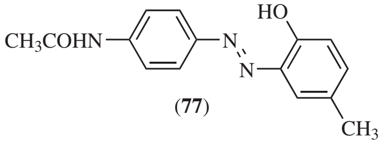
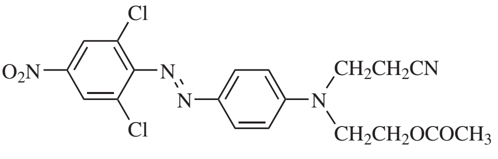


(**77**)

Water. Salt (NaCl) is essential in the isolation of water-soluble acid, direct, and reactive dyes from their aqueous reaction mass during the manufacturing process. However, wastewater containing a salt concentration of 1 g/L or higher is known to exhibit aquatic toxicity (125). The most effective and efficient methods for removing salt are reverse osmosis, ultrafiltration, and hyperfiltration. This produces clean wastewater for use in other plant processes. Associated with the lower water usage was a reduction in amount of wastewater treatment at the tertiary biodegradation/PACT treatment facility and a recovery of 500 lb dye/day. This combination afforded an annual savings of more than $1 million (126–129).

As an indirect “salt removal” method, reactive dyes requiring less salt in the dye application process have been developed (130).

5.8. Energy Savings. One example of an interesting approach in this area has involved the preparation of dye filter cakes having a higher percent solids (less water). This has been accomplished by modifying the crystal form or habit (size), resulting in less energy (steam or electricity) required to dry dye cakes prior to grinding and making powders. Also, in the case of disperse dyes, higher percent solids has eliminated the need for drying prior to standardization into disperse dye pastes or spray-dried granules. It has been reported that the surfactant Surfynol 104E (2,4,7,9-tetramethyl-5-decyne-4-7-diol) can be used to facilitate the formation of high percent solids for Disperse Orange 30 (**78**) (131).



(**78**)

Similarly, it has been shown that disperse dyes such as Disperse Blue 79 and Disperse Brown 2 can be prepared at high percent solids in the filter cake (132). Such products are more stable and have better dispersion properties following the addition of a nonionic surfactant such as polyoxyethylene-9-octadecenoic acid ester. In related studies, others have found that the use of anionic and nonionic surfactants such as lignin sulfonates, nonylphenol polyglycol ether after coupling results in disperse dyes with high percent solids and good dyeing properties (133).

As a source reduction measure, reactive dyes that require less salt in the dye application process have been developed (130). Such dyes have also been referred to as “environmentally friendly” reactive dyes because they leave behind less color in the final dyebaths. In this regard, dyes having higher affinity for cotton than the traditional low molecular weight reactive dyes (eg, **5**, Fig. 1) are employed. Their structures resemble direct affinity dyes in that they are often azo structures containing multiple reactive groups (eg, **6**, Fig. 1). While these dyes give wastewater containing less salt and dye requiring removal, they can produce hydrolyzed forms with enhanced affinity for cotton, which leads to lengthy wash off times and increased water consumption.

5.9. Dyeing Medium. The conventional method for dyeing polyethylene terephthalate (polyester) fibers involves the use of dyebaths containing water, disperse dye, dispersing agent, and other chemical auxiliaries needed to enhance the efficiency of the dyeing process. After the dyeing step, dyeing auxiliaries remain in the wastewater and consequently add to the cost and complexity of treating the effluent stream. Since the cost of wastewater treatment and the value of water as a raw material are important considerations in dye application, there has been a renewed interest in exploring approaches to the coloration of textiles that involve alternatives to water as the dye transport medium. As part of this search, laboratory and pilot plant studies using supercritical carbon dioxide ($SCCO_2$) have been undertaken for dyeing polyester with disperse dyes. This technique offers advantages besides the elimination of wastewater treatment, which include the use of an environmentally safe medium, CO_2, which can be recycled inexpensively, and elimination of the need for reduction clearing, drying, and chemical auxiliaries. Excellent leveling and fastness properties without the use of dispersants have been reported, and residual dye can be recovered in a form suitable for reuse (134–166).

6. Corporate Programs

6.1. EPA Initiatives. The EPAs P2 Recognition Project serves as a mechanism for recognizing companies for innovative chemistry and technologies that further pollution prevention and other environmental goals. In this regard, officials who oversee the EPA New Chemicals Program, which operates out of the Office of Pollution Prevention and Toxics, hope that rewarding such innovations will stimulate further innovations in industry.

This program, which screens up to 2500 chemicals a year, was used to identify the chemicals proposed for P2 recognition with the aid of the Premanufacture Notice (PMN) P2 screening process and the more detailed new chemical reviews. The New Chemicals Program also includes the Biotechnology Program, which reviews new (ie, intergeneric) microorganisms. The P2 Recognition Project relies heavily on information contained in the PMN on P2 aspects of the new chemical or biotechnology product, although supplemental information has also been considered.

With regard to the elements of a successful candidate and the criteria the EPA uses in identifying new chemical–biotech candidates for P2 recognition, it is clear that the Agency is looking for safer substitutes for chemical and biological products currently in commerce that are either less toxic (as demonstrated by test data on the new product itself) or derived from substances that have lower toxicity. Other considerations include pollution prevention, source reduction or recycling processes that reduce exposures or releases, environmentally beneficial uses of the product, and conservation of energy and water during its manufacture, processing or use. Finally, the Agency recognizes true commercial successes, which requires that the company start production of the PMN substance in order to receive an award. In some cases, promising cases that have not entered commerce are recognized for the achievement they represent, in anticipation that the chemistry or technology will be commercialized.

6.2. ISO 14000. In the future, a significant factor in the implementation of pollution prevention and waste minimization/source reduction measures in the dye, textile, and pigment industries worldwide will be the International Organization for Standardization (ISO) and its ISO 14000 standards. More than 60 countries have agreed to participate in the voluntary standards of this organization. These standards cover environmental auditing, environmental labeling, environmental aspects of product standards, life cycle assessment, and emphasize a strong commitment to pollution prevention (167–170). At least one pigment manufacturer has implemented ISO 14000 in its industrial plants (171).

6.3. Eco-Efficiency.

A corporate program known as "eco-efficiency" has been established. The goals are to achieve a balance between environmental and economic considerations, to manufacture cost-effective products with a minimum amount of raw materials and energy, and to minimize emissions (172). This initiative has also been used as a strategic instrument for determining which product lines and processes are appropriate for future investment from an environmental and economical perspective.

Another example involves the eco-efficiency analysis of phthalocyanine with and without copper metallization (173), which is an international pilot project between the United Nations Industrial Development Organizations (UNIDO) and the United Nations Environment Program (UNEP), to investigate the eco-efficiency of several textile dye works in Morocco (174).

7. Resources

An interesting book has been published that covers approaches and methodologies for implementing pollution prevention and waste minimization programs such as feedstock substitution, improved operational schemes, recycling, by product recovery, energy efficiency for a number of industries, including dye manufacturing and textiles (175). A 24-page report giving a brief overview of the U.S. textile industry, with an emphasis on efforts to incorporate pollution prevention and clean technologies into its manufacturing operations, is also available. This report can be used as a source of general information about the industry and its use of technologies and processes that reduce or prevent pollution (176).

An important organization, the Waste Resource Center (WRRC), located in the North Carolina Division of Pollution Prevention and Environmental Assistance and founded by the EPA and individual states, provides technical pollution prevention training to industries in EPA regions III and IV. Their web site (177) and on-line clearinghouse and P2 Infohouse provide important reports, including 192 references regarding pollution prevention in the synthesis and application of dyes.

Updates to domestic and international environmental regulatory affairs for dyes and pigments are available (98,99,178). In addition, Europe has enacted a number of regulations designed to protect the environment from damage arising from textile production. Of particular importance and concern are matters pertaining to extractable toxic metals resulting from dyeing with metallized azo dyes (179,180).

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