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REMOVAL AND RECOVERY OF DYESTUFFS FROM DYEING WASTEWATERS

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CONTENTS

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ABSTRACT

The toxic nature of some dyestuffs (DSs) has long been recognized. Accordingly, dyeing wastewaters represent a source of water contamination, and should be treated in some way so as to reduce the concentration of the polluting DSs to permissible limits, prior to dumping its wastewater. In addition, some DSs can be recovered for reuse, a point which should represent saving in the overall cost of the dyeing process. Extensive publications on the removal of DSs from dye house wastewaters have been cited in the literature in which many techniques have been applied, biological treatment being the method most widely used as a primary treatment. However, only few publications have been concerned with recovery of DSs from their wastewaters. In the present paper, numerous techniques, if not all, that are presently used for either removal or recovery of DSs have been reviewed, evaluated and compared.

Key Words: Dyestuffs; Wastewater; Removal; Recovery; Adsorption; Complex formation; Chemical precipitation; Flocculation; Coagulation; Membrane separations; Oxidation; Reduction; Electrochemical oxidation; Photocatalytic decolorization; Ozonation; Biological treatment; Ion exchange; Multi treatment processes; Dye bath recycling; Dye bath reconstitution; High exhaustion dyestuffs

1. INTRODUCTION

The growth in industry and the changes in manufacturing processes have resulted in an increase in the volume and complexity of wastewater discharges to the environment.[1] Many traditional and novel treatment processes are being modified and developed to try to eliminate the release to surface waters of the diverse chemical substances found in wastewater discharges.[1] Wastewater treatment is generally classified into four levels—primary, secondary, tertiary and quaternary. Each treatment level is aimed at removing a more specific class of contaminants. Primary treatment involves simple, physical processes that remove suspended solids and entrained oil from a wastewater stream. Secondary treatment is designed to remove soluble material from waste streams that cannot be removed by simple physical means. Tertiary and quaternary treatments are used to polish an effluent to remove a specific contaminant that is not removed in the first and second treatment steps. In addition to these four levels of treatments, there are four classes of treatment technologies—physical, chemical, thermal, and biological. The specific processes selected to remove contaminants from the bulk aqueous phase can be used either singularly or together in various combinations.[2] Decolorizing textile wastewaters has always been a worldwide problem to which many diverse technologies have been applied.[3] The techniques adopted for the disposal of colored effluents from textile dyeing and printing must be brought into line with the need to protect surface waters and ground water.[3] Some of the recent demands that have imposed on textile effluent under German legislation are shown in Table 1.

Various environmental problems, e.g. the concentration of heavy metals and AOX, continue to harass textile finishers. However, the color quality of textile effluents is progressively becoming problem no 1, not because DSs are particularly hazardous, but because they strike the eye—in the final analysis, therefore, for aesthetic and political reasons.[3] Reactive DSs, in particular, present particular difficulties because bath exhaustion is usually poor. After the dyeing process as much as 800 mg/L of (hydrolyzed) DS may remain in the bath. In addition, DSs are removed from the fiber, often in considerable amounts, during the subsequent rinsing and soaping. Although bath exhaustion of 1:1 and 1:2 metal-complex DSs is much higher, the concentration of

Table 1. Limiting Permissible Values for Textile Effluents (Selected Values)[1]

	Discharged Into		Requirements for the Treatment of Branch Streams
	Water Ways	Drains	
AOX (mg/l)	0.5	0.5	≥ 3
Cr (total) (mg/l)	0.5	0.5	≥ 2
Cu (mg/l)	0.5	0.5	≥ 2
Chromaticity[a]			
Yellow (436 nm)	$7\ \mathrm{m}^{-1}$		
Red (525 nm)	$5\ \mathrm{m}^{-1}$		
Blue (620 nm)	$3\ \mathrm{m}^{-1}$		

[a] Spectral absorption coefficient.

Table 2. Methods for Decolorising Effluents Containing Reactive and Metal-Complex Dyes

Method	Reagent, etc.
Adsorption	Activated charcoal Ion exchange resins Modified cotton Biofilters
Precipitation	Iron salts Aluminum salts Bentonite Cationic polymers Iron(s)/chalk Clathrate
Oxidation	Ozone H_2O_2 Cl_2 or HOCl
Reduction	$Na_2S_2O_4$
Electrochemically with iron or aluminium anodes	Electrolysis and flotation

(chelated) heavy metals, especially in deep shades, may greatly exceed the above mentioned permissible limits in the effluent.[3] Amendments to the legislation on wastewater are making the legal requirements for textile wastewater more stringent. In addition to the limits on the metal content and the COD and AOX values, restrictions are also being placed on the color of the effluent.[3] Examples of methods that have been adopted up to now for decolorizing effluents are presented in Table 2.

DSs are known to be a contaminant that may pollute water streams if their wastewater is dumped before treatment to reduce their concentration. Their removal has been investigated by numerous researchers in the last few decades. The majority of the cited literature deals with the removal of DSs while a minority pertains to their recovery for reuse. The various techniques that have been investigated in the literature include: 1) adsorption on activated carbon or other miscellaneous adsorbents; 2) complex formation and precipitation; 3) flocculation and coagulation; 4) membrane separation such as RO, UF, and NF; 5) oxidative methods with various oxidants; 6) electrochemical methods; 7) ozonation; 8) biological treatment; and 9) ion exchange methods and others.

2. ADSORPTION ON ACTIVATED CARBON

Activated carbon has been used to remove a wide variety of contaminants from liquid or gaseous streams. It is typically employed for organic compounds, and one of its common applications is industrial wastewater treatment, in which thermal regeneration is usually employed, since organic contaminants are destroyed in the process. Activated carbon can also be used for chemical recovery and concentration in which case non-destructive regeneration process is used. In general carbon adsorption should be considered as a potential removal process for organic contaminants that are non polar, of low solubility, or of high molecular weight. Accordingly, soluble organic DSs such as methylene blue and textiles DSs are one of the major classes of organic compounds that are generally amenable to adsorption on activated carbon. However, although adsorption methods can frequently decolorize textile effluents, but their application is limited by the high price of adsorbents and the large amounts of waste normally involved. It is precisely the particularly important reactive DSs that are only moderately retained by the commonest adsorbent-activated charcoal—and thus leave a color. Coke is cheaper, but is also only moderately effective. In any event, considerable amounts of coal sludge are formed, and its disposal presents additional problems.[3]

Several classes of DSs have been removed by adsorption on activated carbon. Ozoh et al.[4] investigated the adsorption of cotton fabric DS wastewater on Nigeria agriculture semi-activated carbon. The Kaduma River in Nigeria is in such great environmental stress that the self purifying capacity of the river has been exceeded as a result of industrial discharges. The river water is blue-green and pollution build up is evident on the river banks. Techniques were designed to rid the river of visible signs of pollution by incorporating the principles of adsorption and incineration. Semi-activated carbon from agricultural wastes was used to treat the wastewater. Residual colors, amber, yellow and orange, were obtained and the solute removed was 96–99.8% and the volatile residue removed by carbon treatment was 3–3.8%. Incineration of 1 kg wastewater yielded 40 g solid residue. Adsorption of DS in the wastewater was linear and increased with concentrations of wastewater per unit mass of guinea corn carbon. Replicate results yielded $y = 2.5 + 0.130\ x$ and $y = 2.306 + 0.017\ x$, where x is the logarithmic value of the percentage DSs concentration in wastewater and y is the logarithmic value of adsorption of DS waste per unit weight of adsorbent. For maize carbon the adsorption was linear but decreased with increasing concentrations. Replicate results were $y = 1.583 - 0.21\ x$ and $y = 0.52 - 0.32\ x$, where x and y are the same as above. For cane sugar carbon, the adsorption was independent of concentrations (Figures 1 and 2).

Adsorption experiments for disperse-red-60 DS on powder activated carbon were investigated by Yieh et al.[5] Color removal from synthetic DS

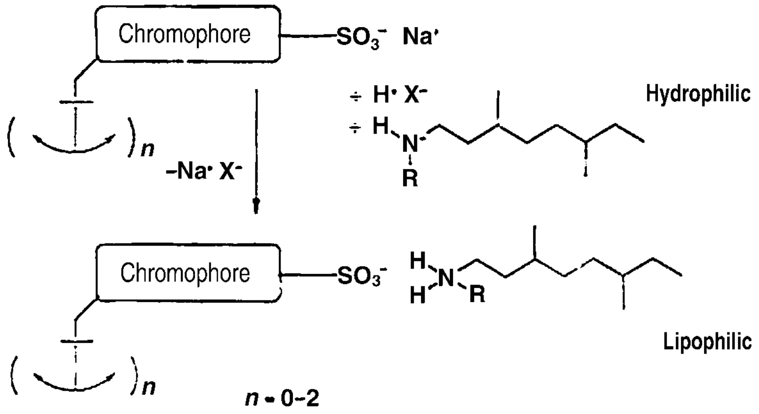


Figure 1. Mechanism of ion pair extraction of dyes containing sulphonate groups with anions.

wastewater from Taiwan textiles industries was investigated by studying the effect of contact time, DS concentration, and the dosage of the powder activated carbon. A film-pore double resistance diffusion model for mass transfer has been used to determine the effective diffusivity for the adsorption of the DS wastewater on powdered activated carbon.

The adsorption of bromothymol blue and crystal violet on activated carbon, and on treated activated carbon was evaluated by Youssef et al.[6] They found that activated carbon removed the DSs considerably, and that the treatment of activated carbon with oxidizing agents like nitric acid decreased

Parameter		Before	After
Extinction at 650 nm (0.5 cm cell)		2.561	0.003
Dye	[mg/l]	816	< 1
Cu	[mg/l]	30	0. 1
AOX	[mg/l]	1.7	0. 3
TOC	[mg/l]	395	150

Figure 2. Treatment of effluent containing Basilen® Turquoise E-B (C.I. Reactive Blue 41) by shaking up with Extractant TX 5096.

its capability for adsorption of DSs. Adsorption of these DSs depends on the pH of the aqueous solution of the DSs and increased with increase of temperature. The crystal violet was more adsorbed than the bromothymol blue. Adsorption was found to obey the Langmuir isotherm over a wide range of equilibrium concentrations.

Fang[7] compared the adsorption of bright yellow which is a cationic DS to that of phenol onto activated carbon, the adsorption of both materials was again affected by pH, and the adsorption of the DS was greater than that of the phenol probably due to its larger molecular weight, greater hydrophobicity and presence of a cationic group in its structure.

The adsorption of reactive DSs, and textile printing wastewater on activated carbon from sake brewing process was studied by Nakaoka et al.[8] The adsorption capacity of the used carbon was found to drop to half or one third of that of virgin carbon or even less. The dissolution of organic substances from the used carbon was 102 mg COD/g and it was reduced to 29 mg COD/g by drying at 105°C for 2 hrs. The dissolution substances were easily biodegradable.

Rao et al.[9] investigated the adsorption of DSs from the DSs utilization and manufacturing industries by various types of activated carbon. They studied the effect of the different types of DSs, the initial concentration of the effluent water and its pH, as well as the temperature on the best available adsorbent. Adsorption of the different DSs was found to follow the Freundlich isotherm.

Wastewater of soluble azo acid, direct, and reactive DSs was treated using a sodium hydrosulphite reduction operation, which was followed by adsorption with carbon by Reife et al.[10]

Tamai et al.[11] synthesized extremely large activated carbon (mesopore ratio higher than 70%), which selectively adsorbed giant molecules like blue acid 90. The activated carbon was prepared by a special method mentioned by the authors.

3. ADSORPTION ON MISCELLANEOUS ADSORBENTS

Numerous adsorbents, other than activated carbon, have been investigated in adsorbing DSs, of which to mention a few are: clay, peat, sawdust, brown coal, fly ash, bagasse pith, silica, aluminium hydroxide, vermiculite and maize cob.

El Guendi[12] investigated the adsorption of cationic DSs such as basic blue 69 and basic red 22 from wastewater onto natural clay. He found that the rate of adsorption was controlled by the boundary layer film diffusion and not by pore diffusion since the external mass transfer coefficient was found to vary linearly with agitation speed. It also varied linearly with clay particle size range, and mass of clay used, which is expected.

Sawdust was used to adsorb Maxilon Blue (a basic DS) in a fixed-bed absorber as well as batchwise by Mansi.[13] The effect of the feed input velocity, the wood particle size and the bed height were studied under isothermal adsorption conditions, and the results were found to obey the Freundlich relationship. Here the controlling step of adsorption at moderate velocity was pore diffusion rather than the external conditions. The best operating conditions were obtained at an intermediate feed velocity of 0.12 cm/s, a particle diameter of 0.018 cm, and a bed height of 10 cm.

Peat was investigated in removing DSs by Ramakrishna,[14] who proved that peat was more effective in removing disperse DSs than activated carbon, and that the surface charge of the adsorbent and the pH had a significant effect on the adsorption of the DSs.

Saskatchewan horticultural peat was also investigated on a laboratory scale in adsorbing a basic and acid DS.[15] Adsorption studies showed that 99% of the basic DS was readily adsorbed in 30 minutes while 48% of the acid DS was adsorbed in 100 minutes. Adsorption of both DSs followed the Langmuir and the Freundlich isotherms.

Cellulosic waste orange peel was used to adsorb congo red, procion orange, and rhodamine B by Namasivyam.[16] The initial DSs concentration, adsorbent dosage, agitation time, and pH were studied. Acidic pH was favorable for the adsorption of the three DSs, while desorption was more efficient at an alkaline pH probably due to functional groups formed at low pH that favor adsorbent–adsorbate interactions. Again adsorption was found to obey both the Langmuir and Freundlich isotherms.

Brown coal was found to successfully adsorb basic DSs.[17] The results obeyed both the Langmuir and the Freundlich isotherms.

Waste egg carton, as an example of a cellulosic domestic waste material was used in adsorbing acid and basic DSs by Mansi et al.[18] They studied the effect of agitation speed on adsorption process. Adsorption obeyed the Freundlich isotherm. The kinetic studies were made using the model suggested by Lagergren.

Adsorption of a dyeing and printing effluent on clay treated by a quaternary ammonium compound was also investigated.[19] The results were successful on a laboratory scale and indicated that the treated clays are efficient in decolorizing the colored effluents as compared to conventional adsorbents.

Porous calcium silicate hydrate was used successfully in the adsorption of DSs by Yoshida et al.[20] The colored liquids were contacted with granules of the adsorbent and the authors recommended the treatment for large amounts of dyeing wastewaters.

Karadag et al.[21] used acrylamide/itaconic acid hydrogel containing different quantities of itaconic acid that have been irradiated with γ radiation to adsorb cationic DSs such as Basic Blue 9, Basic Violet 1 and Basic Blue 12 from their synthetic aqueous solutions. The isotherms obtained were of the S-type, and which are characteristic of weak solute-solid interactions. Acrylamide hydrogel alone did not adsorb any cationic DS, and the adsorption of the DSs increased with the content of itaconic acid in the hydrogels. The work showed that the hydrogels could be used as an adsorbent for water pollutants such as DSs, and that immobilization of these organic contaminants in the hydrogels from wastewater can solve one of the most important environmental problems of the textile industry.

Superswelling hydrogels exhibit a combination of unique physico-chemical properties, thus permitting their wide-ranging and often exceptional possibilities in practical applications such as ecology, biotechnology and medicine. Saraydin et al.[22] studied a convenient method for removing some water-soluble monovalent cationic DSs from aqueous solutions by adsorption on a novel polymeric adsorbent such as acrylamide/maleic acid (AAm/MA) superswelling hydrogel. The potential toxicity of some cationic dyes has been known for many decades. Some cationic DSs are not used because they were found to be carcinogenic.[23] Accordingly, some water-soluble monovalent cationic DSs such as Basic Red 5 (BR-5), Basic Violet 3 (BV-3), and Brilliant Cresyl Blue (BCB), which resemble large molecular DSs found in wastewaters, were used in their adsorption experiments.[22] The AAm/MA hydrogen containing 60 mg MA and irradiated at 5.2 kGy was used for swelling and diffusion studies in water and aqueous solutions of the monovalent cationic DSs. For this superswelling hydrogel the swelling studies indicated that swelling increased in the following order: BR-5 > water > BV-3 > BCB. The diffusion of water and the DSs within the hydrogels was found to have a non-Fickian character. The uptake of the cationic DSs to the AAm/MA superswelling hydrogels was studied by the batch adsorption technique at 25°C. The uptake of DSs within the hydrogel increased in the following order: BR-5 > BV-3 > BCB. In the experiments of the adsorption equilibrium, S-type adsorption in Gile's classification system was found. The binding ratio of the hydrogel/DS systems was gradually increased with the increase of the MA content in the AAm/MA hydrogel and the irradiation dose. Figures 3 and 4 present a diagram of the hydrogel experiment, and the possible complexation process between the hydrogel and DS molecules, respectively.

Saraydin et al.[24] also used an acrylamide/maleic acid hydrogel containing 60 mg maleic acid and irradiated at 5.71 kGy for swelling and diffusion studies in water and solutions of the basic DSs. Swelling studies indicated that swelling increased in the following order: basic red 9 > basic green 4 > cresyl violet > basic blue 20 > water. Diffusion of water and DSs within hydrogels was a non-Fickian character. The uptake of cationic DSs to the hydrogels was studied by the batch adsorption technique at 25°C. In the adsorption experiments Langmuir type adsorption in the Giles classification

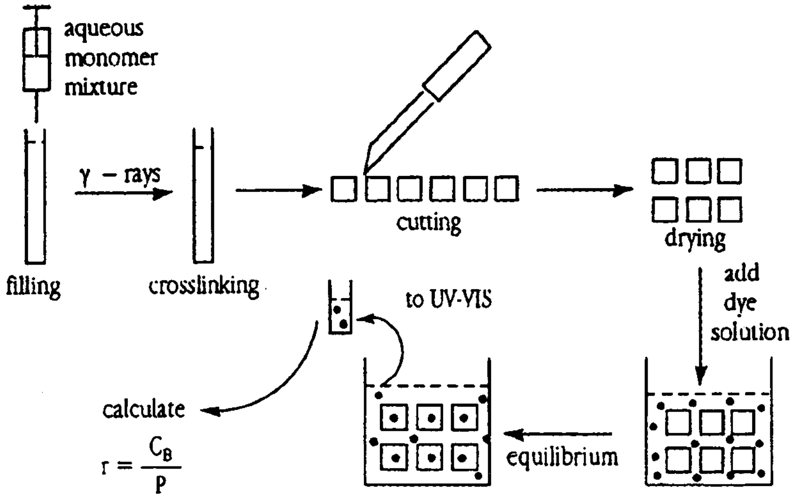


Figure 3. A diagram of the hydrogel experiment.

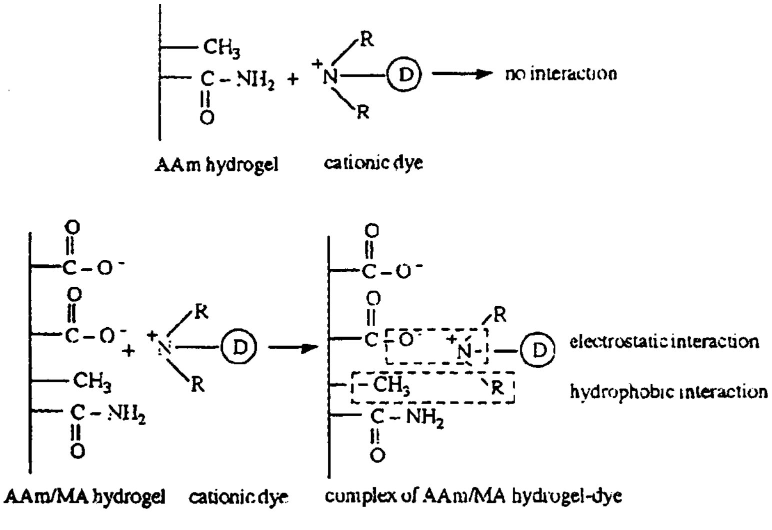


Figure 4. A possible complexation process between the AAm/MA superswelling hydrogel and monovalent cationic dye molecules.

system was found. Some binding and thermodynamic parameters for the hydrogel-DS systems were calculated using the Klotz method. Adsorption studies indicated that monolayer coverages of the hydrogel by these DSs increased in the following order: basic blue 20 > cresyl violet > basic red 9.

Choi et al.[25] investigated the effectiveness of vermiculite as an adsorbent, and its solutions, as a coagulant for removal of color from DS wastewater. In coagulation experiments, it was found that the vermiculite solutions could be applied to the treatment of the wastewater with its content of various cations (as Mg, Fe, Al, Ca, Si). Coagulation with vermiculite produced less sludge at lower coagulant dosage in comparison with conventional inorganic coagulants. For evaluation of adsorption characteristics of vermiculite on basic DS wastewater, adsorption parameters for Langmuir and Freundlich isotherms were determined. The adsorption of basic blue DS on vermiculite was found to conform with both isotherms. The adsorption capacity of vermiculite was found to increase with the decrease of particle size and with increase of temperature and intensity of agitation. The results indicated that vermiculite is an excellent adsorbent for basic blue DS wastewater and only moderately short contact times are required to reach equilibrium at the DS concentrations investigated. In addition, spent vermiculite can be regenerated at high temperature and then be reused, which is a great advantage. Moreover, the cost of applied vermiculite is 11% of that of activated carbon.

Aminated flax and kenaf fibers were investigated in the adsorption of some Remazol DSs by Abo-Shousha et al.[26] The grey flax and kenaf fibers were scoured, bleached, and aminated with polyethyleneimine. The kenaf fibers were found to be more efficient than the flax fibers in the adsorption of Remazol Brilliant Red F3B under various DS concentrations, liquor ratio, pH, and rate of shaking. The amination greatly increased DS removal, and the aminated scoured substrates had the highest ability to remove the DSs among other used substrates. Lowering the pH to 2.5 remarkably improved removal of the DS. The authors suggested that the aminated fibers bounded to the DSs with salt links.

Some DSs (cationic and reactive) were effectively adsorbed on post-vanillin lignin during precipitation of the lignin.[27] Adsorption reached values up to 1.4 g DS/g of adsorbent and the results again obeyed both the Langmuir and Freundlich isotherms.

A supersonic modified montmorillonite in ferric solution was used successfully in adsorption of anionic DSs.[28] The adsorption capacity for direct black DS reached 0.8 g/g, which is considered high.

The adsorption of basic violet 10 and acid red 1 on sulphonated coal and Ganoderma Lucidum (a biosorbent) was also investigated by Mittal et al.[29] The latter was more effective in the adsorption of the basic DS and its adsorption results obeyed the Freundlich isotherm, while the former was more effective in adsorbing the acid DS. The chemical bonds were stronger in the biosorbent than in the sulphonated coal for the basic violet 10. The authors conducted desorption and regeneration by contact with an acid mixture (sulphuric, formic, and other acids) which indicated that the nature of adsorption is chemisorption.

Low cost adsorbents like natural clay, bagasse pith and maize cob were tested in adsorbing Astrazon Blue, Telon Blue and Maxilon Red.[30] The authors claimed the relative costs of removal of the DSs to be only 2–10% of the cost of removal with activated carbon.

Basic DSs were adsorbed successfully on boiler bottom ash by Mall et al.[31] Batch and continuous procedures were employed, and the percentage removal reached 95–100%. The adsorption results obeyed both the Langmuir and Freundlich relations. The authors found that the removal of the DSs increased with the decrease of initial concentration, and pH, speed of agitation and particle size. The kinetics of removal followed the first order kinetic expression, and the breakthrough time increased with increase of bed height and decrease of flowrate. The breakthrough time and bed depth data showed the applicability of BDST model.

Palm-fruit bunch particles were used as a low-cost adsorbent in adsorbing basic red 18 by Nassar et al.[32] The adsorption results followed both Langmuir and Freundlich isotherms. Favorable adsorption for the tested basic DSs by palm-fruit bunch particle system were indicated by the values of the separation factor.

Fly ash as a sorbent-catalyst for the adsorption of four omega chrome DSs, was evaluated by Sur et al.[33] The batchwise adsorption results were found to be first order in nature and obeyed the Langmuir isotherm indicating monolayer adsorption. Both kinetics and diffusional resistances affected the rate of adsorption. The catalytic potential of coal fly ash for the decomposition of hydrogen peroxide was successfully used to regenerate saturated ash particles by peroxidation of the DSs molecules. The loss of adsorption capacity of fly ash was found to be less than 30% after the fifth repeated use and the extent of deactivation was found to vary from ash to ash.

The decolorization of DSs wastewater through the adsorption on fly ash was also investigated by Yan et al.[34] Reactive brilliant X-BR DS was efficiently removed in the adsorption process. The adsorption was found to be dependent on contact time, fly ash amount, pH and initial wastewater concentration. The experimental data obeyed the Langmuir isotherm.

Primary and secondary sludge particles were investigated in the adsorption of anionic new coccine acid red 18.[35] The effect of pH, suspended solids, and ionic strength on the DS adsorption was evaluated. The results showed that the DS adsorption was a fast process, which can reach equilibrium in 30 minutes. The pH was found to be the most important factor affecting DS adsorption; decreasing the pH significantly increased DS adsorption. Greater adsorption was achieved at suspended solids <1 g/L. Increased ionic strength decreased DS adsorption. The multi layer adsorption model allowed calculation of monolayer adsorption capacity and determination of the specific surface area of the various sludge particles.

Chitin is the second most widely occurring natural carbohydrate polymer next to cellulose, and is widely distributed in nature, being the main structural polysaccharide that forms the characteristic exoskeleton of most invertebrates.[36] It has been widely studied as an adsorbent for textile DSs.[37–41] Adsorption of a direct and a reactive green DS (cibacron green T3G-E and Solophenyl green BLE-155%) respectively from wastewater onto three low-cost materials containing chitin were also investigated by Figueiredo et al.[42] The materials were naturally available in Portugal, being also wastes from their seafood industry: Squid and Sepia pens, and Anodonta shells. The isotherms were determined at 20 and 50°C and they well fitted a Langmuir model. Continuous adsorption of the DSs was carried out using the adsorbents squid, sepia pens and anodonta shells in a packed column at 20°C. The adsorption experiments were simulated using a complete model, which includes axial dispersion, external and internal mass transfer resistance and chemical reaction. Results revealed that the squid pen showed the biggest adsorption capacity for both DSs, followed by Sepia pen and Anodonta shell. The isotherms also show that the adsorption capacities of the materials decrease when the grain size increases, probably due to the inaccessibility of the adsorbent micropores by the large DS molecules. This is also confirmed by the parameters used in the mathematical simulations of the continuous column experiments indicating that there is a large and dominating internal resistance. Chitosan, which is produced by deacetylation of chitin, also has the potential as a separator. The unit molecule of chitosan has one amino group.[43] Its saturation capacity as an adsorbent, and which decreases with increasing the degree of cross-linking gives the concentration of the fixed amino group in the adsorbent phase. It is 3–5 times larger than those of commercial weak base ion exchangers. Yoshida et al.[43] developed cross-linked chitosan fibers, which appeared technically and economically feasible in recovering univalent anionic dyes by adsorption. Equilibrium isotherms for adsorption of Acid Orange II (acid dye) on cross-linked chitosan fibers (CFs) were correlated by BET equation for finite layers at $\mathrm{pH}=6.9$ and were almost rectangular at $\mathrm{pH}\leq 4$. The saturation capacities of the DS adsorbed on CFs at $\mathrm{pH}\leq 4$, were around 2 times larger than activated carbon fiber. When $\mathrm{pH}\leq 4$, breakthrough curve was independent of pH of the solution and the breakthrough times are much longer than that at $\mathrm{pH}=6.9$.[43] The authors also demonstrated the effect of feed concentration and temperature by breakthrough curves. The curves indicated that the lower the concentration of the DS is, the longer the breakthrough time becomes, and that the breakthrough time at 323 K is longer than that at 298 K. The results suggest that CF of a higher degree of cross-linking is feasible for recovery of anionic DSs from acid solution. In addition, since the dyeing process, in which acid DSs are used, is normally operated in pH = 3–4 adjusted using acetic acid, it is not necessary to add acetic acid into the wastewater discharged from the dyeing process furthermore.

The decolorization of DSs wastewater by the saccharide caramelization was studied by Tsuchida et al.[44] Decolorization was recommended by the use of saccharides as arabinose, xylose, etc. and/or water soluble starch in the presence of divalent metal ions as Fe, Mn, Co, and Cu. The caramelization was carried out at 20°C and at a controlled pH and it was followed by filtration to obtain a clear liquid.

Adsorption and removal of commercial DSs were studied in aqueous suspensions of fly ash mixtures with a sandy clay loam soil of low organic matter content by Albanis et al.[45] The commercial DSs, Acid Orange 7, Acid Yellow 23, Disperse Blue 79, Basic Yellow 28 and Direct Yellow 28 represent the widely used nitroazo structures. Batch and column experiments were carried out at equilibrium conditions for concentrations of DSs between 5 and 60 mg/L. Adsorption increased with the increase of fly ash content in adsorbent mixtures. The mean removed amounts of DSs by adsorption batch experiments in soil mixture with 20% fly ash content were in the range 53 to 96.8% for different acid, direct, basic and disperse DSs respectively. The removal of DSs from column experiments were found to decrease with increase of the solution concentration from 10 to 50 mg/L at 20°C, showing the process to be highly dependent on the solution concentration. The mean removed amounts of DSs by adsorption in columns of soil mixture with 20% fly ash content and for an initial concentration of DS solution 50 mg/L varied between 33.8% for Acid Yellow 7 to 98.2% for Basic Yellow 28. The results of the batch studies showed that adsorption of azo-DSs (acid, basic, direct and in dispersed solid form) on soil-fly ash is quite satisfactory. The authors stated that the major advantages of an adsorbent system for water pollution control are less investment in terms of both initial cost and land, simple design and easy operation, no effect by toxic substances, and superior removal of organic waste constituents as compared to the conventional biological treatment processes. The adsorption techniques have been found to be useful means for controlling the extent of water pollution due to DSs, and that fly ash is a material showing a pronounced removal of azo DSs from aqueous solutions under alkaline conditions.

4. COMPLEX FORMATION AND CHEMICAL PRECIPITATION

Chemical precipitation is a process by which a soluble substance is converted to the insoluble form either by a chemical reaction or by changes in the composition of the solvent to diminish the solubility of the substance in it. The precipitated solids can then be removed by settling and/or filtration.[46] The method is applicable to the treatment of aqueous hazardous wastes containing toxic constituents that may be converted to an insoluble form. This is not readily applicable to wastewaters containing DSs. Accordingly, the method is not commonly applied for the removal or recovery of DSs from waste streams.[47]

However, few workers have applied precipitation and complex formation as a means of decolorizing DSs in wastewaters. Buschmann et al.[48] decolorized textile wastewater by the formation of DS inclusion compounds by the use of the ligand cucurbituril. The removal of the DSs was possible in the presence of textiles auxiliaries, and the COD was not influenced by the decolorization. They regenerated the ligand by the use of ion-pair extraction and by the oxidative destruction of the DS molecule.

Precipitation of reactive DSs wastewater by the addition of alkaline earth metal salts was also effected.[49] Precipitation was possible at $pH>9.5$. The process was recommended for wastewater from dyeing of textiles containing cellulose fibers.

The treatment of the textile mills effluent with that from the sulfate route titanium dioxide plant, which is composed of 18% sulfuric acid, 16–17% ferrous sulfate and 1–3% titanyl sulfate was also investigated for color removal.[50] Mixing of the two effluents results is a thickened sludge, which is removed and therewith removes most of the color and 65–70% of the COD and BOD. The titanium dioxide manufacturing waste could be pretreated to remove titania hydrate, to remove $FeSO_4.7H_2O$, and to neutralize part of the sulfuric acid using bauxite, scrap iron, iron ore, mill scale, or magnesite.

5. FLOCCULATION AND COAGULATION

Flocculation and coagulation was applied as a means for removing DSs from their wastewaters by numerous researchers. Flocculation is an essential part of any chemical or chemically aided precipitation system, whereby gentle stirring or agitation is used to assist in particle contact after the chemicals have been added.[47] Flocs are formed, which can be separated from water by gravitational settling of the particles that are heavier than water.[47] Common flocculants based on ferrous, ferric, aluminium and calcium salts or bentonite usually do not flocculate reactive dyes completely. Almost quantitative flocculation is feasible with certain cationic polymers, but they necessitate a slight excess of the cationic compound that is toxic for fish, and this is usually undesirable. In addition, sludges formed from dyes and cationic polymers have poor settling characteristics. For this reason, a co-flocculant, e.g.

an iron or aluminium salt, is required, and this further increases the amount of sludge.[3]

Shepperd et al.[51] investigated the removal of DSs by adding a reducing agent to the wastewater, adjusting the pH to 2–7, then adding a particular charge neutralization mixture and adjusting the pH to <3.5, then adding a flocculant to the treated water. The authors recommended using a polyacrylamide flocculant.

Chitosan (extracted from shrimps and crab husks) was also used as a chelating agent for the flocculation of DS from wastewater. The COD removal efficiency was reported to be 85% at $\mathrm{pH} > 7$.[52]

Coagulation, was also carried out as a means for removing and recovering direct DSs from dyeing wastewater, using aluminium containing waste from Vat Golden Yellow ZhKh manufacture for recovery and reuse.[53] The recovered DSs were used in cement dyeing and surface hydrophobization.

The flocculation of Reactive Red X-3B using MGS (a novel flocculating agent prepared by the condensation of dicyandiamide, formaldehyde and thiourea) was carried out by Chen.[54] Addition of 5 gm MGS/gm DS at pH 10 resulted in a supernatant liquid with 100% transmittance indicating complete removal of DSs.

A mixture of polydimethyldiallylammonium chloride and polyaluminium chloride in the presence of 1–5% sulfate and some alkalis was also used for the coagulation of DSs in dyeing wastewater.[55] The supernatant of the treated liquor contained low turbidity and low residual color, indicating efficient DS removal.

In another paper, industrial wastewater containing anionic DSs was treated with a mixture of organic coagulant (mainly containing polydiallyldimethylammonium chloride) and an inorganic coagulant (such as ferric chloride or aluminium sulfate or polyaluminium chloride) at pH 4–5 to effect coagulation effectively.[56] The supernatant treated water was colorless.

The coagulation of reactive DSs present in wastewater was effected by treatment with ferrous sulfate, polyaluminium chloride and polyacrylamide.[57] The removal efficiency reached 84–94% with the addition of 750–950 mg/L ferrous sulfate at a pH 8.0–9.3, and reached 85–93% with the addition of 2 mg/L polyaluminium chloride and 700–900 mg/L polyacrylamide at a pH 5.4–6.6. Coagulation with ferrous sulfate resulted in lower sludge content and increase of turbidity and decreased the effluent dissolved oxygen.

6. MEMBRANE SEPARATIONS

Membrane separation processes are destined to play an increasing role in the reduction and/or recovery of hazardous wastes. These processes include reverse osmosis (RO), hyperfiltration (HF), ultrafiltration (UF), nanofiltration (NF) and others. They can function in several ways: volume reduction, recovery and/or purification of liquid phase, and concentration and/or recovery of the solute.[46] Whereas NF is used to separate water from a feed stream containing inorganic ions, UF is primarily used to separate organic components from water according to size (molecular weight) of organic molecules. UF and HF membranes are manufactured with capability to remove contaminants with molecular weights between 500 and 10,000. They are suitable therefore for recovering DSs from textile-industry effluents.[46]

Kozlov et al.[58] investigated the UF of pigments and acid DSs at 0.2–0.3 MPa and 10–30°C. 98–99% of the pigments were removed whereas, 84% of the acid DSs were removed. The permeate contained a maximum of 25 mg/L DS concentration which required further secondary treatment.

Dyeing effluent treated with a cross flow UF membrane efficiently enabled 97–99% of the permeate to be recycled to the dyeing process.[59]

UF of wastewater containing direct (indigo) DSs, with a nitrocellulose membrane filter having openings <0.3 μm was investigated by Koyama[60] under pressure or diminished pressure. The author was able to recycle the treated effluent.

Majewska-Nowak et al.[61] used capillary modules in a process that involved capillary membranes made of polysulfone (PS) and modified PS for the UF of both synthetic and actual DSs wastewater solution. The synthetic DSs (Direct Black Meta, Helion Grey, and Methyl Orange) solution was ultrafiltered at (0.05, 0.1 and 0.15 MPa) and (0.5, 1, 1.5 m/sec.) linear velocity. The actual textile effluents were filtered for 50 hrs at a pressure of 0.1 MPa and a linear velocity of 1 m/s. The results showed that the increase in the linear velocity generally improves the permeability and selectivity of the membranes, the relationship was pronounced at high molecular weight. The retention coefficient for organic DSs with molecular weight >780 exceeded 92–99% for synthetic DS solutions, while the removal efficiency for the actual DSs solution was 42–65% and 70–98% for the total carbon and the color respectively and the permeability remained at a constant level.

Majewska-Nowak et al.[62] also investigated the UF of organic DSs solution using PS rod type membrane which was cast from 12.5% PS solution and were gelled in a bath containing 1.5% dimethylformamide. The membrane displayed very good transport and separation properties. It retained organic DSs molecules of molecular weights >600 with an efficiency of 96–99% at 0.15 MPa and a volumetric flux around 2.4 m^3/m^2 day. The authors investigated the use of polyvinyl chloride and the polyacrylonitrile membranes, as well, and which were found to display similar transport and separation properties to PS membranes. The authors presented the suggested mechanisms that are likely to govern the separation of organic DSs by these membranes.

Spirally-wound membrane modules were applied in the recovery of dyeing process chemical auxiliaries, water and energy, from a dyeing effluent.[63] 80% of the dyeing process chemical auxiliaries, water and energy, could be recovered. The latter was recovered in the form of hot water at 90°C. The payback time for the process was calculated to be between 18–30 months depending on the degree of automation installed in the unit.

NF acetate membranes were investigated for the recovery of X-36 reactive DS from wastewater by Guo et al.[64] The authors studied the various factors affecting the membrane performance, such as solvent and additives in casting solution, and operating pressures.

RO was also studied for the recovery of textile auxiliary chemicals and water by Thakur et al.[65] A styrene based RO membrane was capable of removing >97% of a disperse DS at 100 ppm concentration and pH 3.2–9.2.

The usage of membrane separation in textile washing processes by RO was found to be the best method to obtain water free from all ions including sodium and chloride ions.[66] NF was found preferable when only DS components are to be removed or when sodium sulfate is used instead of sodium chloride. For the washing processes the wash water should be free from sodium chloride as it diminishes the washing out of the hydrolyzed reactive DSs. For such reason the RO membrane should be used for the washing processes.

7. CHEMICAL OXIDATION AND REDUCTION

Chemical oxidation and reduction processes have been used to treat a wide variety of hazardous wastes. Although the chemicals may be expensive, such treatment can result in the removal of the target chemicals from the waste stream without the production of other process water or waste streams, as is accomplished with ion exchange or activated carbon. The increase in regulations preventing the discharge of toxic chemicals or wastes into the environment may serve to expand the uses of the chemical oxidation and reduction processes. In oxidative processes, an attempt is made to hit weak points in the DS molecule with the aim of destroying the chromophore as selectively as possible or of converting it into a readily biodegradable form.[3] Nowadays, the classical oxidizing agents, chlorine or hypochlorite, are hardly used owing to the formation of organic halogen compounds, and other numerous materials are being used.

Various methods of oxidation and/or reduction have been mentioned in the literature. Hamagushi et al.[67] developed a process that is economic and provides rapid decolorization of dyeing wastewater. The process involved treating wastewater with a reducing agent such as dithionites and sulfites followed by treatment with oxidizing agents as hydrogen peroxide and metal salts. The process provides economical and rapid decolorization of dyeing wastewater.

Poulakis et al.[68] investigated the decolorization of dyehouse wastewater through the use of peracetic acid (PA), hydrogen peroxide (HP) and UV light. The UV decolorization time for Reactive Red 123 was 1 hr, which was reduced to 6–8 minutes by the addition of oxidants as HP and PA respectively. The addition of sodium carbonate to the PA did not alter the reaction rate, but in the case of HP the reaction was slowed down. The reaction time for both oxidants was doubled by the addition of sodium sulfate. Shortening of the treatment time was achieved by the addition of the PA in portions at certain time intervals or continuously. Direct DSs (Orange 39, Blue 243) and the metal complex DS Isolan navy blue S-RL were decolorized in the presence of UV much more rapidly with PA than with HP. The use of PA as a per acid was also used successfully to decolorize textile dyeing wastewater in the presence of a heavy metal catalyst such as cobalt oxide.[69]

The decolorization of 2 non-biodegradable monoazo DSs (Acid Red 1 and Acid Yellow 23) in wastewater by an advanced oxidation process using UV and HP was carried out by Shu et al.[70] The effect of HP dosage, pH, initial DSs concentration, and UV light intensity was studied. It was observed that the decomposition of both azo DSs were a pseudo first order reaction with respect to the azo DS concentrations, and the necessary time for 50% of the DS removal and the observed pseudo first order rate constants were used as parameters to show the efficiency of azo DS treatment.

Decolorization of spent dye bath effluent with small amount of HP at high temperature near the boiling point was also effected.[71] Initial studies showed that azo and anthraquinone DSs were resistant to decolorization with HP alone, whereas the copper phthalothianine based DS was decolorized with the hot HP. The decolorization of the mixture of copper phthalocyanine DS with an anthraquinone DS and an azo DS revealed that the copper contained DS catalysed the oxidation of the other DSs. The ferrous and ferric ions catalysed the decolorization similar to the cupric ion.[71]

The treatment of the dyeing effluent containing reactive DSs with HP and ferrous sulfate as a catalyst at 15:1 molecular ratio was investigated by Achwal.[72] He claimed that the treatment was more economical than oxidation with ozone, or UV light and HP.

Reissig et al.[73] attempted to decolorize dyeing effluent using UV light together with ozone or HP. The Crypur monoazo DSs and the Remazol black reactive DS decolorized within 5–60 minutes through treatment with ozone and HP, while the indanthrene vat DS required a treatment time of 5–6 hours using ozone, HP and UV light. The treatment decreased the TOC and increased bioavailability of monoazo and reactive DSs but had little impact on vat DSs.

Organic wastewater containing pigments, which are resistant to biological treatment such as activated sludge or aeration was decolorized by the use of UV radiation together with HP or ozone as oxidation promoters by Kotani.[74]

The discoloration of aqueous DS solutions induced by UV light in the presence of ferric ions and humic acid was studied under the conditions typical for natural surface waters with high dissolved organic carbon concentrations.[75] The presence of ferric ions and humic acid in the DS solutions significantly enhance discoloration efficiency. The discoloration rate of DS solutions decreased with increasing pH values in the pH range 3–6, while it increased with increasing concentrations of ferric ions over the range 2×10^{-4}–2×10^{-5} mol/L. The optimal concentration of humic acid under the examined condition was 0.5 mg/L and the initial concentration of the DS solution also had some effects on the discoloration efficiency of the DSs.

Lin et al.[76] investigated the treatment of wastewater from a secondary wastewater plant of a dyeing and finishing mill for possible reuse. The purification of the effluent was carried out by a combined Fenton process, chemical coagulation and ion exchange. The Fenton process and the coagulation removed the color, turbidity and COD, while the ion exchange is used further to lower the COD and the iron ions concentration, total hardness, suspended solids, and total dissolved solids. The treated water quality was good enough to be reused in the textiles processes.

The utilization of the Fenton reaction for the degradation of some DSs produced by Bayer and Sandoz was also investigated.[77] The mean decolorization of the DS solutions was above 98%. The optimum conditions were at pH 3, HP to ferrous sulfate ratio of 1:(1–2) at 24°C and 1 hour reaction time. The addition of flocculant during the neutralization stage improved the results. The reduction in COD ranged from 24% to 94% depending on the type of DSs and wastewater.

Michelsen et al.[78] used a pilot plant with a cascading sequence of continuously stirred tank reactors for the chemical decolorization and removal of metals and dissolved organic carbon from the concentrated dyeing waste discharge through the use of oxidizing and reducing agents. The oxidizing agent was Fenton's reagent, and the reducing agents were thiourea dioxide and sodium hydrosulfite. Ferrous sulfate was premixed with the DS wastewater before overflowing to the first reactor. A feedback control system based on color remaining in the discharge was used to regulate the added reactants. Transmittance was measured at several wavelengths (590, 540 and 438 nm) and the American Dye Manufacturers Institute (ADMI) value was calculated. The results demonstrated that ADMI measurements could not be made on dark solutions (over 3000 ADMI) in the pilot plant and typically one wavelength was used for control. DOC removal was used as a means for determining the biological activity in aerated reactors following color removal. The initial pilot studies were conducted using Navy 106 jet-dye waste. Reductive pre-treatment with thiourea dioxide resulted in 92.2% color removal with color returning upon aeration for an overall color removal of 76.6%. The oxidative treatment resulted in a color removal of 98.8% with overall color removal of 96.8% after the aerobic treatment. DOC removal in aerobic treatment improved with oxidative pre-treatment relative to reductive pre-treatment on navy 106 jet-DS concentrates. On site operation of the pilot plant on other DS wastes showed color removals >95%, and DOC removals of 38 and 19% respectively, for an azo-based red DS waste concentrates and copper-phthalocyanine-based DS, Ming Jade. The soluble copper concentration in the Ming Jade was decreased from 19.2 ppm to 4.5 ppm. The results showed that, continuous oxidative pre-treatment with a 15 minute residence time was controllable and more effective than reductive treatment for color removal.

The prevention of the pollution from colored wastewater containing DSs was studied through the evaluation of the color and the determination of the composition of the colored compounds, by capillary electrophoresis and electrokinetic chromatography.[79] Oxidation of the colored wastewater with Fenton's reagent and electrolytic and wet oxidations was effected.

Decolorization of dyeing wastewater with Fenton's reagent was also investigated.[80] Five types of simulated wastewater, separately prepared with disperse, reactive, direct, acid and basic DSs were treated. The best pH value for decolorization was less than 3.5, the average percentage COD removal was 90% and the average percentage decolorization was over 97%. The results from treating DS wastewater from actual dyeing and finishing mills are similar to those in the laboratory. Increase of temperature increased the rate of decolorization.

HP and iron powder system was also used in decolorization of commercial DS wastewater.[81] The decolorization kinetics and mechanisms of the DSs were studied. The oxidation kinetics and mechanism of Reactive Red 120, Direct Blue 160 and Acid Blue 40 was investigated in a batch reactor. The optimum pH was 2–3 depending upon the DS molecular structure and the iron dissolution rate. The iron metal optimum concentration was 0.001–1 gm/L. The initial oxidation rates were obtained according to a pseudo first order reaction kinetics. The structure of the DS was found to influence the kinetics of the oxidation. The results suggested that the substituted anthraquinone ring in Acid Blue 40 is readily destroyed than the azo DS. The color change during the decolorization may result from the formation of DS complexes with the iron species. The iron powder together with HP were more efficient in decolorization than the Fenton's reagent due to the continuous dissolution of the iron powder and adsorption of the DS on the iron powder, despite the fact that the Fenton' reaction was the major process contributing to decolorization.

Decolorizing dyeing effluents, by a coagulation step, followed by the oxidation of the non-separated colored part in the filtrate by chlorine dioxide gas, was also effected by Santo et al.[82] The resulting decolorized water quality was good enough to be reused.

Ogawa et al.[83] investigated the decolorization of wastewater containing pigments by passing through an apparatus generating chlorine dioxide together with an optional treatment with a polymer flocculant.

Catalytic air oxidation was also used using manganese oxide catalyst at normal temperature and pressure as performed by Xu et al. for the decolorization of dyeing wastewater.[84] The degree of decolorization was over 90%.

8. ELECTROCHEMICAL METHODS

Interest in the use of electrochemical processes for the treatment of wastewaters containing organic pollutants is continuing to grow. The anodic oxidation of waters containing phenol is well documented.[85,86] The implementation of electrochemical processes in the treatment of wastewaters can result in the destruction of the organic contaminant and lead to a total reduction in the COD and BOD of the effluent.[87–89] The method is simple and the process operating requirements and area are significantly less than conventional treatment processes.[1] Dye house effluents normally contain significant quantities of dissolved organic DSs. They are often highly colored and have a high COD. The complex nature of some of the reactive DSs used in industry results in an effluent, which can be bio-resistant, highly colored and unacceptable for discharge into surface waters.[1]

Water electrolysis with corrodible iron electrodes forms highly oxidative oxygen together with ferrous ions, which have an additional catalytic effect that oxidize the DSs. The pH change near the iron anode precipitates ferrous and ferric hydroxide (or aluminum hydroxide in case of aluminum anode) which acts as flocculants. Resultant flocs are separated from the aqueous phase by flotation with the O_2 and H_2 gases produced at the electrodes.

The electrochemical oxidation of DSs wastewater was studied by various researchers. Jia et al.[90] devised a method for generating radicals on activated carbon fiber electrodes in combination of flocculation for the removal of DSs from wastewater. HP was used for the generation of OH radicals and an aluminium-iron flocculant was used for flocculation. The color removal was more than 90% and the TOC removal was around 60%.

The decolorization of wastewater containing DSs with the in situ generation of OH radicals was also studied by Chen et al.[91] Methyl orange was studied as a model DS. Decolorization was due to the chemical reaction with the OH radicals generated from the decomposition of HP, which was formed from the cathodic reduction of the oxygen. Agitation rate, ferrous ions concentration and concentration of the methyl orange were the major factors affecting the decolorization. However the oxygen partial pressure and the temperature did not affect the decolorization significantly. Direct current in the range from 0125 to 0.375 mA/cm^2 or potential at about 90 mV (Ag/AgCl) was optimal.

Dyeing wastewater treatment by a process that comprises pH adjustment (acidic), filtration, removal of coarse particles and electrolysis, was investigated by Takaoka.[92] The wastewater is mixed with sodium chloride prior to electrolysis to generate hypochlorous acid. The electrolysis unit contained many alternating anodes and cathodes and one or both sides of the electrodes had spaces for storing plant-derived charcoal. Flocculation is proceeded during electrolysis and the floc is settled in a floc maturing tank. Degradation and decolorization of azo-complex DSs in a micro-electrolysis cylinder filled with activated carbon and zeolite powder was effected by Yang et al.[93] The efficiency of decolorization and degradation increased with increase of the applied potential, the electrolyte concentration, the retention time and with the decrease of the DS concentration in the effluent.

Kolesnikov et al.[94] investigated the removal of organic DSs from wastewater by electro-flotation. The method is based on particle adhesion by the highly dispersed micro-bubbles of oxygen and nitrogen generated during electrolysis. The authors compared the operating characteristics and pollutants concentrations before and after treatment.

An apparatus for the treatment of dyeing effluent was designed by Hatano et al.[95] The apparatus includes a pump supplying wastewater, a pH adjusting means, a supply for sodium chloride, an electrolytic cell to decompose the DSs acidified with hydrochloric acid, and a means for separating colloids from wastewater. The DS is decomposed by the hypochlorous acid generated from the electrolysis. The positive electrode could be made from charcoal or a metal like iron or aluminium. In case of using the metal electrode the electrolysis will result in the formation of metal chloride coagulant.

Allen et al.[1] demonstrated the success of the electrochemical reduction of the color imparted by organic DSs in wastewater by the use of a simple cell, which is shown in Figure 5. The process has been able to reduce color from organics from levels as high as 200 ppm down to zero (see Figure 6). The rate of removal has been shown to be a pseudo-first-order reaction. The rate constant has been related to the concentration of electrolyte (Figure 7) and also the type of electrolyte used in the cell (Figure 8). The rate constant increases as the electrolyte concentration increases and also as the initial DS concentration is reduced. In addition, the half-life for oxidation at low concentration is reported to be significantly less at low DS concentrations and at high electrolyte concentrations.

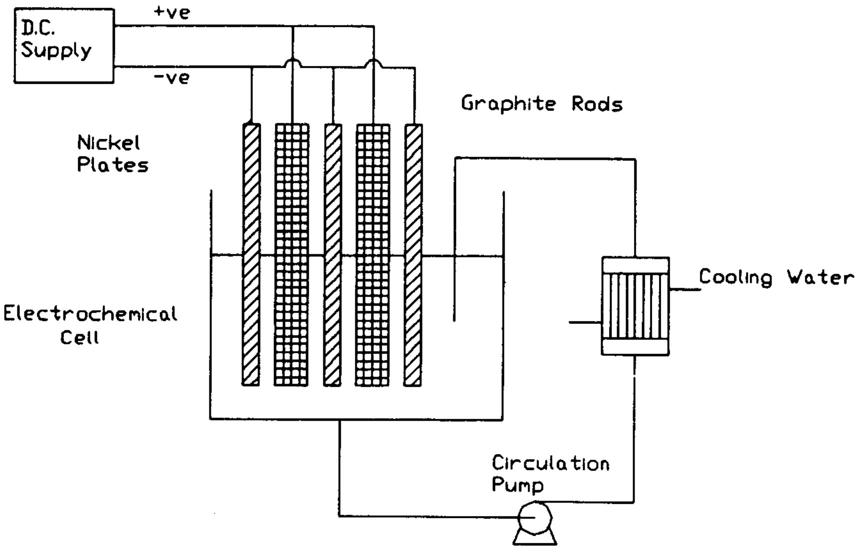


Figure 5. The electrolytic cell used in the electrooxidation process.

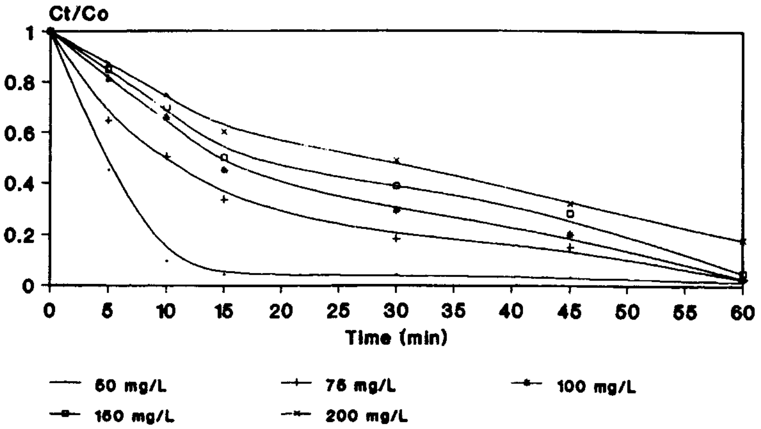


Figure 6. Concentration decay curves for Acid Red 88. ─■─ 50 mg dm^{-3}; ─┼─ 75 mg dm^{-3}; ─☆─ 100 mg dm^{-3};─□─ 150 mg dm^{-3}; ─×─ 200 mg dm^{-3}.

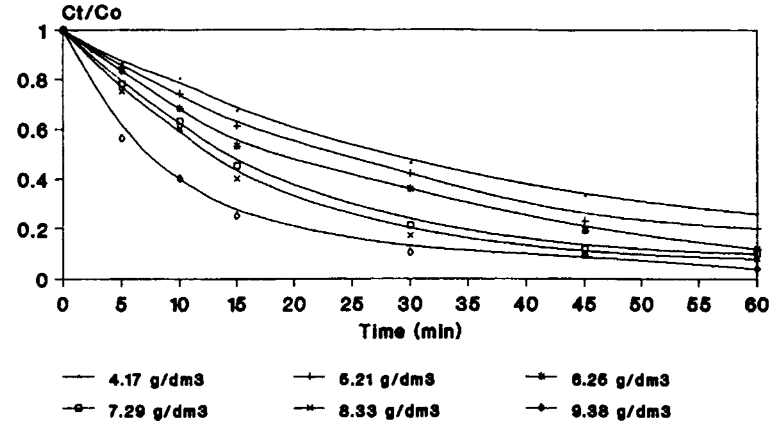


Figure 7. Effect of concentration of electrolyte on the concentration of Acid Red 88. —■— 4.17 mg dm^{-3}; —+— 5.21 g dm^{-3}; —☆— 6.25 g dm^{-3}; —⊟— 7.29 g dm^{-3}; —×— 8.33 g dm^{-3}; —◇— g dm^{-3}.

A micro electrolytic cell containing iron was used to treat dyeing wastewater for 30 minutes at pH 5–6 followed by precipitation and filtration.[96] The method resulted in a COD removal of 75% and a color removal of 99%. The method costs were claimed 30% less than the conventional coagulation-biological method.

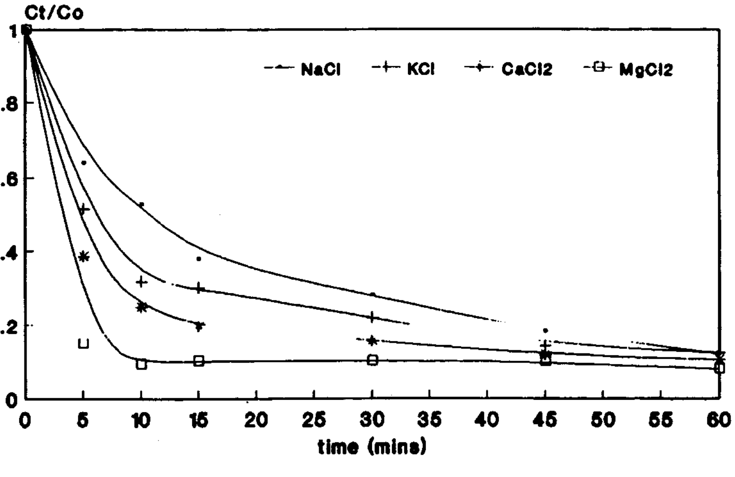


Figure 8. Effect of different electrolytes on the rate of oxidation.

9. PHOTO CATALYTIC DECOLORIZATION

More than 3×10^8 pounds of DSs are produced annually in the United States. DSs pose a potential environmental hazard since their manufacturing produces and involves a variety of organic chemicals, some of which have been shown to be carcinogenic.[97] DS manufacturing plants, textile plants, and newsprint recycling mills discharge DSs in their process water, which must be treated before it can be released into the aqueous environment.

Over the past decade, photo assisted catalytic degradation of organic compounds in aqueous solutions has been a subject of interest. Several studies have dealt with the fundamentals of the photo catalytic process, the effects and optimization of various reaction parameters, analysis of the degradation pathways, and the identification of the intermediates and final degradation products. Since the direct use of concentrated solar energy to supply the energy needed to drive chemical reactions is possible, a study to establish an efficient and practical method for using highly concentrated sunlight to completely mineralize several organic DSs, was also indicated by Reeves et al.[97] They have evaluated the ability of highly concentrated solar energy to destroy a variety of organic DSs through the photo assisted catalytic action of TiO_2. Figure 9 clarifies the strong effect of both light and catalyst together on the destruction of malachite green. The DSs, which were chosen (malachite green, crystal violet, methyl orange, Congo red, methylene blue, sodium alizarinsulfonate, and fluorescein) represent the major structural families of

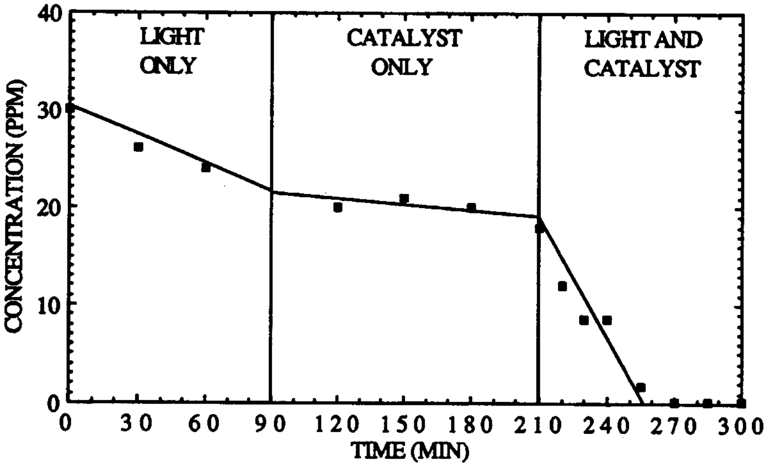


Figure 9. Effect of concentrated simulated solar radiation and presence of TiO_2 (Degussa P25, 0.2% by weight) on destruction rate of 30-ppm malachite green in water.

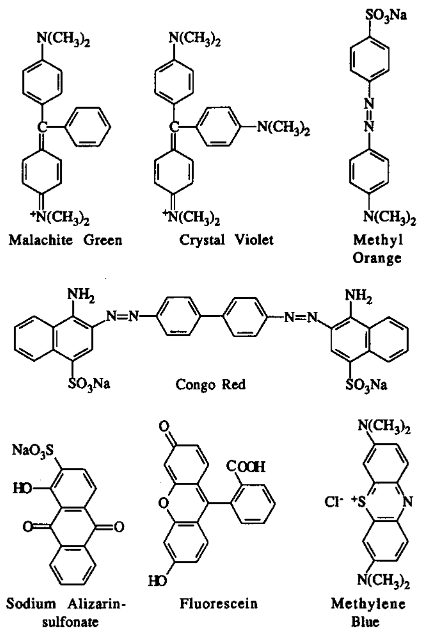


Figure 10. Structures of organic dyes used in this study.

organic DSs. Figure 10 presents structures of DSs used in their study. Table 3 shows that all the DSs were destroyed completely in less than 20 minutes. A variety of parameters including the type of TiO_2 and degree of catalyst loadings, as well as the effect of flux on the rate of the reaction, have been evaluated and optimized. The increase in the flux resulted in an increase in the

Table 3. Destruction Rates of Various Dyes in the Solar Simulator

Dye Solution Initial Conc. 30 ppm	Class of Dye	Time for Concentration Reach <1 ppm (min)
Malachite green	Triarylmethyl cationic	10
Crystal violet	Triarylmethyl cationic	15
Methyl orange	Azo	5
Congo red	Azo	10
Methylene blue	Heterocyclic	15
Sodium alizarinsulfonate	Anthraquinoid	5
Fluorescein	Phthalein	12

Catalyst used was Degussa P25 TiO2 (0.2% by weight).

rate of decomposition of the DSs. They also described reactors utilizing a solar simulator system and a concentrated natural solar system. There was a significant rate increase as flux increased from 15 suns (solar simulator) to 150 suns (solar dish concentration) with the increase in the rate of decomposition being slightly greater than the square root of the increase in flux. The authors concluded that a potential exists for the use of highly concentrated sunlight in the removal of textiles DSs and biological stains from wastewater.

The degradation of organic DSs by solar energy was studied by several researchers. Uygur[98] exposed 11 reactive DSs to different pH values in daylight and in the dark, laser radiation, UV radiation, and UV radiation with HP application at alkaline pH and at acidic pH values. It was observed that the decolorization at pH 2 is faster than at other pH values, and the decolorization at daylight is faster than that in the dark. The best decolorization was obtained by UV and HP at pH 1.

Photo catalytic degradation of reactive DSs was also carried out with solar irradiated titanium dioxide.[99] The decolorization efficiency was affected by pH, amount of catalyst and light intensity. The reactive DSs decolorized rapidly through the cleavage of the azo bond, but the intermediates needed more time for further degradation. The main products were alkanes and alkyl amines, which could be more easily biologically degraded. The authors observed that the toxicity decreased after photo degradation.

10. OZONATION

Ozone has been used for more than 85 years, primarily for the disinfections of municipal drinking water. At present there are more than 1200 water plants using ozone for disinfections and color and odor removal as well as 100 wastewater plants using ozone worldwide. Because textile wastewaters contain a variety of organic DSs and chemical additives, textile DS wastewater are extremely complicated and difficult to treat. Of the many unit treatment processes for textile wastewaters, the most recent is treatment by ozone. Process selection depends on the type and concentration of DS wastewater needed for acceptable discharge. Ozone combined with hydrogen peroxide or UV has been used for the decolorization of wastewater. Ozone and/or coagulation was used to treat textiles wastewaters at several manufacturing plants to obtain various degrees of effluent quality from opaque to crystal clear. The object was to recycle rather than discharge the wastewater. Twenty test runs were completed with eight different DSs and 100% wastewater recycling. Energy savings were obtained as a result to treating the water and returning it to the system. Dyed products were acceptable.

Ozonation has been accomplished in several ways. Decolorization of dyeing wastewater by spraying the wastewater into an ozone atmosphere was one way, which causes the oxidation of the DSs on contacting with ozone, followed by decomposition of the ozone.[100]

Decolorization of dyeing wastewater was also carried out by mixing the colored wastewater with water containing sufficient dissolved ozone in a main ozone reactor for ozone aeration.[101]

The decolorization of 16 soluble DSs by ozonation at an ozone flow rate of 0.5 L/min. using 18.7 mg/L ozone at 20–24°C was carried out by Takahishi et al.[102] The decolorization rate was measured by the absorbance, dilution and Pt-Co methods. The decolorization rate and was found to be pseudo first order reaction with respect to ozone dosage. The color measured by the three methods correlated with each other.

Gähr et al.[103] also investigated ozonation of textile wastewater. The author claimed the ozonation method to comply with the new German law for textiles wastewater treatment. Table 4 presents the limiting parameters for textile wastewater in Germany, while Table 5 gives a short overview of potential steps for wastewater treatment of selected effluents organized according to the textile finishing processes.

Decolorization of DSs solutions with either ozone or chlorine was investigated by Namboordi et al.[104] The common disperse and direct DSs were dispersed or dissolved in distilled water and treated with sodium hypochlorite or ozone. The rate and extent of colour removal were determined. The effect of pH, temperature, and DS solubility in the treatment of medium were measured during chlorination. In an aqueous medium chlorine caused rapid removal of a portion of disperse DS color and the remaining colour was resistant to chlorination. Complete decolorization of disperse DSs in aqueous ethyl alcohol was obtained with low doses of chlorine. This indicated that the DS solubility in water was an important factor in the resistance of disperse DSs to decolorization. Complete decolorization of direct DSs was obtained

Table 4. Parameters for Textile Wastewater in Germany

Colour: 436 nm (yellow)	7 m^{-1}
525 nm (red)	5 m^{-1}
620 nm (blue)	3 m^{-1}
Chemical oxygen demand (COD)	160 mg/l
Bio/chemical oxygen demand (BOD_5)	25 mg/l
Halogenated organic compounds (AOX)	0.5 mg/l
Aromatic compounds (benzene, phenol etc.)	0.1 mg/l
Chrome, copper, nickel	each 0.5 mg/l
Phosphorus	2 mg/l
Ammonia nitrogen	10 mg/l
No carriers, alkylphenol surfactants, arsenic, mercury	

Table 5. Treatment Techniques for Textile Wastewaters

Pretreatment	Dyeing	Printing	Finishing
Elimination of sizes via ultrafiltration Biological treatment Oxidation Combustion	Oxidation -Ozone -Peroxide/UV Anaerobic treatment Coagulation/precipitation: -Fe/Al-compounds -Quart, ammonia compounds Membranes: -Ultrafiltration -Nanofiltration Adsorption: -Activated carbon -Lignite -Ion pair extraction	Recycling of scour and rinse waters Anaerobic treatment of concentrated residues (Other methods see dyeing category)	Low pressure oxidation Precipitation via electrolytes at higher temperatures (90°C)

with low doses of chlorine at room temperature. For chromium complexed acid black 60 a significant amount of residual colour was observed and the increase of chlorine concentration and the lowering of the pH had only minimal effect during discoloration. Ozonation completely decolorized direct and disperse DS in short time periods relative to chlorination. Ozonation was found to lower the pH and to raise the conductivity of the DS solutions. Also acid, disperse, reactive and direct DSs were bleached with either Cl_2 or O_3.[105] Chlorine was found effective with the acid and direct DSs and some disperse DSs, whereas ozone was effective for all four classes of DSs. The authors also discussed the possibility of reuse of the spent dye-bath water after bleaching.

The efficiency of various contacting systems in ozonation was compared by McHugh et al.[106] Decolorization of acid red 49 was undertaken in cylindrical bubble column with an external recirculation loop. The reactor was operated batchwise with respect to the DS solution and continuously with respect to the gas phase. The stoichiometry of the system was deducted from the mass balances. The authors found that sparging of O_3 gave the highest mean ozone utilization efficiency.

The degradation of commercial azo DSs in water using ozonation and UV enhanced ozonation process.[107] Degradation of eight non-biodegradable azo DSs was investigated in a pilot scale photochemical reactor. The UV light did not enhance significantly the degradation ability of the ozonation reaction. No degradation was observed when the azo DS solution was irradiated with UV alone. The ozone dose and the azo DS concentration was found important. The degradation rate of azo DSs was found to be first order with respect to azo DS and ozone concentrations and the pH of the solution was decreased while the azo DSs degraded. The necessary time for the removal of 50% of the azo DSs and rate constants were used to determine the decomposition rate for each azo DS as a function of various conditions.

Ozone treatment of textiles effluents was also studied by Langley et al.[108] Ozone effectively eliminated color and odor, and destroyed many organic DSs. Trial was carried at municipal wastewater treatment plants where the dye-houses wastewater contribute a significant burden to the facility. Ozone reduced color by around 90% and reduced fecal coliform to levels equal or lower to chlorine treatment. The authors presented a study on ozone chemistry and design concepts and costs for ozonation systems.

Ozonation of dyeing and printing wastewater resulted in 99% color removal and 90% COD removal as reported by Cu.[109]

Various advanced oxidation processes for dyeing wastewater resulted in a TOC degradation according to the following order: UV and Fenton reagent > UV and ozone > UV, and HP = UV and titanium dioxide.[110] The addition of iron to ozone and UV gave no additional effect on the DS waste degradation.

The treatment of dyeing wastewater by ozone produced by surface electric discharge from high frequency high voltage pulse source, significantly decreased the COD value to less than 100 mg/L of the effluent.[111]

Zima et al.[112] studied the composition of textile dyeing wastewaters and the treatment practices specially with ozonation treatment. According to them the optimum ozone dosage required to remove 80–90% of the DSs was 100–200 mg ozone/m^3.

The effect of various variables in the ozonation of acid DSs was investigated by Beltran De Heridia et al.[113] The decomposition of the DS increased with increase in the stirring rate, ozone flow rate and partial pressure, and temperature. When the pH promoted the formation of the hydroxyl ions, the DS degradation was accelerated. The decomposition products were carboxylic acids and carbonyl compounds. The efficiency of the COD removal was over 60% for all the studied DSs after one-hour ozonation.

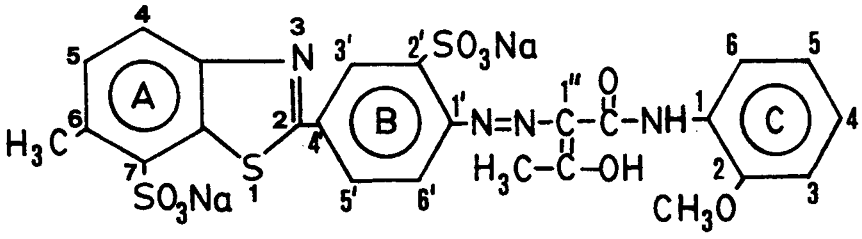
Sid'ko et al.[114] removed of DSs by ozonation with 23–27 mg/L ozone followed by batch adsorption on granular activated carbon of 0.25–0.5 nm. The authors revealed the dependence of the decolorization efficiency on the pH. Adsorption was ineffective in the removal of the DSs ozonation products when the ozonation was carried out at an alkaline pH, whereas adsorption on activated carbon gave an additional 40–60% reduction in the COD if the ozonation was done at neutral or acidic pH levels.

Zima et al.[115] studied the design and operation of an installation for decolorization by ozonation of textile mill wastewater. The designed degree of decolorization was obtained at energy of 4.25–5.6 KW/m^3 of wastewater.

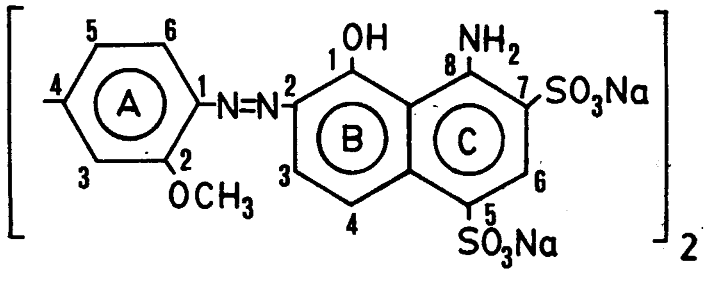
A great part of the textile industrial wastewater pollution is due to the presence of DSs, being constituted by low-biodegradable complex molecular structures with poly-substituted aromatic rings. As is known, aromaticity can be related to the precursor character of organohalogenated compounds, when some organic complex molecules are treated with chlorine. This problem is eliminated to a great extent by using ozone as oxidizing agent.[116] Previous researchers have shown ozonation as one of the best methods for DS destruction in treatment plants.[117]

The influence of the variables affecting ozonation of three azoic DSs: acid black 52, direct blue 1 and direct yellow 27 on the rate of decolorization was studied by Sotelo et al.[118] Ozonation was conducted in an agitated tank. Figure 11 shows the molecular structures of the three DSs. Results indicated that at the most favorable conditions (900 rpm and 90 L/hr) a 92% reduction in the DS concentration is observed in 5 minutes. It was also noted that only a 0.5% O_3 in the gas permits a 75% destruction in 8 minutes. Figure 12 presents the action of O_3 on the azoic dye molecule. The figure shows that O_3 can attack organics, both directly (dipolar addition, electrophilic aromatic substitution)[119] or via radical chain, by means of the hydroxyl radicals generated in

DIRECT YELLOW 27 λ = 398 nm



DIRECT BLUE 1 λ = 620 nm



ACID BLACK 52 λ = 537 nm

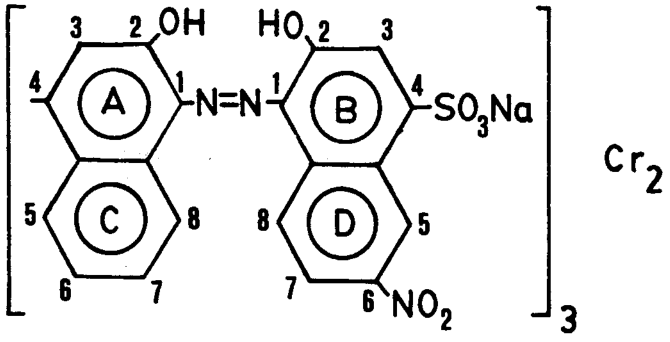


Figure 11. Azoic dye molecule structures and wavelength at which absorbances of their aqueous solutions are measured.

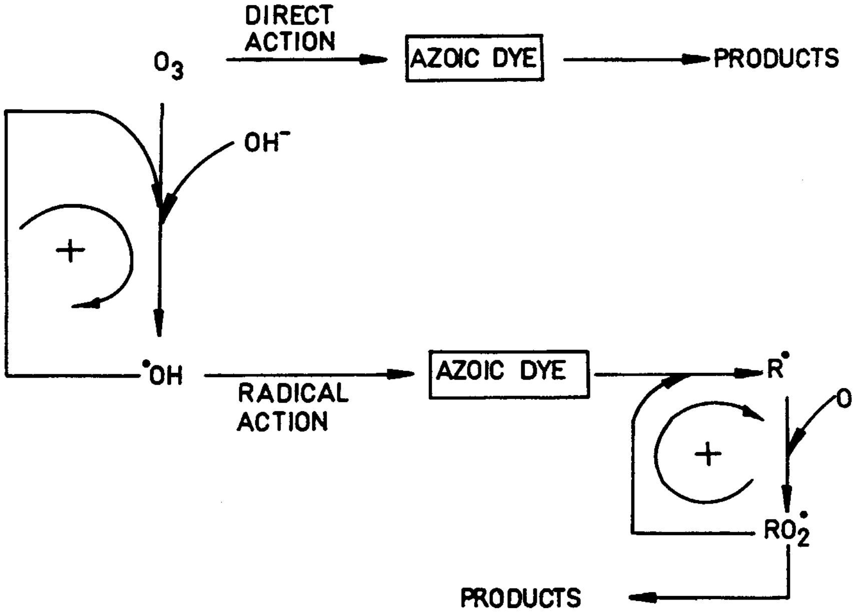


Figure 12. Ozone actions on azoic dye molecule.

its decomposition. Their work showed that the use of O_3 to eliminate azoic DSs in textile wastewater effluents is an advantageous method because it provides high decolorization rates and aromaticity reduction and, therefore, converts them in more bio-degradable substances, mainly low molecular weight aldehydes and carboxylic compounds.

The ozonation of solophenyl DS solution was studied by El Ebiary et al.[120] The reaction was a pseudo first order reaction and the chemical reaction rate constants were determined with respect to the ozone and the DS and found to be 0.03 and 0.06 min^{-1} respectively. From the knowledge of the physical mass transfer coefficient and the effects of the chemical reaction on the mass transfer, a proposed mathematical model was used to describe the overall reaction process. The mass transfer coefficient was 0.69 min^{-1}, which was increased according to the global reaction rate of ozone in the treated solution.

Treatment of dyeing wastewater through ozonation and UV radiation was also investigated by Kos et al.[121] Two different textiles wastewater samples from a polish knitting company were tested and the effluents before and after the treatment were analysed according to the Polish standard. The best results were obtained from the simultaneous ozonation and UV radiation.

Goheen et al.[122] investigated the degradation of various organic DSs by corona discharge. Several DS solutions were exposed to corona discharge, the light absorbance decreased for all organic DSs with time. Methylene blue, malachite green and new coccine were studied. The highest reaction rates were observed with the highest stirring rate, lowest salinity, smallest electrode spacing, and an environment containing enhanced levels of oxygen. The current was higher in the presence of nitrogen than in the presence of oxygen (for the same voltage) but the reaction of methylene blue did not proceed unless oxygen was present.

Pulsed corona discharge was also applied in the decolorization of dyeing wastewater.[123] The non-equilibrium plasma produced by pulsed high voltage discharge was allowed to contact the dyeing wastewater. The DS wastewater decolorized rapidly. The decolorizaion rate was over 95% when the wastewater was treated at a pulsed peak voltage of 38 KV for 40 seconds. The decolorization rate was affected by the pH of the wastewater. The suitable pH range was <4 or >7. The addition of sulfate ions increased the decolorization rate whereas the addition of chloride ions decreased the decolorization rate.

11. BIOLOGICAL METHODS

Industrial wastewaters containing biodegradable organic compounds such as DSs are quite often treated by biological processes. Either aerobic or anaerobic methods are used according to the characteristics of the wastewater and the level of the treatment needed. Aerobic processes generally are more appropriate for treating wastewaters containing COD less than about 3000 mg/L or BOD concentration less than about 2000 mg/L. Anaerobic processes generally are more suitable for treating high-strength wastewaters. In an increasing number of cases, anaerobic processes are used for pretreating high strength wastewaters to a level suitable for further treatment to aerobic processes. Design and satisfactory operation require consideration of a number of factors including solid retention time, organic loading rate and effluent waste characteristics, effluent and biomass recycle, media type, specific surface area and placement for fixed film processes, equalization, influent waste distribution, waste sludge withdrawal, operating temperature, and desired final end products (CO_2, N_2, CH_4, etc…).

Nigam et al.[124] isolated a microbial consortium PDW that was capable of rapid decolorization of important DSs under anaerobic condition. The decolorization was dependent upon the presence of a carbon and energy source in addition to the textile DSs. The PDW was capable of decolorizing DSs in the presence of cheap carbon sources such as lactose, starch and distillery waste. PDW removed 76% of color from textile plant effluent after 3 days.

The acclimation of a mixture of sewage and soil micro organisms to several azo DSs was investigated by Rakmi et al.[125] The acclimated culture was transferred to a continuous process, which was operated at various conditions. Colorless effluent was produced. The microbial studies showed the culture to consist of four species, Pseudomonas aeruginosa, Pseudomonas oryzihabitans, Acinetobacter calcoaceticus, and Citrobacter freundii. The metabolite analysis revealed that the DS had undergone azo bond cleavage followed by carboxylation, hydroxylation, and acetylation of the aromatic products.

Wu et al.[126] separated the purple non-sulphur photosynthetic bacteria from the activated sludge in an aeration tank at the Shanxi dyeing wastewater treatment plant. Twelve from fourteen DSs were decolorized under dark anaerobic conditions with efficiency over 75%. The effect of variables as temperature, pH...etc. on the decolorization and the decolorization mechanism were studied.

Treatment of dyeing wastewater in an anaerobic reactor containing purple nonsulphur photosynthetic bacteria followed by contact aeration and sand filtration was carried out by Wu et al.[127] It gave a 92% color removal and a 90% COD removal.

Das et al.[128] used the white rot fungus Phanerochaete chrysosporium NCIM 1197 to decolorize congo red, crystal violet and cresol red in malt extraction broth medium and in czapek dox medium supplemented with 3% glucose (CDG) or sucrose (CDS). Under static aerobic condition the fungus removed 70% of the congo red, 64% of the crystal violet and 96% of the cresol red, in 20, 17 and 12 days respectively. In an aerobic column bioreactor with a multistage inoculum holder, the organism efficiently decolorized 92% of crystal violet in 9 days in both CDG and CDS medium. The presence of increasing concentrations of lead ions in the medium (<20 ppm) gradually inhibited the decolorization. At 6 ppm lead ions concentration, only 4.5% inhibition of decolorization (compared to the control set without lead ions) was noticed but total biosorption of lead ions was effected.

Xian et al.[129] isolated 13 bacteria strains from the activated sludge and biofilm from the textile wastewater treatment plants. The strains had ability to decolorize DSs. They were identified as Aleromonas, Klebseila, Pseudomonas, Enterobacter, Alcaligene, and Corynebacterium. The strains D33, D32, D4 of Alteromonas can decolorize 20 types of DSs (2.6 mg DS/gm of wet cells-h) the optimum pH was 7–8 and the optimum temperature was 37°C. The growth of bacteria was 3 times better in stirred cultures than in static cultures, and the decolorization rate was 4–9 times higher in the latter than in the former. The examination of the reaction products of diamond chrome red B and diamond navy blue RRN indicated the possibility of biodegradation of these DSs by Enterobacter D17.

Decolorization of dyeing wastewater by mixed bacterial cells immobilized in polyvinyl alcohol was effected by Liu et al.[130] The mixed bacteria including Pseudomonas, Citrobacteria, and Bacillus immobilized in polyvinyl alcohol carrier granules were effective in decolorizing dyeing wastewater at 30–40°C and pH 7 with a hydraulic retention time less than 3 hours. The polyvinyl alcohol granules maintained the color removal efficiency at 70–80% for over one month.

Kakuta et al.[131] investigated the azo DSs wastewater treatment with immobilized yeast strain identified as candida curvata. The yeast strain decomposed methylene blue, chrysoidine, new coccine, orange I, orange II, acid blue 92, acid blue 111, acid red 37, direct blue 168 and direct red 2. Immobilizing the strain on granular ceramics maintained a high decolorizing efficiency for 90 days for 0.01% chrysoidine solution, and for 30 days for a mixture of DSs.

Biodegradation of direct, acid, reactive, disperse and vat DSs by the white rot fungus P-Chrysosporium ATCC 24,725 was investigated by Chen et al.[132] All these DSs were either totally or partially decolorized by the treatment.

Nakaoka et al.[133] investigated the degradation of four kinds of Reactive DSs by anaerobic microorganisms. The dyeing wastewater was treated by a sludge preincubated under aerobic conditions. The samples were anaerobically incubated in a 100 ml syringe containing an inorganic medium inoculated with the sludge. The susceptibility of DSs to biodegradation decreased in the following order monoazo > diazo > anthraquinone. The decolorization was greatly improved with the addition of yeast extract or desizing wastewater to the medium as an organic nutrient. The decolorization was 70–80% in an anaerobic reactor using desizing wastewater.

Sangaleti et al.[134] investigated the removal of the azo DS Reactive Red 120 by the use of a mixed bacterial culture previously aerobically grown in the presence of this DS. They found that some ecological factors affect the DS decolorization. The most effective removal of the DS was achieved at 28°C and pH 6.8 by using 0.2 volume fraction of culture inoculum and by the addition of 0.1 volume fraction of nutrient broth.

FitzGerald et al.[135] studied the mineralization of the azo DSs Acid Orange 10, Acid Red 14, and Acid Red 18 by the use of a two-stage anaerobic-aerobic laboratory scale reactor. The reactors consisted of a fixed film-fluidized bed reactor followed by an aerobic suspended growth activated-sludge reactor. The results indicate that DS decolorization greater than 90% took place at the first stage for the two red DSs and over 65% decolorization for the orange DS. There was a very little additional decolorization in the second stage; the analysis for metabolic intermediates indicated an extensive (over 99%) removal in the first stage for all the reactors. The COD removal in the reactors reached 85% in the first stage with very little additional removal in the second stage.

A cost-effective treatment of dyeing wastewater by the use of an anaerobic-aerobic treatment was also investigated by Zhu et al.[136] The anaerobic stage was carried out in an up-flow anaerobic sludge blanket (UASB) reactor and the aerobic stage was conducted using a conventional activated sludge process. The treatment involved a raw dyeing wastewater of 1150–1300 mg COD/L and 500-fold chromaticity (which is the number of dilution times required for a solution to reach the color of a reference tap water). Under the condition of hydraulic retention time 6–10 hours at the anaerobic stage, over 60% of the COD was removed and the chromaticity was reduced by a factor of 5–10. By additional 6 hours aeration treatment the COD removal was 85–90% and the chromaticity was further reduced 20 folds. The spectroscopic analysis of effluent and influent revealed that the decolorization of the DSs in wastewater mainly took place at the anaerobic stage and was achieved through biological degradation.

Three DSs solution (Acid Yellow 17, Basic Blue 3 and Basic Red 2) were treated in a UASB reactor, followed by a semi-continuous aerobic activated sludge tank by An et al.[137] When the hydraulic retention time (HRT) in the aerobic stage was less than 12 hours no significant color removal was observed. In the anaerobic stage, Acid Yellow 17, Basic Blue 3, and Basic Red 2 were removed by 20, 72 and 78% respectively. Wastewater from a DS manufacturing plant (1200 mg/L COD and color of 500 degree) was treated in a UASB reactor (4.5 L) and an activated sludge tank (5 L), the COD and the color were removed by >83% and >90% respectively at a COD loading rate of 5.3 Kg COD/m^3 day in the anaerobic stage and a HRT of 6–10 hours at the anaerobic stage and 6.5 hours at the aerobic stage. The anaerobic stage of the anaerobic/aerobic system removed both color and COD. In addition it also improved biodegradability of DSs for further aerobic treatment.

The effect of concentrations of yeast extracts, inorganic salts and initial concentrations of DSs in wastewater on the microbial decolorization of wastewater from the dyeing or DSs production processes under anaerobic conditions was studied by Nakaoka et al.[138] A bottom mud from a river near a dyeing plant was used as a microbial source. Injection tubes of 100 ml were used as anaerobic incubation tubes. The decolorization of Reactive Orange 12, Reactive Yellow 2, Yellow 17 and Orange 1 was inhibited by the use of 2% sodium sulfate. The DSs were decolorized at initial concentrations of 40 units (absorbance of 413 nm). Yeast extracts over 100 mg stimulated the decolorization.

Mo et al.[139] studied the effect of algae plus different metal ions on the decolorization of azo DSs with algae. The results showed that the systems of algae with metal ion had much higher rates and higher efficiencies in the decolorization of azo DSs solutions than when using algae alone and that the type and concentration of the metal ion played an important role in the decolorization of the azo DSs.

Knapp et al.[140] investigated the decolorization of DSs by wood-rotting basidiomycete fungi. The ability of 7 isolates of wood-rotting fungi to decolorize a wide range of structurally different DSs was studied. All isolates decolorized some DSs and the DSs were decolorized to some extent. Color removal efficiency varied from 100% to only 50% for chrysophenine. Some decolorization was extremely rapid. Two isolates reduced the A625 of a solution of brilliant green from 57 to 0.5 in 1 day. No one isolate proved to be best for all types of DSs. Some were poor in most tests. Phanerochaete chrysosporium was among the least effective of the isolates. The un-optimized screening system used mycelial mats pre-grown on malt extract medium and supplied with an energy source, glucose together with the DSs.

Walker[141] studied the decolorization of a simulated aqueous discharge from a carpet printing plant composed of a ternary solution of acid DSs. The effluent was treated with a biological activated carbon process to remove color in an aerobic stirred tank configuration. The bacteria immobilized on granular activated carbon, on sand particles, on granular activated carbon with no biological activity, and free bacterial cells were investigated. The bacterium used in this study was Pseudomonas putida (NCIMB 9776). Results indicated that the biological activated carbon system performed a combination of conventional granular activated carbon adsorption and biological wastewater treatment processes. For biodegradable anthraquinone DSs, the enhanced color removal was due to higher DSs utilization rates caused by increased substrate concentrations at the granule surface of the biological activated carbon systems. For non-biodegradable azo DSs, increased bio-sorption was observed in biological activated carbon systems versus conventional immobilized systems.

12. ION EXCHANGE

The role of ion-exchange is usually to reduce the magnitude of a problem by converting a hazardous waste into a form in which it can be reused, leaving behind a less toxic substance in its place, or to facilitate ultimate disposal by reducing the hydraulic flow of the stream bearing the toxic substance. Ion exchange is nevertheless a very versatile and effective tool for the treatment of aqueous hazardous wastes. Although ion exchange has become widely accepted as a standard method for purifying water for certain applications, its potential and indeed, actual use in treating hazardous waste has not been nearly so widely recognized. Nevertheless, the ion exchange process has tremendous potential in this application.[46]

Unlike many other separation processes such as evaporation and reverse osmosis that remove the water from the polluting species, ion exchange usually removes the pollutants from the water. Since the offending pollutant is often present in low concentration, ion exchange is often more efficient in treating large flows of hazardous waste stream than many other processes.

Another significant feature of the ion-exchange process is that it has the ability to separate, as well as concentrate pollutants.[46]

However by far the greatest utility of ion-exchange has been the treatment of inorganic wastes, because the molecular weights of any organics is too high to permit ion exchange at practical rates in polar solutions. There are a number of applications of ion exchange to the treatment of organic wastes but usually the mechanism is one of adsorption by the resin as opposed to true ion exchange.

Fang et al.[142] decolorized anionic DSs by the use of a cationic polymer. Methyl orange, acid red 3 MB and mordant blue I were decolorized by the use of the polymer poly (2-trimethylammonium methyl methacrylate chloride) (PTMAC). The results showed that the relative molecular mass and the cationic ionization degree affect the decolorization. The decolorization rate relates to the intensity and wavelength of the absorption peak.

Shishido[143] purified colored wastewater with an ion-exchanger filter. The filter has a layer of charged granules of tourmaline (Zeolite) and/or an adsorptive natural stone on a permeable bed material in a tank. The filter adsorbed DSs, lead and copper from the wastewater.

The use of an H-type cation-exchanger resin for the removal of pigments from dyeing effluent was applied by Higozaki et al.[144] The resin consisted of monovinyl-polyvinyl copolymer as base material with less than 8% polyvinyl monomers cross-linking agents. The resin was prepared by sulfonation and H-type conversion.

Farag et al.[145] investigated the removal of acid DS (Polar Red) by the use of anion-exchanger formulation containing starch/methylenediacrylamide/dimethylaminoethyl methacrylate. The best results were obtained with aqueous DS concentration of 100 mg/L and anion-exchanger of 500 L/kg with stirring for 3 hours at pH 7.5. Freundlich adsorption isotherms for the Polar Red and other DSs were obtained. The anion-exchanger proved to be a low cost agent suitable for the removal of DSs and other pollutants as heavy metal cations and toxic anions.

Cationic DSs were decolorized using polystyrene based cation-exchange fibers under static and dynamic conditions by Zhang et al.[146] The fiber was regenerated easily with an efficiency over 90%.

Removal of acid DSs with long chain amines was investigated by Kermer et al.[147] Reactive Red 120, Reactive Violet 38, Acid Green 12, Acid Green 194 and Direct Blue 86 were removed by amines containing more than 6 carbon atoms as diisotridecyl amine, and isotridecylamine optionally in water soluble solvents followed by the addition of calcium oxide. The organic phase is removed leaving purified water. The solids are filtered out from the solvent, which can then be recycled. The decolorization efficiency was over 99%.

The removal of anionic DSs from wastewater by ion pair extraction with long chain amines was also effected by Steenken-Richter et al.[148] The most effective removal was achieved at pH 1.5–4 with primary and secondary amines, and pH 3.5–5 with tertiary amines. The metal complex DSs can be recovered from the organic phase by extraction with sodium hydroxide and reused in dyeing. The spent amines were practically colorless and can be reused.

Weltrowski et al.[149] adsorbed heavy metals and DSs on a reactive filter. Acid, direct, mordant, metal complex and reactive DSs were tested. In the first step the solutions of 23 of these DSs were filtered through the filter. The best results were obtained for acid, mordant and reactive DSs. In the second step, the solutions of DSs and auxiliaries usually used in the dyeing processes were filtered. All tested auxiliaries, except sodium sulfate were compatible with the filtration process. Adsorption of dichromate ions used in mordant dyeing was also tested. The flow rate of 40 ml/min corresponding to a superficial velocity of 8 L/m^2 min was the optimal filtration velocity. Desorption was effected with 0.1 N sodium hydroxide solution. High desorption rates were obtained with all classes of DSs except the non-hydrolyzed reactive DSs which were probably fixed with covalent bonds. For the other DSs an ion exchange fixation mechanism was suggested. The tests confirmed the utility of this filter for textile effluent treatment.

Acid Orange II wastewater was decolorized with PVAF anion-exchange fibers.[150] The PVAF had superior ability to decolorize the DS solution and can be easily regenerated. Adsorption obeyed the Langmuir isotherm. The thermodynamic parameter of decolorization at different temperatures was evaluated. The dynamic behaviour of the DS-PVAF system was found to follow the Bangham equation.

Cellulose modified with quaternary ammonium groups was used in the adsorption of anionic DSs by Lazzlo.[151] Adsorption was followed by the regeneration with bisulphate mediated borohydride. The ion exchangers based on cellulose or lignocellulose have strong affinity for anionic DSs but the restoration of the exchanger is very poor using low cost conventional regenerants. The experiments carried on two monoazo DSs (acid orange 7 and reactive red 180) showed that the exchanger was fully regenerated with the redox treatment (KBH_4/$NaHSO_3$) from the acid orange 7 and restored 74% of the exchanger from the adsorption of the red 180 which was 95% restored with a subsequent wash with sodium hydroxide or sodium perchlorate. HPLC tests confirmed that the redox treatment reductively cleaved the DSs azo bonds in the red 180. The bisulphate formed a stable adduct with the acid orange 7 but did not cleave the azo bond. The results indicated that the reduction of monoazo DSs is an efficient method to regenerate the DSs binding capacity of the quaternized cellulosics used to decolorize textiles wastewater.

13. MULTI-TREATMENT PROCESSES

Combination of methods used to remove or recover DSs from wastewater have been investigated by several researchers, with the aim of increasing the separation efficiency of the DSs.

The textile industry consumes a considerable amount of water in the manufacturing process. The water is primarily used in the dyeing and finishing operations in which the cloths are dyed and processed to finished products. In a typical dyeing and finishing mill, about 100 L of water are consumed on the average for every ton of cloth processed.[152] The water used in the dyeing and finishing processes eventually ends up as wastewater, which needs to be treated before final discharge. Accordingly, treatment of wastewater effluent from the secondary wastewater treatment plant of a dyeing and finishing mill, was investigated for possible reuse by Lin and Chen.[153] The treatment system employed consists of the Fenton process, chemical coagulation and ion exchange. The Fenton process and chemical coagulation are intended primarily to remove color, turbidity (NTU) and COD concentration of wastewater effluent while ion exchange is used to further lower the COD and Fe ion concentrations, total hardness, conductivity, alkalinity, SS and TDS of wastewater. Experimental results throughout the present study have indicated that the combined chemical treatment methods are very effective and are capable of elevating water quality of the treated wastewater effluent to the reuse standard of the textile industry. Table 6 shows the water quality change after the various treatment steps.

A combined process of jet aeration-biological contact oxidation-flotation-filtration has proven to be an effective method for BOD, COD and sulfides removal from dyeing wastewater.[154]

Table 6. Water Quality Change After Various Treatment Steps

	Original Wastewater	Fenion Treatment	Chemical Coagulation	Ion Exchange	Reuse Standard
COD, mg/l	133	43.8	42.8	9.3	10
COD removal, %	–	67.1	67.8	93	–
NTU	9.4	–	0.7	0.5	1
Conductivity, μmho/cm	4500	4960	5450	1	10
Color removal, %	–	–	97.7	100	–
Hardness, mg/l	42.1	–	45.8	8.9	10
Alkalinity, mg/l	310	–	72	4	50
Fe conc., mg/l	0.15	0.98	0.11	0.03	0.1
TDS, mg/l	2810	–	3490	30	50
SS, mg/l	26.4	–	0	0	0

The pre-treatment of dyeing wastewater by a chemical or biological method followed by mixing with ultra fine activated carbon then decolorization by a cationic polymer after which the wastewater is passed through a sand filter for decolorization was investigated by Shigeru et al.[155]

Decolorization of dyeing wastewater was also effected by chemical precipitation, chemical oxidation, adsorption and a combination of the three techniques together.[156]

Treatment of highly concentrated dyeing wastewater by a combined process consisting of coagulation-precipitation, biological contact oxidation, pressurized air flotation and filtration was also applied by Tong et al.[157] The COD and color removal efficiency were 96% and 90% respectively. The COD removal efficiency was found to greatly increase with the increase of the specific surface area of the fiber fillers in the biological contactors.

14. DYE BATH RECYCLING AND RECONSTITUTION

The reconstitution and the reuse of the spent dye bath chemicals and DSs is one of the routes to recover the spent chemicals and DSs and to reduce pollution problems.

Yang et al.[158] investigated the reuse of hydrolyzed (spent) reactive DSs for dyeing nylon 6, nylon 66 and wool as acid DSs. The DSs tested were the reactive black 5, yellow 3, red 2, blue 19, and the acid black 1 and blue 25. The fresh acid DSs have the same parent structure as the reactive DSs and were tested as a comparison to the dyeing behavior of the hydrolyzed reactive DSs. The effects of dyeing conditions such as temperature, pH, types and concentrations of electrolytes were evaluated. The dyeing results were claimed to give similar results to the fresh acid DSs.

The reconstitution of the exhausted reactive DSs bath with fresh reactive DSs and its reuse was effected by Burkinshaw et al.[159] The reconstituted dye bath should be ideally identical with the fresh DS bath, which contains both hydrolyzed and reactive DSs. The dyeing behaviour of the residual DS in the exhausted reactive dye bath differed from that of the fresh reactive DSs.

Mazur et al.[160] studied the proposal of analyzing the dyeing wastewater to determine the concentration of the DSs of the exhausted dye baths, which offers the possibility of recycling the dye baths in the course of the technological process.

15. HIGH EXHAUSTION DYESTUFFS

High exhaustion DSs are one route that lowers pollution problems. Imada et al.[161] discussed the approach of using reactive DSs with higher fixation power to the cotton fabrics in order to reduce the dyeing effluent level and obtain better fastness properties, which is satisfactory for both environmental and economical considerations of the dyer as it can easily be decolorized during effluent treatment. The bi-functional reactive DSs with a vinyl sulfone reactive group and a monochlorotriazine reactive group are a good example for this approach. Prabu et al.[162] also recommended the use of high exhaustion reactive DSs to obtain higher fixation on cotton and lower pollution problems. The authors recommended acidification of the effluent before adsorption.

16. CONCLUSIONS

In this paper, the different techniques for the removal or recovery of DSs from wastewaters have been presented, evaluated and compared. The following section presents the most important conclusions arrived at regarding all the aforementioned techniques.

Normal textile dyeing and finishing operations are such that the DSs used in a mill can vary from day to day and sometimes even several times a day mainly because of the batch-wise nature of the dyeing process. Frequent changes of DS and chemicals used in the dyeing process cause considerable variation in the wastewater characteristics, particularly the pH, color and wastewater BOD and COD concentrations.[163] A large pH swing is especially troublesome because the pH tolerance of conventional biological and chemical treatment systems are very limited. Hence without proper pH adjustment, normal operation of the treatment process is essentially impossible.

Strong color is another important component of the textile wastewater, which is very difficult to deal with. The combination of the strong color and highly dissolved solid content results in high turbidity of the waste effluent. The DSs are highly structured polymers and very difficult to decompose biologically. Hence, there is relatively little change of these DS molecules in an activated sludge process.[163] A strong color of the wastewater effluent, if not removed, would cause disturbance to the ecological system of the receiving waters. Color removal by activated carbon, hydrogen peroxide, sodium hypochlorite and other chemical agents has been widely practiced in the textile industry.[164–170] However, the cost of the polishing operation using these chemicals is high.

Traditional activated sludge and chemical methods (such as chemical coagulation and decolorization) have been widely used for dealing with the textile wastewaters.[163] These methods are intended to treat the textile wastewater to a level that meets the discharge standards required by the government. However, due to dwindling supply and increasing demand of water in the textile industries, a better alternative is attempt to further elevate the water quality of wastewater effluent from a secondary wastewater treatment plant to a higher standard for reuse. Thus far very little attention has been paid to this respect.

Adsorption methods can frequently decolorize textile effluents, but their application is limited by the high price of adsorbents and the large amounts of waste normally involved. It is precisely the particularly important reactive DSs that are only moderately retained by the commonest adsorbent—activated carbon—and thus leave a residual color. Activated carbon is relatively an expensive adsorbent and the adsorption capacity of the used carbon usually decreases to 70–80% of that of the virgin carbon. Coke is cheaper, but is also only moderately effective. In any event, considerable amounts of coal sludge are formed, and its disposal presents additional problems.[3] Other adsorbents as clays, sawdust, vermiculite, waste orange peel, bagasse pith, and maize cob are more economic than activated carbon. Some adsorbents as post-vanillin lignin have very high affinity for DSs. The DSs adsorption by adsorbents as clays is controlled by boundary layer film diffusion, while for other adsorbents as sawdust the DSs adsorption is controlled by pore diffusion. The adsorption is sometimes of chemical nature as that of aminated flax and kenaf fibers.

Common flocculants based on ferrous, ferric, aluminium and calcium salts or bentonite usually do not flocculate reactive DSs completely. Almost quantitative flocculation is feasible with certain cationic polymers, but they necessitate a slight excess of the cationic compound that is toxic for fish, and this is usually undesirable. In addition, sludges formed from DSs and cationic polymers have poor settling characteristics. For this reason, a co-flocculant, e.g. an iron or aluminium salt, is required, and this further increases the amount of sludge.[3]

The oxidation methods are a successful solution for the decolorization of DSs that are stable to bio-degradation. The Fenton reagent is available in all dyehouses and successfully decolorize DSs, the reuse of the water after decolorization necessitates a coagulation stage to reduce COD and an ion-exchange stage to remove hardness and Fe ions. In oxidative processes, an attempt is made to hit weak points in the DS molecule with the aim of destroying the chromophore as selectively as possible or of converting it into a readily biodegradable form. Nowadays, the classical oxidizing agents, chlorine or hypochlorite, are hardly used owing to the formation of organic halogen compounds. Numerous studies on textile and other industrial effluents have been devoted to hydrogen peroxide and ozone as oxidizing agents. Fenton's reagent (Fe^{2+} ions) or ultraviolet radiation is required to activate the hydrogen peroxide with the formation of hydroxy radicals. Owing to its toxicity and the risk of explosion, numerous safety precautions must be observed if ozone is used. Quantitative exploitation of the ozone must be ensured by very fine distribution of the gas in the reactor.

If due consideration is given to these aspects, good to very good results are generally achieved in decolorizing with ozone or hydrogen peroxide. However, the oxidation processes are not sufficiently selective. In other words, all other organic substances are oxidized simultaneously with the DSs, and the costs involved are thus considerable. It has been described in the literature that toxic derivatives of organic substances may also occur if ozone is the oxidizing agent. However, it is well known that ozone is a powerful oxidant, its oxidizing potential is nearly twice as high as that of chlorine. Ozone alone and in combination with ultraviolet light, catalysts, ultrasound or activated carbon has been successfully applied to a myriad of industrial discharges. Ozonation is one of the most effective methods to decolorize textile wastewaters. The major advantage is that ozone can be applied directly in its gaseous sate and therefore doesn't increase the volume of wastewater and sludge. It is advantageous that ozone reacts preferably with refractory substances, this means substances, which are not bio-degradable. In fact, wastewater of textile processes contain large amounts of refractory substances and halogenated organic compounds.[103] It is faster than other oxidation methods and it removes color and decreases COD to permissible limits. The complete solubility of the DSs is imperative to achieve an efficient decolorization.

Azo dyes, in particular, can be decomposed by reduction processes, and the effluent concerned can thus be decolorized. The decomposition products, which are aromatic amines, may be carcinogenic, but traditional manufacturers no longer produce textile DSs that give rise to carcinogenic amines when they are decomposed by reduction. Nevertheless, reduction processes for decolorizing effluents have not yet found a foothold due to some reasons as: 1) High cost of reducing agents; 2) Problems involved by derivatives of the reducing agent, e.g. sulfite; and 3) Unsatisfactory or reversible decolorization, particularly of anthraquinone DSs.

Recently, electrochemical processes have also been offered for decolorizing textile effluents. The electrochemical oxidation by the hypochlorous acid resulting from the electrolysis of the sodium chloride solutions successfully decolorizes DSs. The fixed capital cost for these units is 30% of that of the biological units.

The ion exchange resins are used successfully with systems producing large amounts of wastewater. The DSs adsorbed by the long chain amine liquid exchanger were successfully regenerated for reuse, whereas other ion-exchangers necessitated strong oxidative and reductive regenerants, which are destructive for the DSs.

Membrane processes have many cost effective applications in the textile industry. They are fast processes with a short residence time, as no adsorption or reaction time steps are required. They are modular in construction and their capacity can be easily enlarged. Membrane separation successfully recovers the majority of the DSs and the expected payback time for such units is around 2–3 years. However, membranes are subject to fouling due to partial adsorption of DSs and surfactants and subject to scaling by silicates and other chemicals, which are usually present in the dyeing wastewater.

Membrane separations are used for the recycling of valuable components from dyeing wastewater. The membrane process is usually integrated in a total wastewater treatment where some selected streams are directed to the membrane units for recovery purposes.

Ultrafiltration membranes are capable of separating many DSs such as vat, acid, pre-metallized, disperse and direct DSs. Nanofiltration membranes can be used to separate reactive and cationic DSs. Reverse osmosis membranes remove all the DSs and the common salt from the wastewater. The membranes are packaged in several configurations, the most common are spirally wound, hollow fiber and tubular membranes. Spiral configurations are generally the least expensive to buy and to operate because of the high packing density and turbulence promotion generated by the feed spacer. Spiral modules are susceptible to plugging of the module with colloidal or fibrous material. Hollow fiber membranes are the next most economical and are limited to relatively low pressures resulting in lower fluxes. Tubular modules are extremely durable and have long life and high fluxes but are generally more expensive to purchase and operate.

Concentrated sunlight has a promising potential in the removal of DSs and biological stains from wastewater.

The biological methods require a large fixed capital but they have low operation costs. The anaerobic treatment is more efficient in decolorization and COD removal than the aerobic treatment, but a combination of both treatments gives best results.

The dye bath reconstitution and the bi-functional DSs are routes for conducting the dyeing operations with a minimization of DSs in the dyeing effluents.

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