TREATMENT OF A REACTIVE DYE, A DISPERSE DYE, AND THEIR MIXTURES USING H_2O_2/pyridine/Cu(II) SYSTEM

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by

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LIST OF ABBREVIATIONS

ANOVA	Analysis of Variance
AOP	Advanced Oxidation Process
AOX	Absorbable Organic Halide
BDD	Boron Doped Diamond
BOD	Biochemical Oxygen Demand
CCD	Central Composite Design
CI	Colour Index
COD	Chemical Oxygen Demand
DD	Disperse Dye
DO	Dissolved Oxygen
DOE	Design of Experiments
FT-IR	Fourier Transform Infra Red
GC-MS	Gas Chromatograph Mass Spectometry
KHP	Potassium hydrogen phthalate
NF	Nanofiltration
RD	Reactive Dye
RO	Reverse Osmosis
RSM	Response Surface Methodology
SBR	Sequencing Batch Reactor
SS	Suspended Solids
TOC	Total Organic Carbon
TSS	Total Suspended Solids
UV	Ultraviolet

LIST OF SYMBOLS

H_2O_2	hydrogen peroxide
Cu(II)	cuprous
OH	hydroxyl group
OH^*	hydroxyl radical
))))	sonolytic oxidation
e^-_{aq}	hydrated electron
λ_{max}	maximum absorption wavelength

PENGOLAHAN SISA PEWARNA REAKTIF, SERAKAN, DAN CAMPURANNYA MENGGUNAKAN SISTEM H_2O_2/pyridine/Cu(II)

ABSTRAK

Sistem H_2O_2/pyridine/Cu(II), merupakan satu siri proses pengoksidaan lanjutan (AOP) yang melibatkan gabungan penggunaan pengelat ligan dengan logam bagi membentuk kompleks logam peralihan yang menghasilkan radikal reaktif. Sistem ini diguna bagi menilai kecekapan pengolahan 1 g/L sisa pewarna sintetik yang terdiri daripada satu bahan pewarna kelas reaktif (Cibacron Red FN-R), kelas serakan (Terasil Red R), serta gabungan pewarna reaktif (RD) dan pewarna serakan (DD) dalam 3 nisbah yang berlainan (RD: DD = 0.25: 0.75, 0.50: 0.50, dan 0.75: 0.25), serta satu sisa pewarna dari industri tekstil. Pewarna reaktif dan serakan dipilih dalam ujikaji in disebabkan kedua-dua bahan pewarna ini diguna secara meluas berbanding dengan pewarna-pewarna yang lain hasil daripada pencapaian mereka yang memberangsangkan. Keputusan ujikaji adalah berdasarkan peratus pengurangan konsentrasi keperluan oksigen kimia (COD), peratus penyahwarnaan, serta jumlah sisa yang terjana. Parameter pengendalian optima diperoleh melalui penggunaan rekabentuk ujikaji statistik. Parameter pengendalian optima ialah 0.059 M [H_2O_2]/ 0.087 M [pyridine]/ 0.0171 M [Cu(II)] bagi sisa pewarna reaktif, 0.0055 M [H_2O_2]/ 0.038 M [pyridine]/ 0.00168 M [Cu(II)] bagi sisa pewarna serakan, 0.004 M [H_2O_2]/ 0.05 M [pyridine]/ 0.0186 M [Cu(II)] bagi (RD: DD = 0.75:0.25), 0.024 M [H_2O_2]/ 0.106 M [pyridine]/ 0.019 M [Cu(II)] bagi (RD: DD = 0.50:0.50), 0.002 M [H_2O_2]/ 0.066 M [pyridine]/ 0.0018 M [Cu(II)] bagi (RD: DD = 0.25:0.75), serta pH 10/ 0.0023 M [H_2O_2]/ 0.0073 M [pyridine]/ 0.0123 M [Cu(II)] bagi sisa pewarna industri. Sistem ini didapati berupaya mengurangkan konsentrasi COD sisa pewarna dalam lingkungan 73 % – 92 %, serta mencapai peratus penyahwarnaan 93 % – 99 % dalam keadaan optima bagi sisa pewarna yang dikaji manakala jumlah sisa yang dijana bagi sisa-sisa pewarna sintetik berada dalam lingkungan 20 mg/L – 330 mg/L dan 260 mg/L – 555 mg/L bagi sisa pewarna industri. Rekabentuk 2^4 faktorial penuh dan metodologi permukaan sambutan (RSM) dengan menggunakan rekabentuk ujikaji gabungan pusat (CCD) telah digunakan dalam analisis penapisan dan pengotiman ujikaji. Kecekapan pengolahan didapati tidak bergantung kepada pH bagi kesemua pewarna sintetik.

TREATMENT OF A REACTIVE DYE, A DISPERSE DYE, AND THEIR MIXTURES USING H_2O_2/pyridine/Cu(II) SYSTEM

ABSTRACT

The H_2O_2/pyridine/Cu(II) system is a series of advanced oxidation processes involving the use of a chelating ligand, combined with a transition metal, forming the transition metal complexes to produce reactive radicals. This system was used to assess the efficiency of the treatment of a 1 g/L synthetic dye wastewater comprising of a reactive dye, (Cibacron Red FN-R), a disperse dye (Terasil Red R), mixtures of a reactive dye (RD) and a disperse dye (DD) in three different ratios (RD: DD = 0.25: 0.75, 0.50: 0.50, and 0.75: 0.25), and a real industrial dye wastewater. Reactive and disperse dye powders were selected to be used in this study as these two dyes are used widely as compared to dyes from other classes due to their superior performance. Experimental results are assessed in terms of percentage chemical oxygen demand (COD) reduction, decolourization, and the amount of sludge produced. Optimal operating parameters were obtained using statistical design of experiment. The optimal parameters were 0.059 M [H_2O_2]/ 0.087 M [pyridine]/ 0.0171 M [Cu(II)] for reactive dye wastewater, 0.0055 M [H_2O_2]/ 0.038 M [pyridine]/ 0.00168 M [Cu(II)] for synthetic disperse dye wastewater, 0.004 M [H_2O_2]/ 0.05 M [pyridine]/ 0.0186 M [Cu(II)] for (RD: DD = 0.75:0.25), 0.024 M [H_2O_2]/ 0.106 M [pyridine]/ 0.019 M [Cu(II)] for (RD: DD = 0.50:0.50), 0.002 M [H_2O_2]/ 0.066 M [pyridine]/ 0.0018 M [Cu(II)] for (RD: DD = 0.25:0.75), and pH 10/ 0.0023 M [H_2O_2]/ 0.0073 M [pyridine]/ 0.0123 M [Cu(II)] for industrial dye wastewater. This system was found to be capable in reducing the concentration of COD of the dye wastewater within the range of 73 % – 92%, and achieving 93 % –

99 % in decolourization at the respective optimal conditions of process variables of the wastewaters being studied, while the amount of sludge produced for synthetic dyes was within the range 20 mg/L – 330 mg/L, and industrial dye wastewater at 260 mg/L – 555 mg/L. Full 2^4 factorial design and the response surface methodology using central composite design (CCD) were utilized in the screening and optimization of this study. Treatment efficiency was found to be pH independent for all synthetic dyes.

CHAPTER ONE

INTRODUCTION

1.1 GENERAL

At present, approximately 50% of water supply is being used by household while another 50% for industrial and agricultural activities. Increase in the world’s population, placed pressure for the industries to reclaim and reuse some of its wastewater or face the prospect of being shutdown. This was due to the combined pressures of increasing water and wastewater costs and increasing regulatory requirements of discharged wastewater (Pagga and Taeger, 1994).

The textile industry is one that demands large quantities of water, and produce large amounts of wastewater. Dye compounds are synthetic organic compounds with complex molecular structures and large molecular weights. These properties augment treatment difficulties of dye wastewater (Banat et al., 1996; Anjaneyulu et al., 2005).

Dyeing wastewater causes serious environmental problems due to its high colour, large amount of suspended solids (SS), and high chemical oxygen demand (COD) (Kim et al., 2004a). The increase of public concern as well as tighter regulations has challenged the environmental research community to explore new lines in reducing environmental problems associated with such wastewater.

At present, there are various technologies available in the treatment of dye wastewater. Among them are adsorption, ion-exchange, Fenton oxidation, ozonation, coagulation and precipitation, cucurbituril, aerobic and anaerobic processes, and membrane filtration (Anjaneyulu et al., 2005). The negative aspects of these technologies are that either they lack the efficiency in reducing the many diversed pollutants in the dye wastewater or when the treatment technology appears to be promising, the cost of operation is very high thus prohibiting the particular technology to be applied to the large scale wastewater common to the this industry.

1.2 DYE COMPOUNDS

Dyes are exclusively organic compounds. Foundation of synthetic dye is attributed to William Henry Perkin on his discovery of a purple dye named Aniline Purple, which was later known as Mauveine in 1856. Since most organic pigments are chemically and structurally related closely to dyes, confusions between dyes and pigments exist where, the terms dye and dyeing are much better known by the lay public than the more technical expressions pigments (Christie, 2001).

Dyes are applied to various substrates (textiles, leather, paper, hair, etc) from a liquid in which they are completely or at least partly, soluble. In contrast to pigments, dyes possess a specific affinity to a given substrate (Heinrich, 2003).

Pigments on the other hand consist of small particles that are practically insoluble in the media in which they are applied. Therefore, they have to be attached to a substrate by means of additional compounds e.g. by polymers in paints or plastics (Heinrich, 2003). There are two types of pigments (Bogacki et al., 2004):

a) Homogeneous pigments

These pigments contain the same type of pigment particles, e.g. colourful metal oxides, metallic powders, and etc.

b) Mixtures

Pigments under this category can be obtained either by chemical coating by the stain of an appropriate carrier such as the active, highly dispersed silica, precipitated calcium carbonate or by mechanical mixing of intensely staining pigment with a filler.

1.3 CLASSIFICATION OF DYES

A well-known system of classification used internationally for dyes is the Colour Index (CI), devised by the Society of Dyers and Colourists in 1924. It classifies dyes by first assigning a generic name determined by its application characteristics, before assigning a CI constitution number based on its chemical structure if known (Easton, 2005). Companies need to register (free of charge) with the Society of Dyers and Colourists if they wish to use CI numbers and generic names.

The commercial name of a dye normally consists of (Giles, 1971):

a) The brand name, often an indication of the dye class as well as the manufacturers.
b) Colour of the dyes, example red, blue, or yellow.
c) One or more suffix letters (of German origin) and figures indicating:
    i) Shade of colour, referred to as secondary colours. Example, B, G, R (B = Blau = Blue; G = Gelb = Yellow; R = Rot = Red) representing the three secondary colours. A blue colour may be described as R (reddish) or 2R (more reddish) or G (yellowish), and so on. Similarly for red or yellow colour which may be described in various degrees. For instance, suffix G applied to yellow denotes greenness.
    ii) Special qualities, for instance, F = fine; FF = superfine
    iii) Strength of dye, for example 150, 200 or 250%. This indicates the increased dye strength of a brand, for instance containing less salt or diluents in the proportions given.

Textile industries consume a large amount of dyes where the choices of dyes depend very much on the colour shade, types of fibres, dyeing process, as well as economic considerations (Steiner and Miskie, 1974).

1.4 NATURE OF TEXTILE EFFLUENT

In a textile processing plant, the main sources of wastewater originate from the washing and bleaching of natural fibers and from the dyeing and finishing steps. These processes generate wastewater of diverse and great chemical complexities due to the many varieties of fibers, dyes, process aids and finishing products in use (Philippe et al., 1998). Textile wastewaters by nature are known to contain colour, persistent organics, toxicants, surfactants, absorbable organic halide (AOX) and heavy metals (Slokar and Le Marechal, 1998).

1.4.1 Colour

The most notable contribution to the science of colour and constitution was due to Witt who in 1876 proposed that dyes contained two types of group namely chromophore and auxochrome which are responsible for their colour. Chromophore is a group of atoms principally responsible for the colour of the dye and auxochromes are the 'salt forming' groups of atoms whose role is to provide an essential enhancement of the colour (Christie, 2001).

Further contribution was made by Hewitt and Mitchell who proposed in 1907 that conjugation is essential for the colour of a dye molecule. In 1928, Dilthey and Witzinger in their refinement to Witt's theory on chromophore and auxochrome recognized that chromophore is an electron withdrawing group and auxochromes are usually electron releasing groups and that both of them are linked to one another through a conjugated system (Christie, 2001). By increasing the electron-withdrawing power of the chromophore, by increasing the electron releasing power of the auxochromes and by extending the length of the conjugation will result in a shift of the adsorption band to longer wavelength, causing changes of the colour (Christie, 2001).

The most important chromophores are the azo (-N = N-), carbonyl (C = O), methine (-CH=), and nitro (NO_2) groups. Presence of common auxochrome groups such as hydroxyl (OH) and amino (NR_2) groups may shift the existing wavelength to a longer wavelength thus increases the intensity of the colour (Raghavacharya, 1997; Christie, 2001).

Colour absorbs the sunlight responsible in the photosynthesis of aquatic plants, preventing it from penetrating into the water. This causes serious threat to the ecosystem. Dye is also visible even at low concentration; hence, the treatment of wastewater containing dye must meet not only legal standards but aesthetic standards as well (Gulen et al., 2007).

1.4.2 Persistent Organics

Shifts in process chemicals used by the textile industries had resulted in an increase of the biodegradability of dye wastewaters (Philippe et al., 1998). The persistent organics present in the effluents belong to diverse chemical classes**,** each used in relatively small amounts.

Apart from dye molecules, these molecules include dyeing auxiliaries such as polyacrylates, phosphonates, sequestering agents such as EDTA, denocculation agents such as lignin or naphtalenesulfonates, antistatic agents for synthetic fibers, carriers in disperse dyeing of polyester, fixing agents in direct dyeing of cotton, preservatives such as substituted phenols and a large number of finishing auxiliaries such as waterproofing (Porter and Snider, 1976; Correia et al., 1994; Churchley, 1999).

1.4.3 Toxicants

A series of bioassays assessing the acute, sublethal, and chronic toxicity at various trophic levels showed that textile effluent was highly toxic using the typical LC_{50} (96 hr) values amount to 5-6 % (v/v) with bleaching, dyeing or mixed textile effluents using freshwater fish as test organism (Costan et al., 1993). Textile effluents comprised of many organic constituents and additives. These substances contained toxicants such as biocides which in turn contributed to the overall toxicity of the textile effluent (Gulen et al., 2007).

1.4.4 Surfactants

Wet processing in the textile industry such as sizing, spinning, weaving, desizing, dyeing, scouring, and washing, consume large amount of surfactants. Surfactants are divided into two groups namely anionic and non-ionic. Alkyl phenol ethoxylates was the largest non-ionic substances used in most textile processes where this substance may biodegraded to alkyl phenols which tend to absorb and eventually accumulated in the sewage sludge (Philippe et al., 1998).

1.4.5 Absorbable Organic Halide (AOX)

AOX consists of a collection of organic compounds in which one or more chlorine atoms are attached. AOX compounds are formed only when chlorinated compounds were used in the bleaching process. Example of AOX is sodium hypochlorite which was used commonly due to superior whiteness, and lower cost. Certain reactive dyes are also AOX and given this carcinogenic nature, the discharge of AOX are restricted in a number of countries (Philippe et al., 1998).

1.4.6 Heavy Metals

Heavy metals were known to have toxic effects to the receiving environment. Heavy metals are introduced into the wastewater of textile manufacturing through the use of premetalized dyes and heavy metal afterwashes, which are used to increase the light fastness of the finished product. Typical dye bath effluents contained Chromium (Cr), Copper (Cu), Nickel (Ni) and Zinc (Zn). These heavy metals may cause detrimental effects on all forms of life upon discharge to the environment (Philippe et al., 1998; Pamukoglu and Kargi, 2007). Although trace amounts (µg/L) of certain metal ions such as copper, zinc, iron, nickel and cobalt are required by some organisms as cofactors for the enzymatic activities, however heavy metal ions at (mg/L) level are known to be toxic to most of the organisms due to irreversible enzyme inhibitors by heavy metal ions (Pamukoglu and Kargi, 2007).

1.5 SYNTHETIC TEXTILE WASTEWATER

Synthetic dye solutions had been used by most researchers in their investigation of treatment technologies since synthetic solutions was useful in obtaining information on how individual dyes react to different types of treatment. Apart from this, constant composition of a synthetic solution enables the specific study of treatment efficiency on a particular treatment technology.

1.6 TREATMENT METHODS

In general, there are three classifications of wastewater treatment methods. These comprise of physical, chemical and biological treatment. The main drawback with these technologies is that they generally lack the broad scope of treatment efficiency required to reduce all the diverse pollutants present in textile wastewater.

However, when one approach does look promising, often then the capital cost, or operating cost become prohibitive when applied to the large scale water needs common to this industry (Correia et al., 1994).

1.6.1 Physical Treatment

Adsorption is a favourable technique as it is an economically feasible process that produces a high quality product and its efficiency in the removal of pollutants to stable compounds (Choy et al., 1999). Adsorbents such as activated carbon which are available both commercially and some low cost adsorbents prepared from sugarcane baggase were widely used in the removal of organic pollutants from wastewater (Satyawali and Balakrishnan, 2008).

1.6.2 Chemical Treatment

Chemical treatment such as coagulation, flocculation, and ozonation are quite effective in the treatment of textile wastewater although some of the mentioned application is limited with their high operating costs. Nevertheless, it was mandatory to apply these processes to overcome the inadequacy of other treatment systems (Bali and Bünyamin, 2007).

1.6.3 Biological Treatment

Biological methods are generally cheaper to apply in the removal of organics and colour from dyeing and textile wastewater. However, dyeing wastewater cannot be readily degraded by the conventional biological processes such as trickling filters and activated sludge process, because the structures of most commercial dye compounds are very complex and many dyes are of non-biodegradable in nature due to their chemical nature and molecular size (Kim et al., 2004b). Though biological treatment process is generally efficient in BOD removal, however, it is considered unsatisfactory because of the low efficiency, low reaction rate of treatment as well as the result in sludge bulking (Kumar et al., 2008).

1.7 OBJECTIVES OF STUDY

Most dye compounds are highly structured polymers. They are very difficult to break down biologically and can hardly be treated efficiently by any means of physical, chemical or biological methods (Lin and Lin, 1993).

The term AOP (Advanced Oxidation Process) was first invented by Glaze in 1987 involving the generation of highly reactive radicals (OH^*) as the main oxidants in all chemical oxidations (Glaze et al., 1987). The OH^* is capable in the complete oxidizing of less reactive pollutants principally by means of electrophilic addition to unsaturated bonds, addition to unsaturated bonds, addition to aromatic rings, abstraction of hydrogen, or by electron transfer (Bossmann et al., 1998; Pignatello et al., 2006). End products generally comprised of carbon dioxide, water and inorganic ions, without large residues generation (Hoigné 1997).

Among the many different AOP’s, the Fenton process is considered the most commonly used technology in the treatment of highly contaminated wastewaters (Bossmann et al., 1998). Fenton reagent is popular since iron is an abundant element, non toxic and safe and is considered a “clean” reagent (Huston and Pignatello 1999). Once the treatment is over, dissolved iron can be removed by precipitation by increasing the pH of the media (Malato et al., 2003) while hydrogen peroxide on the other hand decomposes to O_2 and H_2O (Huston and Pignatello 1999; Pignatello et al., 2006). Limitation of this technology includes the necessity of pH changes, and the possible iron sludge generation at the end of treatment (Pignatello et al., 2006).

Since dyes are organic molecules, they can be the target of hydroxyl radical attack. For this reason, the AOP was selected in this study of the treatment of dye wastewater. In this study, another series of AOP known as the H_2O_2/pyridine/Cu(II) system was employed whereby treatment efficiencies were measured in terms of COD reduction, colour removal, and the amount of sludge produced on a single reactive dye, a disperse dye, their mixtures in 3 different ratios, and finally on an actual industrial dye wastewater.

In practice, real dye wastewater contains mixture of dyes. Therefore, in this study, two classes of most widely used dyes namely the reactive dye (RD) and disperse dye (DD) were combined in three different ratios of (RD: DD) = (0.25: 0.75), (0.50: 0.50), and (0.75: 0.25) to obtain an idea of the trend in terms of the composition of the types of dyes used in relation to the treatment efficiency using this system.

Based on the theoretical knowledge acquired from literature studies the H_2O_2/pyridine/Cu(II) system offers new perspective in the field of environmental study in which the application of this system could provide an easy degradation and the possibility of working without pH adjustments (Nerud et al., 2001; Verma et al., 2004a; Bali and Bünyamin, 2007 a, b). This finding was important especially when it comes to the large scale application of this system.

Therefore, the main aim of the present study is to determine the effectiveness of the H_2O_2/pyridine/Cu(II) system, in reducing the COD concentration as well as colour removal of a reactive dye, a disperse dye and their mixtures. The effects of operating factors such as pH, the concentrations of H_2O_2, pyridine, and Cu(II) used in this treatment system were also studied.

The specific objectives of this study include:

1) To determine the percentage of COD reduction of a disperse dye, reactive dye and their mixtures using this proposed treatment system.
2) To determine the percentage of Colour removal of a disperse dye, reactive dye and their mixtures using this proposed treatment system.
3) To determine the quantity of sludge produced by a disperse dye, reactive dye and their mixtures using this proposed treatment system.
4) To optimize this treatment method in order to achieve optimum treatment efficiencies of a disperse dye, reactive dye and their mixtures.

CHAPTER TWO

LITERATURE REVIEW

This chapter outlines the science and technology used in the treatment of dye wastewater to upgrade its quality in order to meet specific water quality standards.

2.1 TEXTILE DYES

Dyes are used in the colouration of a wide range of substrates, including paper, leather, and plastics but by far their most important outlet is on textiles. Textile materials are used in a wide variety of products, including all types of clothing, curtains, and carpets (Christie, 2001).

2.1.1 Textile Fibres

Textile fibres may be classified as follows (Christie, 2001):

i) Natural

The most important natural fibres are either of animal origin, for example wool and silk or of vegetable origin such as cotton which is a cellulosic fibre.

ii) Semi-synthetic

Semi-synthetic fibres used today are derived from cellulose as the starting material of which the two most important of these being viscose rayon and cellulose acetate.

iii) Synthetic

The most important completely synthetic fibres are polyester, polyamides (nylon) and acrylic fibres.

Although textile fibres share the common feature that they are made up of polymeric organic molecules, however, the physical and chemical nature of the polymers involved vary widely. This is why each type of fibre essentially requires its own application classes of dyes.

2.1.2 Dye Classes

A good dye gives a colour that is fast, which means it resists fading by water, light, perspiration and other factors. Main dye classes according to their applications are categorized as acid dyes, azoic dyes, basic dyes, direct dyes, disperse dyes, mordant dyes, reactive dyes, sulphur dyes, and vat dyes. The dye classes, textile fibres (substrates) and method of applications can be seen in Table 2.1 (Kirk, 1993).

Table 2.1: Dye classes and their types of fibres and application methods

Class	Types of fibres	Method of application
Acid	Nylon, wool, silk, and leather	Usually from neutral to acidic dye baths
Azoic	Cotton, rayon, cellulose acetate, and polyester	Fibre impregnated with coupling component and treated with stabilized diazonium salt
Basic	Paper, polyacrylonitrilemodified nylon, polyester, and inks	Applied from acidic dye baths
Direct	Cotton, rayon, paper, leather, and nylon	Applied from neutral or slight alkaline baths containing additional electrolyte
Disperse	Polyester, polyamide, acetate, acrylic, and plastics.	Fine aqueous dispersions applied by high temperature, pressure or lower

		temperature carrier methods.
Mordant	Wool, leather, and anodized aluminium	Applied in conjunction with chelating Cr salts
Reactive	Cotton, wool, silk, and nylon	Reactive site on dye reacts with functional group on fibre to bind dye covalently under influence of heat and pH (alkaline)
Sulfur	Cotton and rayon	Aromatic substrate vetted with sodium sulfide and re-oxidized to insoluble sulfur-containing products on fibre
Vat	Cotton, rayon, and wool	Water-insoluble dyes solubilised by reducing with sodium hydrosulfite, then exhausted on fibre and re-oxidized

2.1.2.1 Acid Dye

Acid dyes are a large class of dyes applied from acidic solutions to polyamide fibres. These dyes are used in the dyeing of wool, silk and nylon where they are typically applied in a bath that may range from neutral to strongly acidic and at near boiling temperature. Acid dyes range from poor to excellent colour fastness and from dull tones to brilliant shades (Kirk, 1993).

2.1.2.2 Azoic Dye

Also known as naphthol dyes, azoic dyes in fact are chemically synthesized inside the fibre and are not truly dyes, but insoluble pigments. Naphthol component which is soluble is applied to the fibre. Then a solution of diazo salt is used to develop the colour. Components used can be very toxic before they react to form the pigment (Kirk, 1993).

2.1.2.3 Basic Dye

Also known as cationic dyes, basic dyes are primarily used for acrylic fibres. They can also be used on certain nylon, and protein fibres. This dye has excellent colour fastness on acrylic while fastness on natural fibres is generally poor (Kirk, 1993).

2.1.2.4 Direct Dye

Direct dyes have high substantivity which meant that dyes from this class have high tendency to move onto fibres without the need for other chemicals to bond the dye to the fibre and therefore, have poor washfastness (Kirk, 1993).

2.1.2.5 Disperse Dye

The use of disperse dyes had increased in the textile industry ever since the discovery of synthetic fibers. Most of them contain amino or substituted amino groups. Dyes in this class are almost totally insoluble in water. Disperse dyes exist as dispersion of microscopic particles with only a tiny amount of solution at any time in the dye bath. These are the only dyes effective for polyester while some types are used for nylon and acetate. Disperse dyes can be applied to most synthetic fibers using simple exhaustion techniques. Polyester is dyed with disperse dyes by boiling it with carrier chemicals or by heating in a temperature of 103ºC which requires elevated pressure. Thermosol dyeing, in which the fabric is padded with dye liquor before being heated to 200 ºC for 90 seconds is also used for polyester and for colouring the polyester component of poly-cotton blends (Christie, 2001).

Disperse dyes belong mainly to three chemical classes namely nitoarylamine, azo, and anthraquinone. Dyes from this class cause environmental concern due to their widespread use, their degradation products, such as toxic aromatic amines and their low removal rate during biological aerobic treatment (Arslan 2001).

2.1.2.6 Mordant Dye

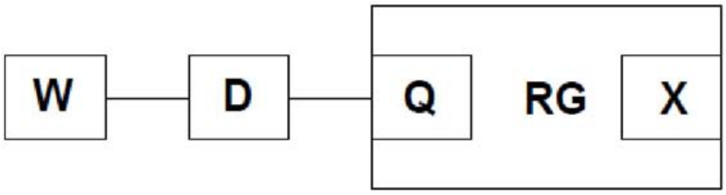
Mordant dye as its name suggests require the use of mordant; a chemical that aids attachment of a dyestuff to fibres by bonding to both fibre and dye. Example of a mordant is chromium, being used exclusively as mordant on wool. Many natural dyes require a mordant in which it can significantly influence the hue produced with a particular dyestuff (Kirk, 1993).

2.1.2.7 Reactive Dye

Reactive dyes are characterize by their readily water solubility as well as their high stability and persistence due to their complex structure. Since they are designed to resist degradation, this enables them to have high resistance against degradation by any means (Brown and Hamburger, 1987). Although reactive dyes in nature are non toxic, however under anaerobic conditions, they may break down into aromatic amines which are potentially carcinogenic and toxic (Pinheiro et al., 2004; Frank P and Villaverde 2005).

Reactive dyes are characterized as containing one or more groups capable of forming covalent bonds with the hydroxyl groups of cellulosic fibres with the amino, hydroxyl, and mercapto groups of protein fibres, and with the amino groups of polyamides (Zollinger, 1991; Waring and Hallas, 1994).

The structural feature of a reactive dye is shown in Figure 2.1 (Zollinger, 1991).



RG : electrophilic reactive group

Q : bridge link

X : nucleofugic leaving group

D : chromogen

W : water solubilizing group

Figure 2.1: Structural feature of a reactive dye

Structural feature of reactive dye comprised of 2 main parts namely the chromogen and the reactive group. The reactive group bonded to the chromogen by a bridge link generally contains an amino group responsible for the interaction with fibre (Zollinger, 1991).

Reactive dye attaches to the fibre by forming a covalent bond and are known for their bright colours with excellent washfastness even though with poor resistance to chlorine bleach. Most reactive dyes are intended specifically for wool. Reactive dyes of the same family can be mixed to produce wide range of colours while maintaining good application characteristics. However, reactivity among families varies widely therefore, some are easily applied at room temperature, some at boiling temperature while others at intermediate temperature. The largest commercial drawbacks to reactive dyes are that they require large amounts of electrolyte in most processes and extensive rinsing and hot washing after dyeing to remove unfixed and hydrolyzed dye (Christie, 2001).

2.1.2.8 Sulfur Dye

Sulfur dyes are a class of dye made by reacting sulfur with organic compounds in which most are of unknown chemical structure. Sulfur dyes are insoluble in water and had to be converted to a soluble form for application. They are generally dull in colours but inexpensive, have good washfastness but sensitive to bleach. Sulfur dyes may decompose under warm, humid conditions to form acid but this can be prevented by making the finished fabric slightly alkaline. Dyes under this class are often used commercially on cellulosic fabrics (Kirk, 1993).

2.1.2.9 Vat Dye

A class of dyes that are converted from the form of water insoluble pigment to a soluble form using a reducing agent, immersed to fabric, then converting back to the insoluble form by oxidation. Example of common vat dye is indigo, the blue of blue jeans. Vat dyes are very washfast and have good resistance to chlorine bleach. Multiple applications of dye may be required to build strong shades because of limited substantivity (Kirk, 1993).

2.2 TREATMENT OF DYE WASTEWATER

Dye molecules are highly structured polymers. Therefore, they are very difficult to break down biologically and cannot be treated efficiently by any activated sludge process or any combination of physical, chemical or biological methods (Lin and Lin, 1993).

As more environmental restrictions are being imposed, choices of dye wastewater treatment processes becomes of greater importance. These choices may well depend not only on the desired results, but on the type, amount, and cost of handling the waste resulting from the particular process. Furthermore, all these considerations have to be made while keeping in mind the public's increasing concern about the environment (Morelli, 1996).

With the current progress in both the technology and equipment required, treatment options are more varied bearing in mind that what seemed to be a good solution in one location, may well be detrimental in another (Morelli, 1996). There are three main treatments involved namely physical treatment, chemical treatment and biological treatment. Table 2.2 shows a comparison between all the treatments used in the treatment of dye wastewater.

Table 2.2: Comparison of different treatment process

Treatment	Advantages	Limitations	References
PHYSICAL 1) Adsorption 1.1) Activated Carbon	- Proven as one of the most effective and reliable physical treatment method.	- Reactivation of carbon results in 10-15% loss of sorbent and therefore it has to be regenerated to make it cost effective.	(Gómez et al., 2007)
1.2) Baggase	- Ability to absorb waste chemicals - Good alternatives for expensive absorbents	- Post treatment disposal	(Singh and Tiwari, 2001)
1.3) Peat	- Cellular structure of peat enables it to absorb polar organic compounds in dye - No activation required and less cost	- More inefficient as compared with activated carbon	(Bousher et al., 1997)

Treatment	Advantages	Limitations	References
1.4) Wood Chips	- Good removal of organics - Good sorbent for dyes and colour causing polar organics	- Longer contact times needed due to their hardness - Large amount needed for treatment	(Bousher et al., 1997) (Nigam et al., 2000)
2) Ion Exchange	- The resin contains high concentration of acid sites, which makes them an effective catalyst for facile reaction.	- Not applicable for wide range of dyes - High operating cost	(Ali et al., 2007)
3) Membrane Filtration	- Reclamation of textile effluent with good permeate qualities	- Flux decline	(Goksen et al., 2006)
CHEMICAL 1) Coagulation and precipitation	- Good removal of colourants and other dissolve organic compounds	- High cost of chemicals for pH adjustments & high sludge problem.	(Tan et al., 2000)
2) Cucurbituril	- Presence of organic substances does not interfere with the formation of complexes.	- High cost	(Slokar et al., 2001)

Treatment	Advantages	Limitations	References
3) Oxidation 3.1) Fenton	- Strong oxidizing species are able to break large toxic organics into small molecules	- High sludge production	(Anand et al., 2008)
3.2) Ozonation	- Able to convert bio-refractory dyes in wastewater into biodegradable species	- Short half life demanding continuous application	(Wu et al., 2008)
3.3) Sodium Hypochlorite (NaOCl)	- Effectively attack the amino group of dye molecule by Cl^+	- Require use of Chlorine and the release of aromatic amines.	(Robinson et al., 2001)
3.4) Electro-chemical Oxidation	- Lower temperature and do not require any additional chemicals - End products are non hazardous	- Rapid loss of efficacy due to surface fouling.	(Marco and Giacomo, 2008)
3.5) Photocatalysis	- Mild operating conditions; can be powered by sunlight. - Effective in removing colour and COD.	- Effective for small amount of colourants.	(Secula et al., 2008)

Treatment	Advantages	Limitations	References
3.6) Sonolysis	- Simple to use	- Extreme conditions needed	(Aline et al., 2006)
3.7) Irradiation	- Simple and efficient in eliminating a wide variety of organic contaminants and disinfect harmful microorganisms	- Requires high cost and maintenance	(László and Erzsébet, 2008)
3.8) H_2O_2/Pyridine/Cu(II) system	- Effective in treating synthetic dyes - Unaffected at a wide range of pH	- Effective for all dyes except Rifacion Yellow HE-4R and Levafix Yellow Brown E-3RL	(Bali and Bünyamin, 2007a)
BIOLOGICAL 1) Aerobic	- Colour removal is facilitate with COD reduction	- Heavy metals in dye molecules will inactivate the microorganisms	(Anjaneyulu et al., 2005)
2) Anaerobic	- Production of biogas which can be reused to provide heat and power.	- Longer acclimatization phase	(Bras et al., 2005)

Treatment	**Advantages**	**Limitations**	**References**
3) Single cell	- Effective for specific colourant removal	- Cannot cope in large volumes of coloured effluents.	(Anjaneyulu et al., 2005)
4) Enzymatic treatment	- Able to remove compounds that can interfere with downstream treatment process.	- Tedious method during enzyme isolation and purification.	(Anjaneyulu et al., 2005)
5) Redox Mediators	- Easily available and enhances treatment by increasing efficiency of electron transfer.	- Depends on the biological activity of the system.	(Anjaneyulu et al., 2005)