

**ADSORPTION STUDIES OF DYES USING CLAY-BASED AND ACTIVATED
CARBON ADSORBENTS**

YASMIN BINTI CHE ANI

UNIVERSITI SAINS MALAYSIA

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**ADSORPTION STUDIES OF DYES USING CLAY-BASED AND ACTIVATED
CARBON ADSORBENTS**

by

YASMIN BINTI CHE ANI

**Thesis submitted in fulfillment of the
requirements for the degree
of Master of Science**

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NOMENCLATURE

Symbol	Description	Unit
a_L	Langmuir isotherm constant	[L/mg]
C_o	The highest initial dye concentration	[mg/L]
C_e	The equilibrium concentration of dye	[mg/L]
C_i	The initial concentration of dye	[mg/L]
C_t	The concentration of dye at time, t	[mg/L]
E_a	Activation energy	[kJ/mol]
K_c	Equilibrium distribution coefficient	[-]
K_f	Freundlich isotherm constant	[(mg/g(L/mg) ^{1/n})]
K_L	Langmuir isotherm constant	[L/mg]
k_p	Intraparticle diffusion rate constant	[g/mg hr ^{1/2}]
k_1	Equilibrium rate constant of pseudo-first sorption	[L/min]
k_2	Equilibrium rate constant of pseudo-second sorption	[g/mg min]
n	Adsorption tendency	[-]
q_e	Amount of dye sorbed at equilibrium	[mg/g]
q_t	Amount of dye sorbed at time, t	[mg/g]
R	Universal Gas constant, 8.314	[J/mol K]
R_L	Dimensionless constant separation factor	[-]
R^2	Correlation coefficient	[-]
T	Absolute temperature	[K]
t	Time	[hrs or min]
V	The volume of the solution	[L]
W	The weight of adsorbent	[g]
X_m	Monolayer capacity of the adsorbent	[mg/g]
ΔG	Free energy Gibbs	[kJ/mol]

ΔH	Enthalpy	[kJ/mol]
ΔS	Entropy	[J/mol K]
Δq	Normalized standard deviation	[-]
λ	Wavelength	[nm]

LIST OF ABBREVIATION

Acid Blue 29	AB29
Acid hydrochloric	HCl
Activated carbon cloths	ACCs
Aluminium oxide	Al ₂ O ₃
Basic Blue 66	BB66
Brunauer-Emmett-Teller	BET
Calcium oxide	CaO
Chemical index	C.I.
Chemical oxygen demand	COD
Diphosphorus pentoxide	P ₂ O ₅
Direct Red 2	DR2
Direct Yellow 12	DY12
Energy disperse X-ray	EDX
Ferum oxide	Fe ₂ O ₃
Fourier transform infrared	FT-IR
Hours	hrs
Hydrogen peroxide	H ₂ O ₂
Infra Red	IR
International Union of Pure and Applied Chemistry	IUPAC
Kelvin	K
Lignin peroxides	LiP
Lost on ignition	LOI
Magnesium oxide	MgO
Manganese dependent peroxides	MnP
Mangan dioxide	MnO ₂
Methylene Blue	MB

Nano filtration	NF
Polychlorinated biphenyls	PCBs
Polyvinyl alcohol	PVA
Potassium bromide	KBr
Potassium oxide	K_2O
Scanning electron microscopy	SEM
Sodium hydroxide	NaOH
Sodium hypochloride	NaOCl
Sodium oxide	Na_2O
Solid state fermentation	SSF
Solophenyl Green	SG
Silica dioxide	SiO_2
Strontium oxide	SrO
Titanium dioxide	TiO_2
Ultraviolet	UV
X-ray Fluorescence	X-RF
Zinc oxide	ZnO
Zirconium dioxide	ZrO_2

KAJIAN PENJERAPAN UNTUK PENCELUP MENGGUNAKAN BAHAN PENJERAP BERASASKAN TANAH LIAT DAN KARBON TERAKTIF

ABSTRAK

Objektif kajian ini adalah untuk mengkaji penyingkiran pencelup 'Basic Blue 66' (BB66), 'Acid Blue 29' (AB29) dan 'Direct Red 2' (DR2) dari air sisa sintetik melalui penjerapan oleh penjerap tanah liat dan karbon teraktif. Parameter operasi yang dikaji termasuklah kepekatan awal, (10–600 mg/L), suhu, (30, 45 dan 55°C) dan pH, (2–10). Ujikaji secara kelompok telah dijalankan. Data ujikaji garis sesuhu dianalisis menggunakan model garis sesuhu 'Langmuir' dan 'Freundlich'. Ia menunjukkan bahawa model garis sesuhu 'Langmuir' padan data dengan baik bagi ketiga-tiga pencelup oleh kedua-dua penjerap. Faktor pemisah tidak berdimensi, R_L yang dikira menunjukkan bahawa penjerapan ketiga-tiga pencelup oleh kedua-dua penjerap adalah baik. Persamaan kinetik pseudo tertib pertama, pseudo tertib kedua dan model resapan intrazarah digunakan untuk mengkaji data eksperimen kepekatan awal yang berlainan. Data menunjukkan bahawa bagi kedua-dua penjerap mematuhi persamaan kinetik pseudo tertib kedua. Analisis termodinamik telah dijalankan untuk semua sistem pencelup-penjerap. Ia menunjukkan bahawa proses penjerapan ketiga-tiga pencelup bagi karbon teraktif adalah serap haba secara semulajadi. Nilai ΔH untuk penjerapan pencelup BB66, AB29 dan DR2 oleh karbon teraktif ialah masing-masing, 41.5, 48.8 dan 27.0 kJ/mol. Manakala bagi tanah liat, proses penjerapan untuk pencelup BB66 dan DR2 adalah serap haba kecuali untuk pencelup AB29. Nilai ΔH untuk penjerapan pencelup BB66, DR2 dan AB29 oleh tanah liat ialah masing-masing, 51.6, 26.6 dan -14.5 kJ/mol. Prestasi kedua-dua penjerap untuk menjerap pencelup BB66, AB29 dan DR2 juga dibandingkan. Ia menunjukkan bahawa keupayaan penjerapan oleh karbon teraktif untuk menjerap kedua-dua BB66 dan AB29 adalah lebih tinggi daripada penjerap tanah liat. Manakala, penjerap tanah liat menunjukkan keupayaan penjerapan yang lebih tinggi daripada karbon teraktif untuk penjerapan pencelup DR2. Kawasan permukaan BET dan

taburan saiz liang untuk kedua-dua penjerap diperolehi melalui penjerapan N_2 pada 77K. Morfologi permukaan juga dikaji menggunakan kemikroskopan elektron imbasan (SEM). Komposisi kimia, analisis unsur dan kumpulan berfungsi pada permukaan masing-masing menggunakan teknik X-RF, EDX dan FT-IR

ADSORPTION STUDIES OF DYES USING CLAY-BASED AND ACTIVATED CARBON ADSORBENTS

ABSTRACT

The objective of this study was to investigate the removal of Basic Blue 66 (BB66), Acid Blue 29 (AB29) and Direct Red 2 (DR2) dyes from synthetic wastewater by the adsorption on clay-based and activated carbon adsorbents. The operation parameters investigated included initial concentrations, (10-600 mg/L), temperature, (30, 45 and 55°C) and pH, (2-10). Experimental tests were conducted in a batch process. The experimental isotherms data were analyzed using Langmuir and Freundlich isotherm models. The data was found that Langmuir isotherm model fits the data very well for all three dyes on both adsorbents. The calculated dimensionless separation factor, R_L indicated that the adsorptions of the three dyes onto both adsorbents were favourable. Pseudo-first order, pseudo-second order kinetic equations and intraparticle diffusion model were used to examine the experimental data of different initial concentrations. It was found that the pseudo-second order kinetic equation described the data of dyes adsorption on both adsorbents very well. Thermodynamic analysis was carried out for all dye-adsorbent systems. It was found that the adsorption processes of all three dyes on activated carbon were endothermic in nature. The values of ΔH for BB66, AB29, and DR2 dyes adsorption on activated carbon were 41.5, 48.8 and 27.0 kJ/mol, respectively. The adsorption process for BB66 and DR2 dyes onto clay were endothermic except for AB29 dye. The values of ΔH for BB66, DR2 and AB29 dyes adsorption on clay were 51.6, 26.6 and -14.5 kJ/mol, respectively. The performance of both adsorbents to adsorb BB66, AB29 and DR2 dyes was also compared. It was found that the adsorption capacity of activated carbon to adsorb both BB66 and AB29 was higher than clay adsorbent. While clay adsorbent exhibited higher adsorption capacity than activated carbon for adsorption of DR2 dye. The BET surface areas and pore size distributions for both adsorbents were obtained by N_2 adsorption at 77K.

Surface morphology was also examined using Scanning Electron Microscopy (SEM). The chemical composition, elemental analysis and functional groups of the surface were conducted using X-RF, EDX and FT-IR techniques, respectively.

CHAPTER ONE INTRODUCTION

1.1 Environmental issue

Environmental pollution control has been a concerned issue in many countries. The most concerned environmental pollution is air pollution and wastewater pollution. Air pollution usually comes from open burning especially the forest and vehicles combustion while wastewater pollution comes from the industrial effluent and also from the domestic sewage.

It is an interesting issue since it is one of the most public health concerns. Wastewater pollution gives bad effects on public water supplies which can cause health problem such as diarrhea. While air pollution can cause lung diseases, burning eyes, cough and chest tightness.

Additionally, it is also an esthetic concern caused by odours and discolouration which interferes bathing facilities and recreation. It is also can cause property damage such as the discharge of sewage affects industrial water supplies by changing the character of the water. It is also affect real estate by causing paints to discolour as well as damage to boat. While ashes, smokes and dust can dirty and discolour structures and other property including clothes and furniture. Acid aerosols can eat away stone used on buildings, statues and monuments. Therefore treatment of these pollutions is very important.

1.2 Wastewater pollution

One of the major environmental pollution is wastewater. Wastewater is the spent water after homes, commercial establishments, industries and public institutions which used waters for various purposes. This polluted water comes from the domestic

and also from the industries since the increasing of population and industrial expansion especially from the developed countries.

These contaminants such as heavy metal, cyanide, toxic organics, nitrogen, phosphorous, phenols, suspended solids, colour and turbidity from the industries and untreated sewage sludge from the domestics are become a great concern to the environment and public health. Table 1.1 shows the physical characteristics of wastewater and their sources (Cheremisinoff, 1995).

Table 1.1 Physical Characteristic of Wastewater and Their Sources (Cheremisinoff, 1995)

Physical characteristic	Sources
Colour	Domestics and industrial wastes, natural decay of organic materials
Odour	Decomposing wastewater, industrial wastes
Solids	Domestic water supply, domestic and industrial wastes, soil erosion, inflow-infiltration
Temperature	Domestic and industrial wastes

The environmental issues surrounding the presence of colour in effluent is continuing problem for dyestuff manufactures, dyers, finishers and water companies, because increasingly stringent colour consent standard are being enforced by regulatory bodies to reduce the quality of colour in effluent and water courses. Therefore, Department of Environment, Ministry of Natural Resources and Environment, Malaysia has established interim national water quality standards for Malaysia. For example the maximum contaminant level for colour is 15 colour units. The unit of measurement of colour is the platinum in potassium chloroplatinate (K_2PtCl_6). One milligram per liter of Pt in K_2PtCl_6 is one unit of colour (Sincero and Sincero, 2003). Table 1.2 shows the maximum contaminants levels and their classes and uses (Interim National Water Quality Standards for Malaysia, 2004).

Table 1.2 Maximum contaminants levels and their classes and uses (Interim National Water Quality Standards for Malaysia, 2004)

CLASSES							
PARAMETERS	UNIT	I	IIA	IIB	III	IV	V
Amoniacal Nitrogen	mg/L	0.1	0.3	0.3	0.9	2.7	>2.7
BOD	mg/L	1	3	3	6	12	>12
COD	mg/L	10	25	25	50	100	>100
DO	mg/L	7	5 - 7	5 - 7	3 - 5	<3	<1
pH		6.5 - 8.5	6 - 9	6 - 9	5 - 9	5 - 9	-
Colour	TCU	15	150	150	-	-	-
Elec. Conductivity*	Umhos/cm	1000	1000	-	-	6000	-
Floatables		N	N	N	-	-	-
Odour		N	N	N	-	-	-
Salinity	%	0.5	1	-	-	2	-
Taste		N	N	N	-	-	-
Total Dissolved Solid	mg/L	500	1000	-	-	4000	-
Total Suspended solid	mg/L	25	50	50	150	300	300
Temperature	°C	-	Normal +2°C		Normal +2°C	-	-
Turbidity	NTU	5	50	50		-	-
Faecal Coliform**	counts/100mL	10	100	400	5000 (20000) ^a	5000 (20000) ^a	-
Total Coliform	counts/100mL	100	5000	5000	50000	50000	>50000

Notes

- N No visible floatable materials or debris or No objectionable odour, or No objectionable taste
- * Related parameters, only one recommended for use
- ** Geometric mean
- a Maximum not to be exceeded

Table 1.2 Continued

Class	Uses
CLASS I	Conservation of natural environment water supply 1 – practically no treatment necessary
	Fishery I – very sensitive aquatic species
CLASS IIA	Water Supply II – Conventional treatment required
	Fishery II – sensitive aquatic species
CLASS IIB	Recreational use with body contact
CLASS III	Water Supply III – extensive treatment required
	Fishery III – common, of economic value, and tolerant species livestock drinking
CLASS IV	Irrigation
CLASS V	None of the above

Decolourisation of wastewater has become one of the major issues in wastewater pollution. This is because many industries used dyes to colour their products, such as textiles, rubber, paper, plastics, leather, cosmetics, food and mineral processing industries. Especially, the textile finishing industry has a specific water consumption (approx. 1L/kg of product), part of which is due to dyeing and rinsing processes (Garg *et al.*, 2004a). Of current world production of dyestuffs of ≈ 10 million kg/ year between 1 and 2 million kg of active dye enter the biosphere, either dissolved or suspended in water, every year (Allen *et al.*, 2003).

These dyes are invariably left in the industrial wastes. Since they have a synthetic origin and complex aromatic molecular structures, which make them inert and difficult to biodegrade when discharged into waste streams, people overlook their undesirable nature (Ho and Chiang, 2004). The presence of very low concentrations of dyes in effluent is highly visible and undesirable. Furthermore, some dyes and their degradation products may be carcinogens and toxic and consequently, they are

important sources of water pollutions and their treatment become a major problem for environmental managers.

Some dyes are harmful to aquatic life in rivers where they are discharged. Since, dye can reduce light penetration into the water thereby decreasing the efficiency of photosynthesis in aquatic plants and hence having adverse impact on their growth (Yu *et al.*, 2004). According to Kadirvelu *et al.* (2003) dyes also can cause severe damage to human beings, such as dysfunction of kidney, reproductive systems, liver, brain and central nervous system. The occupational exposure of workers in the textile industry is linked to a higher bladder cancer risk. The use of hair colouring product and breast cancer have also been linked. Hence decolourisation of dye house effluent via the removal of dye has become an important aspect of textile wastewater treatment.

1.3 Methods to remove dyes

Most of dyes are known to be non-biodegradable. Thus the conventional primary and secondary systems are not suitable to treat these effluents (Gürses *et al.*, 2004). Some investigations have focused on the development of a treatment process for dye wastewater, such as biological and advanced oxidation processes. For the former, it has been found that it may be efficient in the removal of suspended solids and reduction of chemical oxygen demand but is largely ineffective in removing colour from wastewater. For the latter, because of the higher organic concentration and complex composition of dye wastewater, the dye wastewater cannot be efficiently purified and treated.

Many physical and chemical processes for colour removal have been applied including coagulation and flocculation, biosorption, photo-decomposition and ultrafiltration, oxidizing agents, membrane and electrochemical. The advantages and

disadvantages of each technique have been extensively reviewed (Robinson *et al.*, 2001). Due to relatively high operating costs and low removal efficiencies using the above-mentioned processes, textile, tannery, pulp and paper industries seldom apply these to treat their effluents.

Adsorption process has been found to be an efficient and economic process to remove dyes, pigments and other colorants (Wang *et al.*, 2003). It is also has been found to be superior to other technique for wastewater treatment in terms of initial costs, simplicity of design, ease of operation and insensitivity to toxic substances (Garg *et al.*, 2004b). Adsorption using activated carbon is rapidly becoming a prominent method of treating aqueous effluents and has been used in industrial processes for variety of separation and purification process.

Activated carbon was usually used as adsorbent for dye removal from wastewater. This could be related to their extended surface area, high adsorption capacity, microporous structure and special surface reactivity (Banat *et al.*, 2003). However, commercial activated carbon remains an expensive material. This has led to a search for low-cost material as alternative adsorbent materials. Ramakrishna and Viraraghavan (1997) investigated the removal of dyes on four low-cost adsorbents, peat, steel plant slag, bentonite clay and fly ash. Nevertheless, studies have been made on decolourisation of wastewater using cost-effective adsorbent system. Some natural adsorbents, such as clays and clay minerals (Gürses *et al.*, 2004) and cross-linked chitosan beads (Chiou *et al.*, 2004) have been examined to match the requirements. Moreover, certain waste materials, such as steel and fertilizer industrial waste (Gupta *et al.*, 2004), sewage sludge (Annadurai *et al.*, 2003) and waste coir pith (Namasivayam *et al.*, 2001) as well as agricultural by-product, such as wheat straw, concorbs and barley husks (Robinson *et al.*, 2002), banana and orange peels (Annadurai, *et al.*, 2002) have recently become the subject of considerable interest.

Their results point towards viable adsorbent, which are both effective as well as economically attractive for colour removal from wastewater.

Of these alternatives, clay seems to be more economically attractive because it is abundant. The ability of clay to refine oils, fats and waxes has been well known. Recently, clay has been accepted as one of the appropriate low-cost adsorbents for the removal of dyes from wastewater. Clay is the main components of the mineral fraction of soils. They are effective natural adsorbents due to their small particle sizes, lamellar structures, and negatively charged surfaces, which make them good cation adsorbents with large reactive surface areas for ion exchange or electrostatic attraction. Adsorption using clay as an adsorbent is an inexpensive methods since some clay derivatives can be easily prepared and regenerated. Clay derivatives also may be promising adsorbents for environmental purification purposes (Gürses *et al.*, 2004).

1.4 Objective of the research

The main purpose of this work was to study the removal of Basic Blue 66 (BB66), Acid Blue 29 (AB29) and Direct Red 2 (DR2) dyes from synthetic wastewater by adsorption technique in batch process. This research has several aims to achieve its desired output and the following objectives have been undertaken to:

1. Study the removal of BB66, AB29 and DR2 dyes from synthetic wastewater using clay-based and commercial activated carbon adsorbents.
2. Establish the adsorption isotherms of the three dyes on both clay-based and commercial activated carbon adsorbents.
3. Study the kinetics and thermodynamics of the adsorption process.
4. Compare the performance of both adsorbents for removal of dyes.

1.5 Organization of the thesis

There are five chapters in the thesis, and each chapter gives important information of the thesis.

Chapter two presents a review of the literature. It is divided into three sections. The first section presents a general definition of dye and the treatment technologies for dye removal. The second section gives a brief explanation on the theory of adsorption process while the last section presents a review on the isotherm models and kinetics of the batch adsorption process.

Chapter three covers the experimental part. This chapter is divided into three sections. The first section presents the materials and chemicals used in the experiments. The second section gives a general description of equipment used for the batch experiment and for characterization of the two adsorbents, while the third section is a general description of the experimental procedures.

Chapter four presents the experimental results together with the discussion. It is grouped into five sections. The first section presents the results for characterization of both clay-based and activated carbon adsorbents. The second section gives results on the equilibrium studies and the third section presents the results on kinetics studies and mechanism. The fourth section gives the results for the thermodynamic studies while last section presents a comparison between clay and activated carbon performance for the adsorption process.

Finally, chapter five gives the conclusions and recommendations of the thesis.

CHAPTER TWO LITERATURE REVIEW

2.1 Colorant

Colorants are characterized by their ability to absorb visible light from 400 to 700 nm, due to this reason that they appear to be coloured. There are two large groups of colorant, which are natural organic and inorganic. Man has used colorants since prehistoric times. However, it was the discovery of mauve by Perkin in 1865, which marked the start of the synthetic dye industry (Zollinger, 1987).

The most important differentiation of colorant is that colorant is either dyes or pigment. These terms are often used indiscriminately, in particular, pigments are quite often considered to be a group of dyes. Ideal pigments are characterized by being practically insoluble in the media in which they are applied. Pigment particles have to be attached to substrates by additional compounds, for example by a polymer in paint, in a plastic or in a melt. Dyes, on the other hand, are applied to various substrates (textile materials, leather, paper and hair) from a liquid in which they are completely, or at least partly, soluble. In contrast to pigments, dyes must possess a specific affinity to the substrate for which they are used (Zollinger, 1987).

2.2 Dye

Dye has been used since the prehistoric times. The prehistoric man used to dye furs, textile and other objects with natural substances, mainly vegetable, but also of animal origin. Nowadays, dyes are not only made from the natural sources but also there are synthetic dyes. They are widely used in many industries such as textile, paper, leather and mineral processing industries to colour their product. Dye is a natural or synthetic colouring material, whether soluble or insoluble, which impart its

colour to a material by staining or being imbibed by it, and which employed from a solution of fine dispersion, sometimes with aid of mordant.

The scale and growth of the dyes industry has been inextricably linked to that of the textile industry. World textile production has grown steadily to an estimated 35×10^6 tons in 1990 (Hunger, 2003a). The two most important textile fibers are cotton, the largest, and polyester. Consequently, dye manufacturers tend to concentrate their efforts on producing dyes for these two fibers. The estimated world production of dyes in 1990 was 1×10^6 tons. The figure is significantly smaller than that for textile fibers because a little dye goes a long way. For example, 1 ton of dye is sufficient to colour 42,000 suits (Hunger, 2003a). In Malaysia dyes have been widely used in textile industries especially in batik industries, which is so popular in the east coast of Malaysia.

2.3 Classification systems for dyes

Dyes can be grouped in accordance with two different principles:

- a) Chemical structure (chemical classification)
- b) Dyeing methods areas of application (colouristic classification)

A review of the whole field of technical dyes shows that the two classifications overlap that there is hardly a chemical class of dye, which occurs solely in one colouristic group, and vice versa.

When classified according to the dyeing method, they may be anionic, direct or disperse dyes, depending on whether they are intended for use on protein, cellulose or polyamide fibers. Moreover, certain reactive dyes with a particular type of chemical structure can be used for several substrates, whilst others with the same type of structure are suitable for only a single substrate.

It is possible to devise a logical method of chemical classification. With some classes of dyes, however, we have abandoned the conventional nomenclature, since it is either wrong (for instance, 'basic' instead of 'cationic' dyes) or insufficiently comprehensive (for example phthalocyanine as a sub group of aza annulene structure).

Both classifications are used by the Colour Index (1971) which lists all dyes and pigments used commercially for large-scale colouration purposes, that is dyeing of textile fibers, for pigment colouration of plastics, paints, printing inks and for the colouration of liquids (solvent and so on).

According to Fu and Viraraghavan (2001) dyes are classified as anionic, cationic and nonionic. Anionic dyes are the direct, acid and reactive dyes. A cationic dye is basic dyes; while a nonionic dye is disperse dyes. Nonionic dyes refer to disperse dyes because they do not ionize in an aqueous medium. The chromophores in anionic and nonionic dyes are mostly azo groups or anthraquinone types. Where, chromophore is the group producing the colour. Table 2.1 summarized the application classes of dyes and their chemical types (Hunger, 2003a).

2. 4 Disadvantages of dyes

Dyes are sometimes being viewed as something other than ordinary chemical. But, actually it is an individual chemical itself like all other chemical such as sodium chloride, acetic acid and benzidine. They are similar in their reactions to some other chemicals, and distinctly different from other. Therefore, there is a possibility that they are toxic. This is because many dyes are made from known carcinogens, such as benzidine and other aromatic compounds (Fu and Viraraghavan, 2001).

Table 2.1 Application Classes of Dyes and Their Chemical Types (Hunger, 2003a).

Class	Substrate	Method of Application	Chemical types
Acid	Nylon, wool, silk, paper, inks and leather.	Usually from neutral to acidic bath.	Azo (including premetallized), anthraquinone, triphenylmethane, azine, xanthene, nitro and nitroso.
Basic	Paper, polyacrylonitrile, modified nylon, polyester and inks.	Applied from acidic dye baths.	cyanine, hemicyanine, diazahemicyanine, diphenylmethane, triarylmethane, azo, azine, xanthene, acridine, oxazine and anthraquinone.
Reactive	Cotton, wool, silk and nylon.	Reactive site on dye reacts with functional group on fiber to bind dye covalently under influence of heat and pH (alkaline).	Azo, anthraquinone, phthalocyanine, formazan, oxazine and basic.
Direct	Cotton, rayon, paper, leather and nylon.	Applied from neutral or slightly alkaline baths containing additional electrolyte.	Azo, phthalocyanine, stilbene, and oxazine.
Disperse	Polyester, polyamide, acetate, acrylic and plastics.	Fine aqueous dispersions often applied by high temperature/pressure or lower temperature carrier methods; dye maybe padded on cloth and baked on or thermo fixed.	Azo, anthraquinone, styryl, nitro and benzodifuranone.
Solvent	Plastics, gasoline, varnishes, lacquers, stains, inks, fats, oils, and waxes.	Dissolution in the substrate	Azo, triphenylmethane, anthraquinone, and phthalocyanine
Sulfur	Cotton and rayon	Aromatic substrate vatted with sodium sulfide and reoxidized to insoluble sulfur-containing products on fiber	Indeterminate structures
Vat	Cotton, rayon and wool	Water-insoluble dyes solubilized by reducing with sodium hydrogensulfite, then exhausted on fiber and reoxidized	Anthraquinone (including polycyclic quinines) and indigoids

According to Daneshvar *et al.* (2003) dye bath effluent, in particular are not only aesthetic pollutants by nature of their colour but also can interfere light penetration through the bodies of water. Hence, dyes disturbing biological process of the aquatic life especially the photosynthesis activity. Furthermore, dyes are also carcinogenic, mutagenic, or teratogenic in various microbiological, fish species. Additionally it also can cause severe damage to human beings such as dysfunction of kidney, reproductive system, liver brain and central nervous system (Kadirvelu *et al.*, 2003). Table 2.2 shows the disadvantages according to different dye class (Robinson *et al.*, 2001).

Table 2.2 Disadvantages of different dye class (Robinson *et al.*, 2001)

Dye class	Disadvantages
Azo groups	Their reductive cleavage of azo linkages is responsible for the formation of toxic amines in the effluent.
Anthraquinone-based dyes	It is most resistant to degradation due to their fused aromatic ring structure and thus remains coloured for a longer time in wastewater.
Basic dyes	It has high brilliance and intensity of colours and is highly visible even in a low concentration.

2.5 Treatment technologies of dyes removal

There are over 100,000 commercially available dyes with a production of over 7×10^5 metric tons per year (Fu *et al.*, 2001; Robinson *et al.*, 2001). From all the industrial wastewater, the effluent from textile industry and dyestuff industry are the one, which is very difficult to treat. This is due to a synthetic origin and complex aromatic molecular structures, which make them more stable and more difficult to be biodegraded. Therefore removal of dyes from the industrial effluents in an economic fashion remains a major problem (Figueiredo *et al.*, 2000).

Conventional biological wastewater treatment systems are inefficient in treating dye wastewater. This is due to the low biodegradability of dye. Usually dye wastewater treated by physical- or chemical-treatment process. These include physical-chemical flocculation combined with flotation, electroflotation, flocculation with Fe (II)/Ca (OH)₂, membrane-filtration, electrokinetic coagulation, precipitation, ozonation and Katox treatment method involving the use of activated carbon and air mixtures (Fu and Viraraghavan, 2001). Robinson *et al.* (2001) have done a review on the widely used methods of removal dye from dye-containing industrial effluents. The methods have been categorized in three categories, which are chemical, biological, and physical.

2.5.1 Chemical method

2.5.1(a) Oxidative processes

This is the most commonly used method of decolourisation by chemical means. This is mainly due to its simplicity of application (Robinson *et al.*, 2001). It was stated that there is a need for more powerful oxidizing methods, such as chlorine, ozone, Fenton's reagent (peroxide and ferrous sulfate), UV/peroxide, UV/ozone, or other oxidizing techniques or combination. This is because modern dyes are resistant to mild oxidation condition, such as exist in biological treatment system. According to Robinson *et al.* (2001) the main oxidizing agent is usually hydrogen peroxide (H₂O₂). This agent needs to be activated by some means, for example, ultra violet light.

Szpyrkowicz *et al.* (2001) has done an experimental work on the destruction of disperse dyes by chemical oxidation using ozone, hypochlorite and Fenton reagent (H₂O₂+Fe²⁺). Their data were compared with the data obtained by electrochemical oxidation. Advanced oxidation process utilizing Fenton's reaction was also investigated for the decolourisation and degradation of H-acid and other dyes (Swaminathan, 2003).

H₂O₂-Fe (II) salts Fenton's reagent

Fenton's reagent is a suitable chemical means of treating wastewaters which are resistant to biological treatment or is poisonous to live biomass (Slokar and Le Marechal, 1997). Chemical separation uses the action of sorption or bonding to remove dissolved dyes from wastewater and has been shown to be effective in decolourising both soluble and insoluble dyes (Pak and Chang, 1999).

One major disadvantage of this method is sludge generation through the flocculation of the reagent and the dye molecules. The sludge, which contains the concentrated impurities, still requires disposal. It has conventionally been incinerated to produce power, but such disposal is seen by some to be far from environmental friendly. The performance is dependent on the final floc formation and its settling quality, although cationic dyes do not coagulate at all. Acid, direct, vat, mordant and reactive dyes usually coagulate, but the resulting floc is poor quality and does not settle well, yielding mediocre results (Raghavacharya, 1997).

Fenton's reagent and UV assisted peroxide techniques have also been evaluated. The limited penetration of UV light into dye solutions in the case of UV/peroxide methods, the cost of the Fenton's reagent approach, and the process complexity in the general have limited the development of these methods.

Nerud *et al.* (2001) have done a study on decolourisation of synthetic dyes by Fenton reagent and the Cu/pyridine/H₂O₂ system. They reported that decolourisation of the dye by Fenton reagent was very effective. Detailed investigations of photodegradation of Direct Yellow 12 (DY12) dye using UV/H₂O₂/Fe²⁺ has been carried out in a photochemical reactor (Rathi *et al.*, 2003). It has been observed that

simultaneous utilization of UV irradiation with Fenton's reagent increases the degradation rate of DY12 dye. The dye quickly loses its colour and there is an appreciable decrease in COD value, indicating that the dissolved organic have been oxidized.

Malik and Saha (2003) also studied the oxidative degradation of direct dyes in aqueous solution using Fenton reagent (Fe^{2+} and H_2O_2). The degradation of two azo reactive dyes also has been evaluated by photo-Fenton and Fenton-like oxidation (Neamtu *et al.*, 2003). While, Kim *et al.* (2004) have done a comparison of disperse and reactive dye removals by chemical coagulation and Fenton oxidation.

Ozonation

The use of ozone was first pioneered in the early 1970s, and it is a very good oxidizing agent due to its high instability (oxidation potential, 2.07) compared to chlorine, another oxidizing agent (1.36), and H_2O_2 (1.78). Oxidation by ozone is capable of degrading chlorinated hydrocarbons, phenols, pesticides and aromatic hydrocarbons (Xu and Lebrun, 1999). The dosage applied to the dye-containing effluent is dependent on the total colour and residual COD to be removed with no residue or sludge formation (Ince and Gönenç, 1997) and no toxic metabolites (Gahrs *et al.*, 1994).

Ozonation leaves the effluent with no colour suitable for discharge into environmental waterways (Xu and Lebrun, 1999). This method shows a preference for double-bonded dye molecules (Slokar and Le Marechal, 1997). While, Muthukumar and Selvakumar (2004) have investigated the effect of presence of inorganic salts namely, sodium chloride and sodium sulphate and their concentration on decolouration

of acid dye effluents by ozonation. It can be concluded that the presence of salt content in the acid dye effluent increases the complete decolouration time and hence decreases the decolouration efficiency of ozone. One major advantage is that ozone can be applied in its gaseous state and therefore does not increase the volume of wastewater and sludge.

Chromophore groups in the dyes are generally organic compounds with conjugated double bonds that can be broken down forming smaller molecules may have increased carcinogenic or toxic properties, and so ozonation may be used alongside a physical method to prevent this. Decolourisation occurs in a relatively short time.

A disadvantage of ozonation is its short half-life, typically being 20 min. This can be further shortened if dyes are present, with stability being affected by the presence of salts, pH, and temperature. In alkaline conditions, ozone decomposition is accelerated, and so careful monitoring of the effluent pH is required (Slokar and Le Marechal, 1997). Better results can be achieved using irradiation (Groff and Byung, 1989) or with a membrane filtration technique (Lopez *et al.*, 1999). One of the major drawbacks with ozonation is cost, continuous ozonation is required due to its short half-life (Xu and Lebrun, 1999).

Photochemical

This method degrades dye molecules to CO₂ and H₂O (Peralto-Zamora *et al.*, 1999) by UV treatment in the presence of H₂O₂. Degradation is caused by the production of high concentration of hydroxyl radicals. UV light may be used to activate chemicals, such as H₂O₂, and the rate of dye removal is influenced by the intensity of

the UV radiation, pH, dye structure and the dye bath composition (Slokar and Le Marechal, 1997). This may be set-up in a batch or continuous column unit (Namboodri and Walsh, 1996). Depending on initial materials and the extent of the decolourisation treatment, additional by-product, such as, halides, metals, inorganic acids, organic aldehydes and organic acids, may be produced (Yang *et al.*, 1998).

The photooxidation of a chlorotriazine reactive azo dye Reactive Orange 4 has been carried out in the presence of H₂O₂ using UV-A light. The effects of the reaction pH, applied H₂O₂ dose, and UV light power have been studied (Muruganadham and Swaminathan, 2004). The advantages of photochemical treatment of dye-containing effluent are; no sludge is produced and foul odours are greatly reduced, UV light activates the destruction of H₂O₂ into two hydroxy radicals:



This causes the chemical oxidation of organic material.

Sodium hypochloride (NaOCl)

This method attacks at the amino group of the dye molecule by the Cl⁺. It initiates and accelerates azo-bond cleavage. This method is unsuitable for disperse dyes. An increase in decolouration is seen with an increase in Cl concentration. The use of Cl for dye removal is becoming less frequent due to the negative effects it has when released into waterways (Slokar and Le Marechal, 1997) and the release of aromatic amines which are carcinogenic, or otherwise toxic molecules (Banat *et al.*, 1999).

Cucurbituril

Cucurbituril was first mentioned by Behrand *et al.* (1905) and then rediscovered in the 1980s by Freeman *et al.* (1981). It is a cyclic polymer of glycoluril and formaldehyde (Karcher *et al.*, 1999a,b). Cucurbituril, so named, because its structure is shaped like a pumpkin (a member of the plant family Cucurbitaceae). The uril, indicates that urea monomer is also part of this compound. Buschmann (1992) showed extraordinarily good sorption capacity of cucurbituril for various types of textile dyes. Cucurbituril is known to form host-guest complexes with aromatic compounds (Mock, 1995) and this may be the mechanism for reactive dye adsorption. Another proposed mechanism is based on hydrophobic interactions or the formation of insoluble cucurbituril dye-action aggregates since adsorption occurs reasonably fast. To be industrially feasible, cucurbituril would need to be incorporated into fixed bed sorption filters (Karcher *et al.*, 1999b).

Like many other chemical methods, cost is a major disadvantage. Cucurbituril was investigated regarding its potential as a sorbent for the removal of reactive dyes from model solutions and authentic wastewaters. The solubility of cucurbituril is low in pure water but increases in the presence of salts (Karcher *et al.*, 2001). Kornmüller *et al.* (2001) have also studied the ozonation and oxidative regeneration of cucurbituril.

Electrochemical destruction

This is a relatively new technique, which was developed in the mid 1990s. It has some significant advantages for use as an effective method for dye removal. There is little or no consumption of chemicals and no sludge build up. The breakdown metabolites are generally not hazardous leaving it safe for treated wastewaters to be released back into waterways. It shows efficient and economical removal of dyes and a

high efficiency for colour removal and degradation of recalcitrant pollutants (Pelegri *et al.*, 1999). Relatively high flow rates cause a direct decrease in dye removal, and the cost of electricity used is comparable to be price of chemicals.

2.5.2 Biological method

2.5.2(a) Decolourisation by white-rot fungi

White-rot fungi are those organisms that are able to degrade lignin, the structural polymer found in woody plants (Barr and Aust, 1994). The most widely studied white-rot fungus, in regards to xenobiotic degradation, is *Phanerochaete chrysosporium*. This fungus is capable of degrading dioxins, polychlorinated biphenyls (PCBs) and other chloro-organics (Reddy, 1995). Davis *et al.* (1993) also showed the potential of using *P. sordida* to treat creosote-contaminated soil. Kirby (1999) has also reported that *P. chrysosporium* had the ability to decolourise artificial textile effluent by up to 99% within 7 days.

White-rot fungi are able to degrade dye using enzymes, such as lignin peroxidases (LiP), manganese dependent peroxidases (MnP). Other enzymes, such as glucose-1-oxidase and glucose-2-oxidase, along with laccase, and a phenoloxidase enzyme (Kirby, 1999). These are the same enzymes used for the lignin degradation (Reddy, 1995). Azo dyes, the largest class of commercially produced dyes, are not readily degraded by micro-organisms but these can be degraded by *P. chrysosporium* (Paszczynski and Crawford, 1995). Other fungi such as, *Hirschioporus larincinus*, *Inonotus hispidus*, *Phlebia tremellosa* and *Coriolus versicolor* have also been shown to decolorise dye-containing effluent (Kirby, 1999).

Although white-rot fungi have been shown to decolourise dyes in liquid fermentations, enzyme production has also been shown to be unreliable. This is mainly due to the unfamiliar environment of liquid fermentations. The ability to utilize these fungi in their natural environment means that they are more likely to be more effective in solid state fermentation (SSF).

Selvam *et al.* (2003) have done a study on decolourisation of azo dyes and a dye industry effluent by white rot fungus *Thelephora* sp. Alginate beads, polyurethane foam, nylon sponge and stainless steel sponge were tested as carrier materials for the white-rot fungus *Trametes hirsuta* for laccase production under submerged fermentation conditions (Rodríguez *et al.*, 2004). They used this fungus for decolourisation of textile dye, Indigo Carmine. Toh *et al.* (2003) have done an investigation on decolourisation of azo dyes by white rot fungi isolated in Singapore. The isolated *Trametes versicolor* CNPR 8107 exhibited the greatest potential in treating dye effluents. While Levin *et al.* (2004) have investigated the decolourising capacity of 26 white rot fungi from Argentina. They reported that only ten strains decolourised all the dyes; all ten strains produced laccase, lignin peroxides and manganese peroxides on solid medium. However, six of the strains could not decolourise any of the dyes.

2.5.2(b) Other microbial cultures

Mixed bacterial cultures from a wide variety of habitats have also been shown to decolourise the diazolinked chromophore of dye molecules in 15 days (Nigam *et al.*, 1996). They demonstrated that a mixture of dyes was decolourised by anaerobic bacteria in 24-30 hrs, using free growing cells or in the form of biofilms on various support materials. Ogawa and Yatome (1990) also demonstrated the use of bacteria

for azo dye biodegradation. These microbial systems have the drawback of requiring a fermentation process, and are therefore unable to cope with larger volumes of textile effluents.

The ability of bacteria to metabolise azo dyes have been investigated by a number of research groups. Under aerobic conditions azo dyes are not readily metabolized although Kulla (1981) reported the ability of *Pseudomonas* strains to aerobically degrade certain azo dyes. However, the intermediates formed by these degradative steps resulted in disruption of metabolic pathways and the dyes were not actually mineralized. Under anaerobic conditions, such as anoxic sediments, many bacteria gratuitously reduce azo dye reportedly by the activity of unspecific, soluble, cytoplasmic reductases, known as azo reductases. These enzymes are reported to result in the production of colourless aromatic amines, which may be toxic, mutagenic, and possibly carcinogenic to animals.

Increasingly literature evidence suggests that additional processes may also be involved in azo dye reduction. It has been reported that many bacteria reduce a variety of sulfonated and non-sulfonated azo dyes under anaerobic conditions without specificity of any significance. In addition many highly charged and high molecular-sized sulfonated and polymeric azo dyes are unlikely to pass the cell membrane. Therefore, both pieces of evidence point to the existence of a reducing activity which is not dependent on the intracellular availability of the azo dye (Keck *et al.*, 1997).

Yeast, such as *Kluyveromyces marxianus*, is capable of decolourising dyes. Banat *et al.* (1999) showed that *K. marxianus* was capable of decolourising Remazol Black B by 78-98%. Zissi *et al.* (1997) also reported that *Bacillus subtilis* could be used

to break down p-amin-oazobenzene, a specific azo dye. Further research using mesophilic and thermophilic microbes has also shown them to degrade and decolourise dyes (Banat *et al.*, 1997).

2.5.2(c) Adsorption by living/dead microbial biomass

The uptake or accumulation of chemicals by microbial mass has been termed biosorption (Kumar *et al.*, 1998). Dead bacteria; yeast and fungi have all been used for the purpose of decolourising dye-containing effluents. Textile dyes vary greatly in their chemistries, and therefore their interactions with micro-organisms depend on the chemistry of a particular dye and the specific chemistry of the microbial biomass (Polman and Brekenridge, 1996). Depending on the dye and the species of micro-organism used different binding rates and capacities will be observed. It can be said that certain dyes have a particular affinity for binding with microbial species.

It had been observed that biomass derived from the thermotolerant ethanol-producing yeast strain, *K.marxianus* IMB3, exhibited a relatively high affinity for heavy metals (Riordan *et al.*, 1998). Biosorption capacities showed that this type of biomass had a significantly high affinity for dye removal, and so widened the spectrum of use for biomass (Bustard *et al.*, 1998).

The use of biomass has its advantages, especially if dye-containing effluent is very toxic. Biomass adsorption is effective when conditions are not always favourable for the growth and maintenance of the microbial population (Modak and Natarajan, 1995). Hu (1992) demonstrated the ability of the bacterial cells to adsorb reactive dyes, while Zhou and Zimmerman (1993) used actinomyces as an adsorbent for decolourisation of effluents containing anthraquinone, phalocyanine and azo dyes.

Biosorption tends to occur reasonably quickly: a few minutes in algae to a few hours in bacteria (Hu, 1996). This is likely to be due to an increase in surface area caused by cell rupture during autoclaving (Polman and Brekenridge, 1996). Fu and Viraraghavan (2002) also used biosorption to remove anionic disazo direct dye, Congo Red from an aqueous solution. They used dead fungus, *Aspergillus niger* which showed that it is a promising biosorbent for dye removal compared to activated carbon. While Waranusantigul *et al.* (2003) used dried *Spirodela polyrrhiza* biomass as an adsorbent for the removal of the basic dye Methylene Blue from aqueous solutions.

2.5.3 Physical method

2.5.3(a) Adsorption

Adsorption techniques have gained favour recently due to their efficiency in the removal pollutants too stable for conventional methods. Adsorption produces a high quality product, and is a process, which is economically feasible (Choy *et al.*, 1999). Also, adsorption process provides an attractive alternative treatment, especially if the adsorbent is inexpensive and readily available (Özacar and Şengil, 2003). Furthermore this process has the edge on the other method due to its sludge free clean operation and complete removal of dyes even from dilute solution (Malik, 2003). Therefore one of the powerful treatment processes for the removal of dyes from water with a low cost is adsorption. Several adsorbents are eligible for such a purpose.

Activated carbon

This is the most commonly used method of dye removal by adsorption (Nasser and El-Geundi, 1991) and is very effective for adsorbing cationic, mordant, and acid dyes and to a slightly lesser extent, disperse, direct, vat, pigment and reactive dyes (Raghavacharya, 1997). According to Malik, (2003) activated carbon is the most

widely used adsorbent for dye removal because of its extended surface area, microporous structure, high adsorption capacity and high degree of surface reactivity. Performance is dependent on the type of activated carbon used and the characteristics of the wastewater. Removal rates can be improved by using massive doses of carbon. Activated carbon, like many other dye-removal treatments, is well suited for one particular waste system and ineffective in another. Activated carbon is also expensive. The carbon also has to be reactivated otherwise disposal of the concentrates has to be considered. Reactivation process results in 10-15% loss of the sorbent.