

**ADSORPTION OF REACTIVE AZO DYES ON CHITOSAN/OIL-PALM ASH
COMPOSITE ADSORBENT: BATCH AND CONTINUOUS STUDIES**

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UNIVERSITI SAINS MALAYSIA

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by

MASITAH BINTI HASAN

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NOMENCLATURE

Symbols	Description	Unit
A	Arrhenius factor	Dimensionless
A_b	Area under breakthrough	Dimensionless
b	Langmuir constant	[L/mg]
B_1	Temkin isotherm constant	[-]
C_0	Initial liquid-phase solute concentration	[mg/L]
C_e	Equilibrium liquid-phase solute concentration	[mg/L]
C_t	Liquid-phase solute concentration at time, t	[mg/L]
C	Effluent liquid-phase solute concentration	[mg/L]
E	Mean energy of adsorption	[kJ/mol]
E_a	Activation energy	[kJ/mol]
k_c	Equilibrium distribution coefficient	[-]
k_f	Pseudo-first-order rate constant	(1/h)
k_s	Pseudo-second-order rate constant	(g/mg h)
k_i	Intraparticle diffusion rate constant	[(g/mg h)]
k	Boharts and Adam rate constant	(1/min)
k_{TH}	Thomas rate constant	mL/(min mg)
K_F	Freundlich isotherm constant	[(mg/g(L/mg) ^{1/n})]
K_t	Equilibrium binding constant	(L/mg)
K_{YN}	Yoon-Nelson rate constant	(1/min)
K	Temperature in Kelvin	(K)
n	Adsorption tendency	Dimensionless
N	Number of measurement	Dimensionless
q_e	Amount adsorbed at equilibrium time	(mg/g)
q_t	Amount adsorbed at time, t	(mg/g)
$q_{e,cal}$	Calculated of amount adsorbed at equilibrium time	(mg/g)

$q_{e,exp}$	Experimental of amount adsorbed at equilibrium time	(mg/g)
$q_{0,cal}$	Calculated of bed capacity in column	(mg/g)
$q_{0,exp}$	Experimental of bed capacity in column	(mg/g)
q_{total}	Total amount of dye adsorbed in column	(mg/g)
q_m	Maximum adsorption capacity (Dubinin-Raduskevich)	(mg/g)
Q_0	Maximum adsorption capacity (monolayer capacity)	(mg/g)
Q	Volumetric flowrate in column	(mL/min)
R	The universal gas constant	(8.314 Jmol ⁻¹ K ⁻¹)
R_L	Separation factor	Dimensionless
R^2	Correlation coefficient	Dimensionless
t	Time	(h or min)
t_{total}	Total flow time in column	(min)
V	Volume of solution	(L)
V_{eff}	Volume of effluent	(L)
W	Mass of dry adsorbent	(g)
ε	Polanyi potential	[-]
τ	The breakthrough time	(min)
ΔG^0	The standard free energy changes	(kJ/mol)
ΔH^0	The enthalphy change	(kJ/mol)
ΔS^0	The entrophy change	(kJ/mol)
λ	Wavelength	(nm)
$\varepsilon \%$	Average percentage errors	Dimensionless
T	Temperature	⁰ C

LIST OF ABBREVIATION

Activated carbons	AC
Absorbance	Abs
Bed depth service time	BDST
Chemical Index	C.I
Energy Disperse X-ray	EXD
Fourier Transform Infrared	FT-IR
Glutaric dialdehyde	GA
International Union of Pure and Applied Chemistry	IUPAC
Mass transfer zone	MTZ
Oil palm ash	OPA
Reactive Blue 19	RB19
Reactive Orange 16	RO16
Reactive Blue 5	RB5
Scanning Electron Microscopy	SEM
Ultraviolet	UV

PENJERAPAN PENCELUP AZO REAKTIF MENGGUNAKAN BAHAN PENJERAP KOMPOSIT CHITOSAN/ABU KELAPA SAWIT: KAJIAN KELOMPOK DAN BERTERUSAN

ABSTRAK

Penjerapan pencelup reaktif biru 19 (RB19), reaktif oren 16 (RO16) dan reaktif hitam (RB5) menggunakan manik-manik komposit chitosan/abu kelapa sawit terpaut silangan dikaji pada kedua-dua keadaan operasi iaitu kelompok dan terus. Kajian penjerapan kelompok dijalankan untuk penjerapan pencelup reaktif pada manik-manik komposit chitosan/abu kelapa sawit terpaut silangan. Pelbagai parameter eksperimen dikaji termasuklah kepekatan awal pencelup (50-500 mg/L), masa sentuh, pH bagi larutan (2-13) dan suhu (30-50 °C). Data-data eksperimen dianalisa menggunakan model garis sesuhu seperti 'Langmuir', 'Freundlich', 'Temkin' dan 'Dubinin-Raduskevich'. Penjerapan pencelup RB19 dan RO16 didapati menuruti model 'Freundlich', manakala pencelup RB5 lebih menunjukkan kesesuaian dengan model garis sesuhu 'Langmuir' dan 'Freundlich'. Model kinetik pseudo tertib pertama, pseudo tertib kedua dan model resapan intra zarah digunakan untuk menganalisa data kinetik. Didapati daripada keseluruhan suhu kajian yang dijalankan pencelup RB19 menuruti model kinetik pseudo tertib pertama pada kepekatan yang rendah, manakala pada kepekatan yang tinggi pula menuruti model kinetik pseudo tertib kedua. Berbeza pula dengan pencelup RO16 dan RB5 yang menuruti model kinetik pseudo tertib pertama untuk keseluruhan kajian kepekatan awal dan suhu yang dijalankan. Walaubagaimanapun, berdasarkan sisihan ternormal piawai, model kinetik pseudo tertib pertama sangat sesuai untuk keseluruhan sistem yang dikaji. Pelbagai parameter termodinamik seperti tenaga Gibbs (ΔG^0), perubahan entalpi (ΔH^0) dan perubahan entropi (ΔS^0) dikira, dimana ianya menunjukkan sistem tersebut adalah spontan dan merupakan proses serap haba untuk pencelup RB19 dan RO16. Walaubagaimanapun, proses luah haba pula didapati berlaku pada penjerapan pencelup RB5. Manik-manik komposit chitosan/abu kelapa sawit terpaut silangan dicirikan oleh Mikroskop Elektron

Imbasan (SEM) dan Spektrosopi Infra-merah Jelmaan Fourier (FT-IR). Spektrum FT-IR yang terhasil menunjukkan penglibatan kumpulan-kumpulan amine dalam penyerapan pencelup RB19, RO16 dan RB5 dan mekanisme yang terlibat adalah interaksi elektrostatik di antara cas positif kumpulan-kumpulan amine dan cas negatif pencelup. Prestasi sesuatu turus adalah berdasarkan konsep lengkung bulus 'breakthrough' untuk penyerapan pencelup RB19, RO16 dan RB5 pada bahan penyerap dalam pelbagai kepekatan awal pencelup (100, 200, 300 mg/L), kadar aliran (5-25 mL/min) dan ketinggian turus bahan penyerap (60, 80, 100 mm). Didapati jumlah bahan pencelup terjerap q_{eq} (mg/g) meningkat dengan peningkatan kepekatan awal pencelup dan ketinggian turus bahan penyerap dan berkurangan dengan peningkatan kadar aliran. Masa separuh hayat, $t_{1/2}$ untuk penyerapan pencelup RB19, RO16 dan RB5 adalah 10, 21 dan 22 minit masing-masing. Model-model seperti Boharts dan Adam, Thomas dan Yoon dan Nelson diaplikasikan pada data-data eksperimen untuk simulasi lengkung bulus. Didapati model Thomas adalah yang terbaik untuk memperihalkan penyerapan pencelup RB19, RO16 dan RB5 pada manik-manik komposit chitosan/abu kelapa sawit terpaut silangan dimana analisa purata ralat peratusan, $\epsilon\%$, adalah kurang daripada 3.1%.

ADSORPTION OF REACTIVE AZO DYES ON CHITOSAN / OIL-PALM ASH COMPOSITE ADSORBENT: BATCH AND CONTINUOUS STUDIES

ABSTRACT

The adsorption of reactive blue 19 (RB19), reactive orange 16 (RO16) and reactive black 5 (RB5) on cross-linked chitosan/oil palm ash composite beads was studied in batch and column modes of operation. Batch adsorption studies were carried out for adsorption of reactive dyes onto cross-linked chitosan/ oil palm ash composite beads. Various experimental parameters were studied including initial dye concentration (50 - 500 mg/L), contact time, pH of solution (2 - 13) and temperature (30 - 50 °C). The experimental data were analyzed using Langmuir, Freundlich, Temkin and Dubinin-Raduskevich isotherm model. The adsorption of RB19 and RO16 was found to follow Freundlich model, while RB5, showed a better fit to the Langmuir and Freundlich isotherm model. Pseudo-first-order, pseudo-second-order kinetic model and intraparticle diffusion model were used to analyze the kinetic data. It was found that the data follow the pseudo-first-order kinetic model at lower concentration, while at higher concentrations, it followed pseudo-second-order kinetic model for RB19 for all temperature studied. Contrary, RO16 and RB5 dye followed pseudo-first-order kinetic model for whole initial concentration and temperature studied. However, based on the standard normalized deviation, the pseudo-second-order kinetic model fitted well for whole system of dyes studied. Various thermodynamic parameters, such as Gibbs energy (ΔG^0), enthalpy change (ΔH^0) and entropy change (ΔS^0), were calculated, which indicated that the present system was spontaneous and endothermic process for RB19 and RO16. However, exothermic process of adsorption of RB5 was observed. The cross-linked chitosan/oil palm ash composite beads were characterized by Scanning Electron microscopy (SEM) and Fourier Transform Infrared (FT-IR) Spectroscopy. Evidence from FT-IR spectra showed the participation of amine groups in the adsorption of RB19, RO16 and RB5 dyes and the mechanism was proposed to be electrostatic interaction between the positive charge amine groups and negative

charge dyes. The performance of column are described through the concept of the breakthrough curve for the adsorption of RB19, RO16 and RB5 on adsorbents under different operating conditions including initial dye concentration (100, 200, 300 mg/L), flowrate (5 – 25 mL/min) and height of adsorbent bed (60, 80, 100 mm). It was found that the amount of adsorbate adsorbed, q_{eq} (mg/g) increased with increasing initial dye concentration and height of adsorbent bed; and decreased with increasing flow rate. The $t_{1/2}$ for the adsorption of RB19, RO16 and RB5 dye was found 10, 21 and 22 min, respectively. Boharts and Adam, Thomas and Yoon and Nelson models were applied to the experimental data to simulate the breakthrough curves. It was found that the Thomas model was best fitted to describe the adsorption of RB19, RO16 and RB5 dyes on cross-linked chitosan/oil palm ash composite beads, which analysis on average percentage error, $\epsilon\%$ give less than 3.1%.

CHAPTER ONE

INTRODUCTION

1.1 Environmental issues in Malaysia

Environmental pollution problems in Malaysia have a long history. River pollution by mine wastewater and sludge began with the rapid development of tin mining, a traditional industry that started at the turn of the century about 100 years ago. In later years, other traditional industries such as natural rubber and palm oil production began in earnest, and wastewater from the factories caused further pollution of rivers and seas. From the late 1960s, Malaysia pursued rapid industrialization supported by foreign investment, but the result of industrialization was a raft of pollution problems, caused by industrial wastewater and other wastes, which became very apparent from the 1970s. In recent years, air pollution caused by the tremendous increase in road traffic that has accompanied economic development, and water pollution from industries wastewater, have become obvious problems that particularly affect urban areas. Another recent problem is haze (smoke and fog caused by particulate matter), which occurred on a large scale for several months in 1997 and caused respiratory complaints and other health problems in the community (US Commercial Service Market Research Worldwide). In this incident, the haze was caused by the huge forest fires on Kalimantan Island and in other parts of Indonesia, across the sea from Malaysia. It is therefore a unique environmental problem that will not be easy to solve. Other problems noted in Malaysia are oil pollution of the sea and deforestation due to regional development of various kinds.

Although Malaysia has a host of environmental problems that demand solution, including those associated with scheduled wastes, the government is implementing more effective pollution controls than other Southeast Asian nations. It is also committing resources to construction of environmental infrastructures, such as sewerage systems to deal with industries wastewater. Given these positive moves,

environmental problems in Malaysia do not appear to be as grave as in the Philippines, Indonesia and Thailand.

Amendments to the Environmental Quality Act (EQA) in 2000 showed that authorities are beginning to accept the necessity of putting the small and medium-sized enterprises (SMEs) out of business for non-compliance. The amendments include a minimum two-fold increase in prison terms and fines, stricter emission standards, auditing requirements, and the ability to close down polluting factories.

1.2 Wastewater Pollutions

One of the major problems concerning environmental pollutants is wastewater problem. Wastewater comes from domestic and industry. In industry, the biggest sources of industrial wastewater come from textiles industries, leather industries, paper, plastic and other dying industries. However, the major sources of industrial wastewater pollution are concentrated on the western coast of Peninsular Malaysia, with nearly 59% of the major sources located in the states of Selangor, Johor and Perak are food and beverage producers, chemical-based industries, paper, palm oil and rubber processing, and textiles (US Commercial Service Market Research Worldwide). Small and medium-sized enterprises (SMEs) are also major contributors to industrial wastewater pollution because of the lack of space and financial resources to install on-site treatment facilities. Moreover, contaminated water also contains organics, bleaches, salts.

Department of Environment, Ministry of Natural Resources and Environment, Malaysia has established interim national water quality standards for Malaysia. Table 1.1 shows the maximum contaminants levels and their classes and uses. For example the maximum contaminant level for colour is 15 colour units (Interim National Water Quality Standards for Malaysia (2004)). The unit of measurement of colour is the platinum in potassium chloroplatinate (K_2PtCl_6). One milligram per litre of Pt in K_2PtCl_6 is one unit of colour (Sincero, 2003).

Table 1.1 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
Ammoniacal 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

TCU True Colour Unit

N No visible flatable 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 1.1 Continued

Class	Uses
CLASS I	Conservation of natural environment water supply 1 - practically no treatment necessary
	Fishery 1 - 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

The main problem found in the decontamination of wastewater is the removal of colour. Various kinds of synthetic dyestuffs appear in the effluents of wastewater in some industries such as textiles, leather, paper-making, plastics, food, rubber, and cosmetic (O'Neill *et al.*, 1999). It has been estimated that about 9 % (or 40,000 tons) of the total amount (450, 000 tons) of dyestuffs produced in the world are discharged in textiles wastewaters (O'Neil *et al.*, 1999). Removing color from wastes is often more important because the presence of small amounts of dyes (below 1ppm) is clearly visible and influences the water environment considerably (Habibi *et al.*, 2005). These coloured compounds are not only aesthetically displeasing, but also impede light penetration in the treatment plants, thus upsetting the biological treatment processes within the treatment plant.

1.3 Methods to remove dyes

Most dyes are non-biodegradable in nature, which are stable to light and oxidation. Therefore, the degradation of dyes in wastewater either traditional chemical

or biological process have not been very effective (Metivier-Pignon *et al.*, 2003; Orthman *et al.*, 2003; Waranusantigul *et al.*, 2003). Dyes are released into wastewaters from various industrial units, mainly from the dye manufacturing and textiles and other fabric finishing (Janos *et al.*, 2003). About half of global production of synthetic textile dyes (700,000 tons per year) are classified into azo compounds that have the chromophore of $-N=N-$ unit in their molecular structure and over 15 % of the textiles dyes are lost in wastewater stream during dyeing operation (Habibi *et al.*, 2005). The dyes are, generally mutagenic and carcinogenic and can cause severe damage to humans beings, such as dysfunction of the kidneys, reproductive system, liver and brain and central nervous system (Kadirvelu *et al.*, 2003).

Reactive dyes are most problematic compounds among other dyes in textile wastewater. Reactive dyes are the largest single group of dyes used in textiles industry. It is highly water-soluble and estimated that 10 - 20% of reactive dyes remains in the wastewater during the production process of these dyes (Koprivanac *et al.*, 2000) and nearly 50 % of reactive dyes may lost to the effluent during dyeing processes of cellulose fibers (Netpradit *et al.*, 2004). Reactive dye wastewater has limited biodegradability in an aerobic environment and many azo dyes under anaerobic conditions decompose into potentially carcinogenic aromatic amines (Netpradit *et al.*, 2003; Panswad *et al.*, 2000).

Many conventional methods such as precipitation, ion exchange, solvent extraction, biosorption, filtration, electrochemical treatment have been applied for removal of contaminants from industrial wastewaters. These methods are either expensive or could not cope with high concentration of contaminants (Alkan *et al.*, 2005). All these methods have significant disadvantages such as incomplete ion removal, requirements and production of toxic sludge or other waste products that require further disposal. Therefore, these methods do not suit the needs of developing countries.

Adsorption process has been a prominent method of treating aqueous effluent in industrial processes (Benkli *et al.*, 2005) for a variety of separation and purification purposes. This technique is also found to be highly efficient for the removal of colour in terms of initial cost, simplicity of design, ease of operation and insensitivity to toxic substances (Garg *et al.*, 2004). Therefore, adsorption using activated carbon is currently of great interest for removal of dyes and pigments.

1.4 Problem Statement

Activated carbon has been the most popular and widely used adsorbent in wastewater treatment applications throughout the world. This is due to its high adsorption capacity, high surface area, microporous structure, and high degree of surface reactivity (Ozcan *et al.*, 2004). In spite of its prolific use, activated carbon remains an expensive material since the higher the quality of activated carbon, the greater it costs. Therefore, this situation makes it no longer attractive to be widely used in small-scale industries because of cost inefficiency. Due to the problems mentioned previously, research interest into the production of alternative adsorbent to replace the costly activated carbon has intensified in recent years. Today, attention has been focused on the low-cost adsorbents as alternative adsorbent materials. Fytianos *et al.*, (2002) investigated the removal of dyes on three low-cost adsorbents, fly ash, bentonite, bleaching earth and also on activated carbon. A large number of low-cost adsorbents have been treated for dyes removal. The successful removal using low cost adsorbents has been carried out by several researchers (Mall *et al.*, 1996 and Bailey *et al.*, 1999). Armagan *et al.*, (2004) have studied the adsorption of reactive azo dyes on zeolite and modified zeolite. Besides that, waste materials from seafood processing industry such as chitosan (Sakkayawong *et al.*, 2005) was used to adsorb anionic dyes. Natural materials such as rice husk, sawdust and palm kernels also occupy a position in the production of inexpensive adsorbents (Davila-Jimenez *et al.*, 2005).

Recently, chitosan that is used as an adsorbent has drawn attentions due to its high contents of amino and hydroxy functional groups showing high potentials of the adsorption of dyes (Uzun *et al.*, 2004), metal ions (Wu *et.al.*, 2000) and proteins (Zeng *et al.*, 1998). Chitosan is the deacetylated form of chitin, which is linear polymer of acetylamino-D-glucose. Other useful features of chitosan include its abundance, non-toxicity, hydro-philicity, biocompatibility, biodegradability and anti-bacterial property (Ravi Kumar, 2000). Moreover, the adsorption of reactive dyes (Reactive Red 189, Reactive Red 222, Reactive Yellow 2 and Reactive Black 5), basic dyes (methylene blue), and acidic dyes (Acid Orange 51, Acid Green 25) in natural solutions using chitosan shows large adsorption capacities (Uzun *et al.*, 2004 and Yoshida *et al.*, 1991). Although chitosan shows better adsorption ability in the bead form than in the flake form due to its higher specific surface area (Wu *et. al.*, 2000), the weak mechanical property (highly swollen in water) and low specific gravity of the beads make them inconvenient for practical use in column mode adsorption.

Besides chitosan, oil palm ash has also been considered as an alternative adsorbent material for low cost adsorbents (Ahmad *et al.*, 2006). This ash is produced after combustion of oil palm fiber and shell as boiler fuel to produce steam for palm oil mill consumption. This solid waste is highly abundant in Malaysia, which is one of the largest palm-oil exporters in the world. Thus, Malaysia generates huge loads of palm ash each year. The oil palm ash showed very high adsorption capacity to remove direct dye (Ahmad *et al.*, 2006). Moreover, the high oxide contents in oil palm ash give its structure the creditibility as a good adsorbent (Zainuddin *et al.*, 2005).

1.5 Research objectives

This research was conducted to study the adsorption of three reactive azo dyes, namely, reactive blue 19 (RB19), reactive orange 16 (RO16) and reactive black 5 (RB5) using the cross-linked chitosan/oil palm ash composite beads in batch and continuous systems. The objectives of the research are to:

- I. synthesize and characterize a cross-linked chitosan/oil palm ash composite beads adsorbents.
- II. study the adsorption of reactive azo dyes (RB19, RO16 and RB5) on cross-linked chitosan/oil palm ash composite beads in batch process under varying operating conditions such as initial concentration and contact time, pH of solution and temperature.
- III. study the isotherm, kinetic and thermodynamic of reactive azo dyes adsorption on cross-linked chitosan/oil palm ash composite beads
- IV. determine the breakthrough characteristic of reactive azo dyes adsorption on cross-linked chitosan/oil palm ash composite beads under varying operating parameters namely, initial concentration, flowrate and height of adsorbent bed and to correlate the experimental results using suitable adsorption dynamic model.

1.6 Organization of the thesis

The thesis has been organized into several chapters:

Chapter 1 introduces the scenario of Malaysia and world's environmental issue and major environmental pollution is wastewater.

Chapter 2 reviews the fundamentals and previous findings. Subdivided into four section, the first section introduces a general definition of dye and the treatment technologies for dye removal. An overview of the adsorption process theory is presented in section two. Meanwhile, section three gives review on the isotherm, kinetics and thermodynamic. Finally, the adsorption continuous system is discussed in section four.

Chapter 3 presents the experimental procedures and analysis required in adsorption study. The first section describes the materials and chemicals used in the experiments. The second section presents description of equipment used for the batch and continuous experiment and the analysis system. The third section explains the experimental procedures and lastly the fourth section describes the analysis techniques performed for characterization of adsorbents.

Chapter 4 presents the experimental results together with the discussion. The detail explanations of the results have been divided into four main sections. The first section gives the results of adsorbent characterization. The second section presents the result and discussion for batch adsorption study including the effect of initial concentration and contact time, pH of solution and temperature. This section also includes discussion on the adsorption isotherm and kinetic studies. The third section discusses the thermodynamic studies. Finally, section four describes the continuous adsorption system including the effect of initial concentration, flow rates, height of adsorbent bed, breakthrough characteristic and also three dynamics models namely, Boharts and Adam, Thomas and Yoon and Nelson model.

Finally, **Chapter 5** gives the conclusions and recommendations of the thesis.

CHAPTER 2

LITERATURE REVIEW

2.0 Colour and the environment

Over the last few decades, society has become increasingly sensitive towards the protection of the environment. Due to this problem, global nowadays has concern about the potential adverse effects to the chemical industry on the environment, although the response in some parts of the world has been much faster and more intense than in others. The colour manufacturing industry represents a relatively small part of the overall chemical industry.

Dyes and pigments are highly visible material. Thus even minor release into the environment may cause the apperance of colour, for example in open waters, which attracts the critical attention of public and local authorities. There is thus the requirement on industry to minimise environmental release of colour, even in cases where a small but visible release might be considered as toxicologically rather innocuous. A major source of release of colour into the environment is associated with the incomplete exhaustion of dyes onto textile fibre from an aqueous dyeing process and the need to reduce the amount of residual dye in textile effluent has thus become a major concern in recent years.

An alternative approach to addressing the problem of colour in textile dyeing effluent has involved the development of effluent treatment methods to remove colour. These method inevitably add to the cost of the overall process and some present the complication associated with the possible toxicity of degradation products.

2.1 Colorants

Man has use natural colorants since prehistoric times. However, in 1856, Perkin's discovery of mauve which marked the start of the modern synthetic dye industry (Hunger, 2003). Colorants are characterized by their ability to adsorb or emit

light in the visible range (400-700nm). Therefore, it is the reason they appear to be coloured. In term of chemical structure, colorants may divided into two groups, which are organic and inorganic colorants. Each of these groups can be further divided into natural and synthethic compounds.

Colorants includes both dyes and pigments. Pigments are insoluble in the materials that they are used to colour, whereas most dyes are soluble in them . The most important, difference between pigments and dyes is that pigments are used as colorants in the physical form in which they manufactured (Zollinger, 1987). Pigments particles have to be attached to substrates by additional compounds, such as by a polymer in a paint. Dyes, on the other hand, are applied to various substrate (textile materials, leather, paper and hair) from liquid in which they completely, or at least partly, soluble. In contrast to pigments, dye must posses a specific affinity to the substrates for which they are used (Zollinger, 1987).

2.2 Dye

Dyes are chemicals which on binding with material will give colour to the material. Dyes are ionic, aromatic organic compounds with structures including aryl rings which delocalised electron systems. The colour of a dye is provided by the presence of chromophore group. They are widely used to colour the substrate such as textile fibre, paper, leather, hair, fur, plastic material, wax, a cosmetic base or a foodstuff.

Dyes are large and important groups of chemicals. Today, there are more than 100,000 available commercially dyes, namely acid, reactive, disperse, vat, metal complex, mordant, direct, basic and sulphur dyes (Aksu *et al.*, 2006). Moreover, it is estimated that 2% from over 7×10^5 tonnes of dyes annually are discharged in effluent from manufacturing operations whilst 10% was discharged from textile and associated industries (Robinson *et al.*, 2001).

2.3 Classification systems for dyes

Dyes are classified usefully in two separate ways, either accordance to to their chemical structure or according to the method of application (dyeing method). In term of chemical structure, dyes may either be inorganic or organic compounds. Both groups can be further subdivided into natural and synthetic representatives.

When classified according to dyeing method, one can be distinguish between anionic, direct, or disperse dyes, depending on whether these substances are use for dyeing protein, cellulose, or polysmide fibers. Furthermore, certain chemically reactive dyes can be used for different substrate, while for the same type of chemical structure are suitable for a single substrate only.

For the two classifications based on chemical structure and on method of application overlap, there is hardly a chemical class of dye which occurs solely in one coloristic group, and vice versa. Furthermore, some coloristic groups can be applied to two or more substrates, whilst others are specified to a single substrate.

Both classifications are used by the Color Index (1971), which lists all dyes and pigments used commercially for large-scale coloration purpose, such as dyeing of textile fibers, for pigment coloration of plastics, paints, printing inks and for the coloration of liquids (solvents). Table 2.1 summarized the application classes and their chemical types (Hunger, 2003). According to Griffiths (1976), colorants can also be classified to the type of electronic excitation occuring on light absorption. However, Luttkke (1985) classified colorants as absorption colorants, fluorescent colorans and energy transfer colorants, depending on whether the light energy absorbed is dissipated predominantly (i.e high quantum yields) by internal conversion, by fluorescence or by intersystem crossing.

Table 2.1 The classification of dyes and chemical types (Hunger, 2003)

Class	Principle substrate	Method of application	Chemical types
Acid	Nylon, wool, silk, paper and leather	Usually from neutral to acidic dyebaths	Azo (including premetallized), anthraquinone, triphenylmethane, azine, xanthene, nitro and nitroso
Basic	Paper, polyacrylonitrile, modified nylon, polyester and inks	Applied from acidic dyebaths	Cyanine, hemicyanine, diazahemicyanine, diphenylmethane, triaryl methane, azo, azine, xanthene, acridine, oxazine, and anthraquinone
Direct	Cotton, rayon, paper, leather and nylon	Applied from neutral or slightly alkaline baths containing additional electrolyte	Azo, anthraquinone, styryl, nitro and benzodifuranone
Disperse	Polyester, polyamide, acetate, acrylic and plastics	Fine aqueous dispersions often applied by high temperature/pressure or lower temperature carried methods; dye may be padded on cloth and baked on thermofixed	Azo, anthraquinone, styryl, nitro and benzodifuranone
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
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 quinones) and indigoids

2.4 Reactive dyes

The first reactive dyes for cellulosic fibres was launched by ICI in 1956 under the trade name Procian. It was the discovery work of Stephen and Rattee which proved that dyes containing the 1,3,5-triazinyl group were capable of reaction with cellulosic fibres under mildly alkaline conditions (Christie, 2001).

Reactive dyes are colored compounds which contain one or two groups capable of forming covalent bonds between a carbon or phosphorus atom of the dye ion or molecule and an oxygen, nitrogen or sulfur atom of a hydroxy, an amino or a mercapto group, respectively, of the substrate. Such covalent bonds are formed with the hydroxyl groups of cellulosic fibers, with the amino, hydroxyl and mercapto groups of protein fibers and the amino groups of polyamides (Zollinger, 1987).

Reactive dyes are used extensively in textiles industries regarding favorable characteristics of bright colour, water-fast, simple application techniques with low energy consumption (Aksu, 2005). According to Aksu *et al.*, (2006), reactive dyes are the largest class of dyes used in textiles industry and it is the azo dyes based on the azo chromogen (-N=N-) and the presence of bright colour due to these azo bonds and associated chromophore.

2.4.1 Structure of reactive dye

There are four important structural features of the molecules in reactive dyes and it can be identified separately. These are the chromogen, the water solubilising group, the bridging group, and the fiber-reactive group (Christie, 2001). Figure 2.1 represent a general schematic representation of the structure of a reactive dye.

The chromogen is the part of the molecule that essentially gives the molecule its colour and may contribute to other features of the dye such as its lightfastness. As encountered in most of the other application classes of textile dyes, these chromogens typically belong to the azo, carbonyl or phthalocyanine chemical.

Most commonly, the water-solubilising group located in the chromogenic part of the reactive dye molecule, although on a number of occasions it is part of the fibre-reactive group. The essential structural characteristic of a reactive dye is a functional group that is capable of reacting chemically with the fibre. This feature is, for obvious reasons, termed the fibre-group and the organic chemistry underlying the reaction of these groups with functionality on the fibre forms.

Commonly the term bridging group is used to identify the group of atoms which is used to link the chromogenic part of the molecule to the fibre-reactive group. In many dyes, the bridging group is the amino (-NH-) group, often for reasons of synthetic convenience.

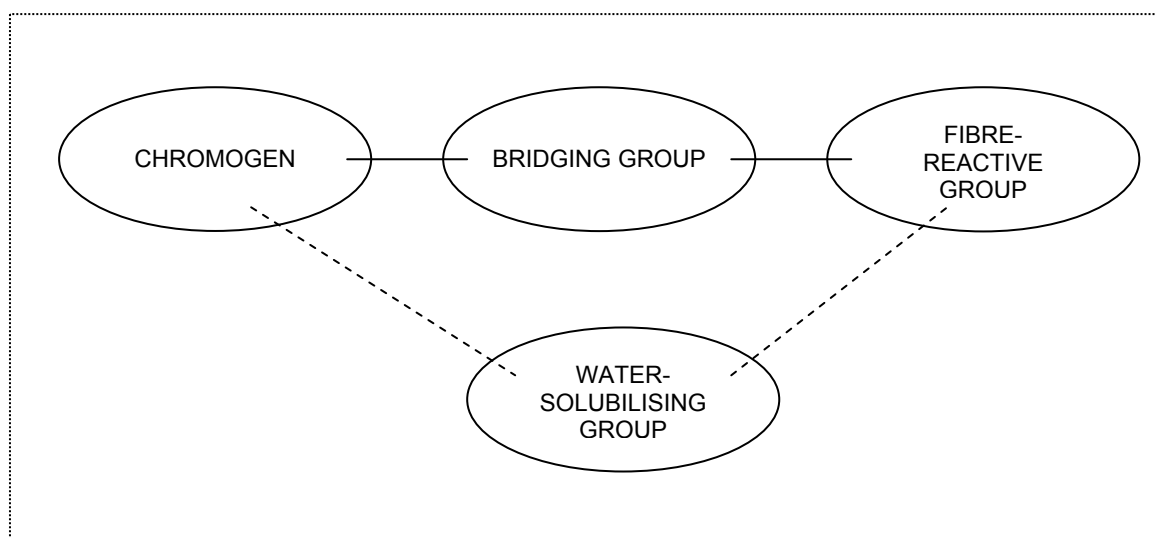


Figure 2.1 General structure of reactive dyes (Christie, 2001)

2.4.2 Dyes classes (chromogen) for reactive dyes

Based on chromophore, reactive dyes can be classified to monoazo and disazo species, metal complexes of azo dyes, formazon dyes, anthraquinones, triphenodioxazines and phthalocyanines. Most reactive dyes fall in the category of azo dyes. Azo dyes based on the azo chromogen (-N=N-) are presently the most important compounds constituting about 20-40% of the total dyes used for coloring (Zollinger (1991) Wu *et al.*, 1998, Beydilli *et al.*, 2000).

Metal complex azo dyes are obtained from a lightfast colors. For example, copper complexes of o,o'-disubstituted azo compounds produce a wide range of colours (yellow, ruby, violet, blue, brown, olive, black). Metal complex dyes are mostly based on chromium, which is carcinogenic (Banat *et al.*, 1996).

Antraquinone-based dyes are significant because of their brilliance, good lightfastness, and chromophore stability under both acidic and basic conditions. Recently, they dominated the market for brilliant blue reactive dyes in spite of their relatively low color strength and comparatively high cost. The shades of commercial reactive antraquinone dyes range from violet to blue, an example C.I. Reactive Blue 19. According to Aksu (2005), an antraquinone-based dyes are most resistant to degradation due to their fused aromatic structures and thus remain coloured for longer time in the wastewater.

Triphenodioxazine dyes are derived from the triphenodioxazine ring system. It have been commercially available since 1928 when Kranzlein discovered dyes with this basic structure augmented by the sulfonic acid groups. Dioxazine chromophores show a sensitivity to acid and base that is more pronounced in dye solutions tahn in the fixed dyes. Generally, triphenodioxazine chromophores show a high degree of agglomeration and thus increased substantivity because of their planar arrangement.

Formazon dyes are derived from 1-(2-carboxyphenyl)formazon, in which all three rings are capable of supporting groups that increase the compound's reactivity and solubility. Moreover, copper complexes of the formazon dyes are another alternatives to reactive athraquinone dyes. They produce red to greenish-blue shades.

The most important characteristic of reactive phthalocyanine dyes is the present of copper or nickel as their central atom. They substituted with sulfonic acid groups and also with reactive groups joined via sulfonamide bridges. Reactive phthalocyanine dyes is a water-soluble which yield brilliant turquoise and green shades.

2.5 Technologies for color removal

There are more than 100,000 commercially available dye exist and more than 7×10^5 tonnes per year are produced annually (Pearce *et al.*, 2003, McMullan *et al.*, 2001). Wastewater containing dyes is very difficult to treat, since the dyes are recalcitrant organic molecules, resistant to aerobic digestion and are stable to light.

A synthetic dyes in wastewater cannot be effeciently decolorized by traditional methods. This is because of the high cost and disposal problems for treating dye wastewater at large scale in the textile and paper industries (Ghoreishi and Haghighi, 2003).

Table 2.2 shows a several reported methods for the removal of pollutants from effluents. The technologies for colour removal can be divided into three categories: biological, chemical and physical (Robinson *et al.*, 2001). All of them have advantages and drawbacks.

2.5.1 Biological method

Biological treatment is the most economical methods compared to other physical and chemical processes. Biodegradation methods such as fungal decolorization, microbial degradation, adsorption by (living or dead) microbial biomass and bioremediation systems are commonly applied to the treatment of industrial effluents because many microorganisms such as bacteria, yeasts, algae and fungi are able to accumulate and degrade different pollutants (McMullan *et al.*, 2001 and Fu and Viraraghavan 2001a).

However, their application is often restricted because of technical constraint. According to Bhattacharyya and Sharma, (2003), biological treatment requires a large land area and is constrained by sensitivity toward diurnal variation as well as toxicity of some chemicals, and less flexibility in design and operation. Further, biological treatment is incapable of obtaining satisfactory color elimination with current conventional biodegradation processes (Robinson *et al.*, 2001). Moreover, although

Table 2.2 Principal existing and emerging processes for dyes removal (Crini,2006)

	Technology	Advantages	Disadvantages
Conventional treatment process	Coagulant Flocculant	Simple, economically feasible	High sludge production, handling and disposal problems
	Biodegradation	Economically attractive, publicly acceptable treatment	Slow process, necessary to create an optimal favorable environment, maintenance and nutrition requirement
	Adsorption on activated carbon	The most effective adsorbent, great, capacity, produce a high-quality treated effluent	Ineffective against disperse and vat dye, the regeneration is expensive and result in loss of the adsorbent, non-destructive process
Establish recovery process	Membrane separation	Remove all dye types, produce a high-quality treated effluent	High pressure, expensive, incapable of treating large volumes
	Ion-exchange	No loss of sorbent on regeneration, effective	Economic constraints, not effective for disperse dye
	Oxidation	Rapid and efficient process	High energy cost, chemical required
Emerging removal processes	Advanced oxidation process	No sludge production, little or no consumption of chemicals, efficiency for recalcitrant dyes	Economically unfeasible, formation of by-products, technical constraints
	Selective bioadsorbents	Economically attractive, regeneration is not necessary, high selectivity	Requires chemical modification, non-destructive process
	Biomass	Low operating cost, good efficiency and selectivity, no toxic effect on microorganisms	Slow process, performance depends on some external factors (pH, salts)

many organic molecules are degraded, many others are recalcitrant due to their complex chemical structure and synthetic organic origin (Ravi Kumar *et al.*, 1998). In particular, due to their xenobiotic nature, azo dyes are not totally degraded.

2.5.2 Chemical methods

Chemical methods including coagulation or flocculation combined with flotation and filtration, precipitation-flocculation with Fe(II)/Ca(OH)_2 , electroflotation, electrokinetic coagulation, conventional oxidation methods by oxidizing agents (ozone), irradiation or electrochemical processes (Crini, 2006). These chemical techniques are often expensive, and although the dyes are removed, accumulation of concentrated sludge creates a disposal problem. There is also the possibility that a secondary pollution problem will arise because of excessive chemical use.

Recently, other emerging techniques, known as advanced oxidation processes, which are based on the generation of very powerful oxidizing agents such as hydroxyl radicals, have been applied with success for the pollutant degradation. Although these methods are efficient for the treatment of waters contaminated with pollutants, they are very costly and commercially unattractive. The high electrical energy demand and the consumption of chemical reagents are common problems.

2.5.3 Physical methods

Different physical methods are also widely used, such as membrane – filtration processes (nanofiltration, reverse osmosis, electrodialysis) and adsorption techniques. The major disadvantages of the membrane processes are: (1) a limited lifetime before membrane fouling occurs and (2) cost of periodic replacement which need to be included in any analysis of their economic viability.

In accordance with the very abundant literature data, liquid-phase adsorption is one of the most popular methods for the removal of pollutants from wastewater since proper design of the adsorption process will produce a high-quality treated effluent.

This process provides an attractive alternative for the treatment of contaminated waters, especially if the sorbent is inexpensive and does not require an additional pre-treatment step before its application.

2.5.3.1 Adsorption

Adsorption is a well known equilibrium separation process and an effective method for water decontamination applications (Dabrowski, 2001). Adsorption has been found to be superior to other techniques for water re-use in terms of initial cost, flexibility and simplicity of design, ease of operation and insensitivity to toxic pollutants. Decolourisation is a result of two mechanisms: adsorption and ion exchange (Slokar and Le Marechal, 1997), and is influenced by many physio-chemical factors such as dye/sorbent interaction, sorbent surface area, particle size, temperature, pH, and contact time (Kumar *et al.*, 1998). Adsorption also does not result in the formation of harmful substance.

Most of the solid adsorbents of great industrial applications possess a complex porous structure that consists of pores of different sizes and shapes. In terms of the adsorption science, total porosity is usually classified into three groups. According to International Union of Pure and Applied Chemistry (IUPAC) recommendation, the micropores are defined as pores of a width ($<2\text{nm}$), mesopores are pores of a width ($2\text{-}50\text{nm}$), but macropores represent pores of a width ($>50\text{nm}$).

However, the importance of porous structure on adsorption of many contaminants in aqueous solution is not well understood. As to physisorption on porous materials, it's generally accepted that adsorption mechanism and process may be significantly different as a consequence of porous structure. In the IUPAC classification of pore size (IUPAC, 1985), the definitions of 'macropores', 'mesopores' and 'micropores' depend on the different adsorption mechanism at pores with specified range of width: in micropores the whole accessible volume is regarded as adsorption space and the process occurs due to micropore filling (Dubinin and Stoeckli, 1980), as

distinct from surface coverage which takes place on the walls of macropores. On the other hand, physisorption in mesopores takes place in two more or less stages (monolayer – multilayer adsorption and capillary condensation). For instance, Sing (1982) concluded that mesopores are thought to be important in air/soil adsorption system for the diffusion of air and the transport and distribution of water, while the wider macropores provide channels for easy removal of surplus water and allow air to penetrate rapidly to the required depth.

Further, a powder is easily recognized as a mass of small dry particles, but the precise definition is inevitably somewhat arbitrary. The term fine powder is also used in an imprecise manner, but it seems reasonable to apply it to a material consisting of particles less than about 1 μ m. The unit mass of a fine powder contains a large number of small particles and exhibits an appreciable surface area.

In addition to the performance, a number of other factors greatly influence the choice and viability of waste materials as adsorbents, for example the cost of processing materials, wastewater selectivity and regeneration of materials. Cost is a very important factor when considering materials for use as adsorbents. It is generally recognized that a material can be deemed 'low-cost' if it requires little processing, is abundant in nature, or is a byproduct or waste material from another industry (Bailey *et al.*, 1999). Here below shows a various of waste materials that have been used as an adsorbent for removal of dyes.

2.5.3.2 Adsorbents for dyes removal

(a) Waste materials from agriculture and industry

The by-products from the agricultural and industrial could be assumed to be low-cost adsorbents since they are abundant in nature, inexpensive, require little processing and effective materials.

(i) Activated carbons from solid wastes

Commercially available activated carbons (AC) are usually derived from natural materials such as wood, coconut shell, lignite or coal, but almost any carbonaceous material may be used as precursor for the preparation of carbon adsorbents (Rozada *et al.*, 2003). Because of its availability and cheapness, coal is the most commonly used precursor for AC production (Carrasco-Marin *et al.*, 1996). Coal is a mixture of carbonaceous materials and mineral matter, resulting from the degradation of plants. The sorption properties of each individual coal are determined by the nature of the origin vegetation and the extent of the physical-chemical changes occurring after deposition (Karaca *et al.*, 2004).

Plentiful agricultural and wood by-products may also offer an inexpensive and renewable additional source of AC. These materials have little or no economic value and often present a disposal problem. Therefore, there is a need to valorize these low-cost by-products. So, their conversion into AC would add economic value, help reduce the cost of waste disposal and most importantly provide a potentially inexpensive alternative to the existing commercial activated carbons. A wide variety of carbons have been prepared from agricultural and wood wastes, such as rice husk (Mohamed, 2004, Guo *et al.*, 2003, corn cob (Juang *et al.*, 2002a) pinewood (Tseng *et al.*, 2003), sawdust (Malik, 2003) and coconut tree sawdust (Kadirvelu *et al.*, 2000, 2003), bamboo-based (Hameed *et al.*, 2007a), rattan sawdust (Hameed *et al.*, 2007b), rubberwood sawdust (Prakash Kumar *et al.*, 2007) and coconut husk, oil palm fibre (Tan *et al.*, 2007).

There are also several reports on the production of AC from various city waste and industrial by-product such as waste PET bottles (Nakagawa *et al.*, 2004), waste tires (Nakagawa *et al.*, 2004) refuse derived fuel (Nakagawa *et al.*, 2004), waste newspaper (Okada *et al.*, 2003) and sewage sludges (Rozada *et al.*, 2003).

The excellent ability and economic promise of the activated carbon prepared from by-products have been recently presented and described. Non-conventional

activated carbons exhibited high sorption properties as shown in Table 2.3. The adsorption capacities of a carbon depend on the different sources of raw materials, the history of its preparation and treatment conditions such as pyrolysis temperature and activation time. Many other factors can also affect the adsorption capacity in the same sorption conditions such as surface chemistry (heteroatom content), surface charge and pore structure.

Table 2.3 Adsorption capacities Q_0 (mg/g) for carbon materials made from solid wastes and coal-based sorbents

Raw material	Dye	Adsorption capacity (mg/g)	References
Cocunut tree flower carbon	Reactive red 120	181.9	Senthilkumaar <i>et al.</i> , 2006
Jute fiber carbon	Reactive red 120	200.0	Senthilkumaar <i>et al.</i> , 2006
Bottom ash coal	Reactive blue 222	3.82	Dincer <i>et al.</i> , 2007
Oil palm fibre	Methylene blue	277.7	Tan <i>et al.</i> , 2007
Bamboo-based	Methylene blue	454.2	Hameed <i>et al.</i> , 2007a
Rattan husk	Methylene blue	294.1	Hameed <i>et al.</i> , 2007b
Bagasse	Basic red 22	942	Juang <i>et al.</i> , 2002a
Lignite coal	Basic blue 9	32	Karaca <i>et al.</i> , 2004
Pinewood	Basic blue 9	556	Tseng <i>et al.</i> , 2003
Rice husk	Basic green 4	511	Guo <i>et al.</i> , 2003
Bagasse	Acid blue 80	391	Valix <i>et al.</i> , 2004

(ii) Agricultural Solid Waste

Raw agricultural solid wastes and waste materials from forest industries such as sawdust and bark have been used as adsorbents. These materials are available in large quantities and may have potential as sorbents due to their physico-chemical characteristics and low-cost.

Sawdust is an abundant by-product of the wood industry that is either used as cooking fuel or as packing material. Sawdust is easily available in the countryside at zero or negligible price (Garg *et al.*, 2004a). It contains various organic compounds (lignin, cellulose and hemicellulose) with polyphenolic groups that might be useful for binding dyes through different mechanisms. Sawdust has proven to be a promising

effective material for the removal of dyes from wastewaters (Ozacar and Sengil, 2005; Garg *et al.*, 2004a,b). Moreover, it is actually an efficient adsorbent that is effective to many types of pollutants, such as dyes, oil, salts, heavy metals and others (Pekkuz *et al.*, 2007)

Another waste product from the timber industry bark is a polyphenol-rich material. Bark is an abundant forest residue which has been found to be effective in removing dyes from water solutions. Because of its low cost and high availability, bark is very attractive as an adsorbent. Bark is an effective adsorbent because of its high tannin content (Morais *et al.*, 2003). The polyhydroxy polyphenol groups of tannin are thought to be the active species in the adsorption process.

Tree fern, an agricultural by-product, has been recently investigated to remove pollutants from aqueous solutions (Ho *et al.*, 2005; Ho, 2003). Tree fern is a complex material containing lignin and cellulose as major constituents.

Other agricultural solid wastes from cheap and readily available resources such as date pits (Banat *et al.*, 2003) corncob (Robinson *et al.*, 2002a), rubber wood sawdust (Vasant Kumar and Sivanesan, 2007), coir pith (Kavitha and Namasivayam, 2007) and hazelnut shell (Ferrero, 2007) have also been successfully employed for the removal of dyes from aqueous solutions.

(iii) Industrial by-products

Because of their low cost and local availability, industrial solid wastes such as metal hydroxide sludge, fly ash and red mud are classified as low cost materials and can be used as adsorbents for dye removal (Namasivayam and Sumitra, 2005)

Recently, Netpradit *et al.*, (2004a) studied the capacity and mechanisms of metal hydroxide sludge in removing azo reactive dyes. The sludge is a dried waste from the electroplating industry, which is produced by precipitation of metal ions in wastewater with calcium hydroxide. It contains insoluble metal hydroxides and other salts. It has been proven that metal hydroxide sludge was an effective positively