

THE EFFECTIVENESS OF NATURAL ADSORBENTS FOR MULTI DYE SYSTEM

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ABSTRACT

Natural materials have been investigated as potential industrial adsorption media. The uses of natural adsorbents in wastewater treatment have received increasing attention and currently offer a very attractive method for pollution remediation. The main purpose of this research was to study the effectiveness of natural adsorbents for the multi dye system removal (synthesis wastewater) by adsorption technique in batch process. The natural adsorbents that had been used were wood ash, papaya seed, coconut husk and clay. The operation parameters investigated included the effect of the pH towards dyes removal performance and optimum dosage of natural adsorbents for multi dye system. Different range of pH that had been used was pH 3 (acidic), pH 7 (neutral) and pH 11 (basic) in different dosage of adsorbents. In this research, the percentage of dye removal for MO showed higher compared than percentage of dye removal for MB. The residual of dye concentration was determined spectrophotometrically by monitoring absorbance changed at maximum wavelength adsorption using UV-Vis spectrophotometer. After analyzed the data, wood ash was found as the effective natural adsorbents in multi dyes system compared with coconut husk, papaya seeds and clay. In pH 3 (acidic), it produced higher percentage of dyes removal. The pH of the solution affects the surface charge of adsorbents as well as the degree of ionization of dyes. The equilibrium data were further analyzed using the linearized form of Freundlich and Langmuir isotherm. The coefficient of correlation R^2 was high for Freundlich and Langmuir isotherm based on pH of adsorbents. The Freundlich isotherm takes place on heterogeneous surface with a non-uniform distribution of heat adsorption over the surface while the Langmuir model based on monolayer, uniform and finite adsorption site assumptions. Lastly, this research indicated that natural adsorbents could be employed as an alternative for wastewater treatments besides it is not only to minimize the cost, but also to improve the profitability.

ABSTRAK

Bahan-bahan semulajadi telah diteliti sebagai potensi media industri penjerapan. Penjerap semulajadi digunakan dalam pemprosesan air kumbahan telah menerima peningkatan perhatian dan saat ini menawarkan kaedah yang sangat menarik untuk perbaikan pencemaran. Tujuan utama dari kajian ini adalah untuk mempelajari keberkesanan penjerap alami untuk menghilangkan sistem multi pewarna (sintesis air sisa) dengan teknik jerapan secara kelompok. Penjerap yang telah digunakan adalah abu kayu, biji betik, sabut kelapa dan tanah liat. Parameter operasi yang diteliti adalah pengaruh pH terhadap prestasi penghapusan pewarna dalam sistem multi pewarna. Perbezaan julat pH yang telah digunakan adalah pH 3 (asid), pH 7 (neutral) dan pH 11 (alkali) dalam dos penjerap yang berbeza. Dalam kajian ini, peratusan removal pewarna untuk MO menunjukkan lebih tinggi berbanding peratusan removal pewarna MB. Baki antara kepekatan pewarna yang telah dijerap ditentukan secara spektrofotometri dengan pemantauan diubah pada panjang gelombang maksimum penjerapan dengan menggunakan spektrofotometer UV-Vis. Setelah menganalisis data, abu kayu dijumpai sebagai penjerap yang berkesan dalam sistem pewarna multi dibandingkan dengan sabut kelapa, biji betik dan tanah liat. Pada pH 3 (asid), abu kayu menghasilkan peratusan yang lebih tinggi penghilangan zat warna. Ph larutan mempengaruhi muatan permukaan penjerap serta darjah pengionan pewarna. Seterusnya, data ujikaji garis sesuhu dianalisis menggunakan model garis sesuhu 'Langmuir' dan 'Freundlich'. Pekali R^2 korelasi tinggi untuk model garis sesuhu Freundlich dan Langmuir berdasarkan pH penjerap. Model garis sesuhu Freundlich terjadi pada permukaan tidak sekata dengan pengedaran tidak seragam dalam haba jerapan di atas permukaan sementara model Langmuir didasarkan pada andaian halaman monolayer, seragam dan terbatas jerapan. Akhir sekali, kajian ini menunjukkan bahawa penjerap semulajadi boleh digunakan sebagai alternatif untuk rawatan air sisa selain itu tidak hanya untuk meminimumkan kos, tetapi juga untuk meningkatkan keuntungan.

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LIST OF SYMBOLS/ABBREVIATION

Symbol	Description
aL	Langmuir isotherm constant
C ₀	The initial concentration of dye
C _e	The equilibrium concentration of dye
HCl	Hydrochloric Acid
K _f	Freundlich isotherm constant
K _L	Langmuir isotherm constant
MB	Methylene Blue
MO	Methyl Orange
n	Adsorption tendency
NaOH	Sodium Hydroxide
No.	Number
q _e	Amount of dye sorbed at equilibrium
q _{max}	Maximum capacity of the adsorbent
R _L	Dimensionless constant separation factor
R ²	Correlation coefficient
T	Absolute temperature
t	Time
UV	Ultraviolet
V	The volume of the solution
W	The weight of adsorbent

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CHAPTER 1

INTRODUCTION

1.1 Environmental issue

Environmental pollution problems in Malaysia have 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 household 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. 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 household wastewater.

1.2 Water Pollution

Water pollution is arguably the most fundamental environmental issue in Malaysia, since the country's pollution problems began with water pollution caused by the three traditional industries of tin mining, natural rubber, and palm oil, as mentioned above. The government's environmental programs therefore give high priority to control of water pollution. Malaysia does not publish exact values of river water quality measurements for individual monitoring sites. Instead, water quality status is published under three rankings (clean, slightly polluted, and polluted), using a Water Quality Index (WQI) based on six parameters: pH, dissolved oxygen (DO), biochemical oxygen demand (BOD), chemical oxygen demand (COD), ammonia nitrogen, and suspended solids (SS).

At present, water quality is monitored regularly at 908 sites on the 117 rivers in the country. Looking at results from Department of Environment (DOE) 1997, which are the most recent published data, 24 of the 117 rivers were classified as clean, 68 as slightly polluted, and 25 as polluted. Comparing these results with the previous year (1996), the number of polluted rivers increased from 13 to 25, and the number of slightly polluted rivers increased from 61 to 68. Low rainfall, which resulted in reduced flow rates in the rivers, was cited as one of the reasons for the increased pollution.

Sources of pollution identified as contributing to BOD loading include the agriculture-based industries (natural rubber and palm oil production, for instance), manufacturing industry, and livestock industry. Similarly, the livestock industry and domestic wastewater are cited as causes of worsening ammonia nitrogen pollution, and civil engineering works and land cultivation are blamed for the deterioration in SS status. Overall trends, however, if weather conditions and other such factors are excluded, show an improvement in river water quality brought about by Malaysia's adoption of wastewater regulations and development of sewerage systems.

In addition, the 1997 results identify a total of 4,932 factories as sources of river water pollution. By industry type, the polluters included 966 food and beverage manufacturing factories (20%), 559 paper factories (11%), and 419 electrical and electronics plants (8%). The breakdown by state shows that Selangor had the highest

number of industrial sources of pollution (1,668 factories), followed by Johor (945) and Negeri Sembilan (371). In terms of individual rivers, the basin of the Klang River which flows through Selangor had the highest number of industrial pollution sources. Rivers in Malaysia generally appear to have high organic pollution loads and high SS concentrations.

1.3 Malaysia's Water Pollution Regulations

Tin mining, palm oil production, and natural rubber production were once the main industries in Malaysia, and because the country's first pollution problem was water pollution caused by these three traditional industries, water pollution is given high priority in Malaysia's environmental regimes. According to 1997 estimates from the Department of Environment (DOE), domestic wastewater contributed approximately 70 percent of organic water pollution as measured by biochemical oxygen demand (BOD) load, followed by pig rearing which contributed 27 percent. Thus, the pollution load due to the manufacturing sector and agriculture-based traditional industries such as palm oil production is minor these days. However, water pollution resulting from rapid industrialization is a growing concern in the community, and wastewater controls focused on industrial wastewater are the most effective in practical terms of all Malaysia's environmental regulations.

Water quality is categorized into six classes, from a level where the natural environment is conserved in which aquatic organisms that are particularly sensitive to environmental changes can live, to a level that can be used as drinking water after advanced treatment, through to a level useable for agricultural irrigation. Water quality standards are defined for approximately 70 parameters, including ammonia nitrogen, BOD, and coliform group number, together with a large number of heavy metals and pesticide components.

Wastewater standards are prescribed as a set of nationally uniform standards divided into two categories: Standard A applies to areas upstream from drinking water intake points, and Standard B applies to areas downstream from drinking water intake points. Each standard covers 23 parameters, including general parameters such as temperature, pH, and suspended solids (SS), as well as BOD, chemical oxygen demand (COD), and various types of heavy metals. Standard B has more lenient

limits than Standard A, but for most parameters even in Standard B, the limits are more stringent than Japan's wastewater standards.

In addition, although it does not prescribe specific wastewater standards, the Environmental Quality (Sewage and Industrial Effluents) Regulations 1979 prohibit discharge into inland waters such as rivers of the following substances: (1) inflammable solvents, (2) tar and other liquids immiscible with water, (3) refuse, garbage, sawdust, timber, and human or animal waste, etc.

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

It is clearly shown that, Malaysia water pollution occurred in high level contamination. The alternatives methods should take before the pollution getting in highly risk and contributes the bad effect to the people that need clean water as their important sources. If we disrupt the temperature balance and precipitation patterns of our current environment, it will make it more difficult to grow food leading to the starvation of million peoples. If we pollute our groundwater with chemicals, then we will be forced to drink chemicals and probably live much shorter life.

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	-
Color	TCU	15	150	150	-	-	-
Elec. Conductivity*	Umho s/cm	1000	1000	-	-	6000	-
Floatables		N	N	N	-	-	-
Odor		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 /100m L	10	100	400	5000 (2000 0) ^a	5000 (200 00) ^a	-
Total Coliform	counts /100m L	100	5000	5000	50000	5000 0	>5000 0

Notes

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

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

1.4 Problem Statement

One of the major problems concerning textile wastewater is colored effluents. Though not particularly toxic, dyes have an adverse aesthetic effect because they are visible pollutants. The presence of color reduces aquatic diversity by blocking the passage of light through water. The main pollution source of textile wastewater comes from dyeing processes, with the degree of coloration being dependent on the color/shade dyed and the type of dye use (Degs *et al.*, 2000). Moreover, some dyes might be toxic to various organisms (Khattri and Singh, 1999).

Concern arises, as many dyes are made from known carcinogens such as benzidine and other aromatic compounds (Baughman and Perenich, 1988). Anthroquinone - based dyes are most resistant to degradation due to their fused

aromatic ring structure. The removal of color from dye-bearing effluents is a major problem due to the difficulty in treating such wastewaters by conventional treatment methods.

The sorption technique is proved to be an effective and attractive process for the treatment of these dye-bearing wastewaters. The most widely used and effective physical method in industry is activated carbon, although running costs are expensive. If the adsorbent material used is of cheaper cost and does not require any expensive additional pretreatment step, this method will become inexpensive.

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). Dyes also can cause severe damage to human beings, such as dysfunction of kidney, reproductive systems, liver, brain and central nervous system. Hence decolourisation of dye house effluent via the removal of dye has become an important aspect of textile wastewater treatment (Kadirvelu *et al.*, 2003).

Natural materials have been investigated as potential adsorption media. The use of natural adsorbents in wastewater treatment has received increasing attention and currently offers a very attractive method for pollution remediation. Besides it is plentiful, inexpensive and available in many countries. Adsorption process has been found to be an efficient and economic process to remove dyes, pigments and other colorants (Wangs *et al.*, 2003). It is also 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.*, 2004).

1.5 Objective

The main purpose of this research was to study the effectiveness of natural adsorbents for the multi dye system removal (synthetic wastewater) by adsorption technique in batch process.

1.6 Scope

To achieve the objective, several scopes have been identified in this research. The scopes of this research are listed as below:

1. To study the effect of multi dye removal with different natural adsorbents.
2. To study the influence of pH toward dye removal performance.
3. To determine the optimum dosage of natural adsorbents for multi dye system.

1.7 Rationale and significant

As a contribution of the environment cleanliness and to save the world from water pollution, this research could help to minimize the pollution. The environment is fundamentally connected to everything we need as human beings to survive. Without green plants, there will simply no oxygen to breathe. If we disrupt the temperature balance and precipitation patterns of our current environment, it will make it more difficult to grow food leading for the million of starvation. If we pollute our groundwater with chemicals, then we will be forced to drink chemicals and probably lead to shorter life.

Also, this research absolutely contributes for economical alternatives. The most widely used and effective physical method for adsorption in industry is activated carbon, although the running costs are expensive. If the adsorbent material used cheaper cost and does not require any expensive additional pretreatment step, this method will become inexpensive. Besides, when we use natural adsorbent it is readily available there will no side effect to our earth. In spite of the scarcity of consistent cost information, the widespread uses of low-cost adsorbents in industries for wastewater treatment applications today are strongly recommended due to their local availability, technical flexibility, engineering applicability, and cost effectiveness. If low-cost adsorbents perform well in removing dyes at low cost, they can be adopted and widely used in industries. It is not only to minimize the cost, but also to improve the profitability.

1.8 Methods to remove dyes

Amongst the numerous techniques of dye removal, adsorption is the procedure of choice and gives the best results as it can be used to remove different types of colouring materials. Recently, numerous approaches have been studied for the development of cheaper and effective adsorbents. Many non-conventional low-cost adsorbents, including natural materials, biosorbents, and waste materials from agriculture and industry, have been proposed by several workers. These materials could be used as adsorbents for the removal of dyes from solution.

Many treatment processes have been applied for the removal of dyes from wastewater such as: photocatalytic degradation (Jain *et al.*, 2003), sonochemical degradation (Abbasi *et al.*, 2008), micellar enhanced ultrafiltration (Zaghbani *et al.*, 2008), cation exchange membranes (Wu *et al.*, 2008), electrochemical degradation (Fan *et al.*, 2008), adsorption/precipitation processes (Zhu *et al.*, 2007), integrated chemical–biological degradation (Sudarjanto *et al.*, 2006), integrated iron (III) photoassisted-biological treatment (Sarria *et al.*, 2003), solar photo-Fenton and biological processes (Garcia-Montano *et al.*, 2008), Fenton-biological treatment scheme (Lodha *et al.*, 2007) and adsorption on activated carbon (Hameed *et al.*, 2008). According to Forgacs (2004), as synthetic dyes in wastewater cannot be efficiently decolorized by traditional methods, the adsorption of synthetic dyes on inexpensive and efficient solid supports was considered as a simple and economical method for their removal from water and wastewater.

Methods of dye wastewater treatment have been reviewed by (Pokhrel and Viraraghavan, 2004), (Robinson *et al.*, 2001), (Slokar and Majcen Le Marechal, 1998), (Delee *et al.*, 1998), (Banat *et al.*, 1996), (Cooper, 1993), (Crini, 2006) and (Gupta and Suhas, 2009). Fungal and bacterial decolorization methods have been reviewed by (Aksu, 2005), (Wesenberg *et al.*, 2003), (Pearce *et al.*, 2003), (McMullan *et al.*, 2001), (Fu and Viraraghavan, 2001) and (Stolz, 2001).

According to Dabrowski (2001), adsorption is a well known equilibrium separation process and an effective method for water decontamination applications. 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. Adsorption also does not result in the formation of harmful substances.

Based on many researches, there are wide ranges of nonconventional low-cost adsorbents about the various types of low-cost materials used for the removal of dyes from the wastewater. Inexpensive, locally available and effective materials could be used in place of commercial adsorbent for the removal dyes solution. In spite of the scarcity of consistent cost information, the widespread uses of low-cost adsorbents in industries for wastewater treatment applications today are strongly recommended due to their local availability, technical flexibility, engineering applicability, and cost effectiveness.

CHAPTER 2

LITERATURE REVIEW

2.1 Dyes

The first human-made (synthetic) organic dye, mauveine, was discovered by William Henry Perkin in 1856. Many thousands of synthetic dyes have since been prepared. Synthetic dyes quickly replaced the traditional natural dyes. Dyes are now classified according to how they are used in the dyeing process.

2.1.1 Classification of dyes

I. Acid dyes

Acid dyes are water-soluble anionic dyes that are applied to fibers such as silk, wool, nylon and modified acrylic fibers using neutral to acid dye baths. Attachment to the fiber is attributed, at least partly, to salt formation between anionic groups in the dyes and cationic groups in the fiber. For example, acid dyes are azo (including premetallized), anthraquinone, triphenylmethane, azine, xanthenes, nitro and nitroso.

II. Basic dyes

Basic dyes are water-soluble cationic dyes that are mainly applied to acrylic fibers, but find some use for wool and silk. Usually acetic acid is added to the dye bath to help the uptake of the dye onto the fiber. Basic dyes are also used in the coloration of paper. For example, basic dyes are cyanine, hemicyanine, diazahemicyanine, triarylmethane, azo, azine, xanthenes, acridine, oxazine, and anthraquinone.

III. Direct dyes

Direct or substantive dyeing is normally carried out in a neutral or slightly alkaline dye bath, at or near boiling point, with the addition of either sodium chloride (NaCl) or sodium sulfate (Na_2SO_4). For example, direct dyes are azo, phthalocyanine, stilbene, and oxazine.

IV. Mordant dyes

Mordant dyes require a mordant, which improves the fastness of the dye against water, light and perspiration. The choice of mordant is very important as different mordants can change the final color significantly. Most natural dyes are mordant dyes and there is therefore a large literature base describing dyeing techniques. The most important mordant dyes are the synthetic mordant dyes, or chrome dyes, used for wool; these comprise some 30% of dyes used for wool, and are especially useful for black and navy shades. The mordant, potassium dichromate, is applied as an after-treatment. It is important to note that many mordants, particularly those in the heavy metal category, can be hazardous to health and extreme care must be taken in using them.

V. Vat dyes

Vat dyes are essentially insoluble in water and incapable of dyeing fibers directly. However, reduction in alkaline liquor produces the water soluble alkali metal salt of the dye, which, in this leuco form, has an affinity for the textile fiber. Subsequent oxidation reforms the original insoluble dye. The color of denim is due to indigo, the original vat dye.

VI. Reactive dyes

Reactive dyes utilize a chromophore attached to a substituent that is capable of directly reacting with the fiber substrate. The covalent bonds that attach reactive dye to natural fibers make them among the most permanent of dyes. "Cold" reactive dyes, such as Procion MX, Cibacron F, and Drimarene K, are very easy to use because the dye can be applied at room temperature. Reactive dyes are by far the best choice for dyeing, cotton and other cellulose fibers at home or in the art studio.

VII. Disperse dyes

Disperse dyes were originally developed for the dyeing of cellulose acetate, and are water insoluble. The dyes are finely ground in the presence of a dispersing agent and sold as a paste, or spray-dried and sold as a powder. Their main use is to dye polyester but they can also be used to dye nylon, cellulose triacetate, and acrylic fibers. In some cases, a dyeing temperature of 130 °C is required, and a pressurized dye bath is used. The very fine particle size gives a large surface area that aids dissolution to allow uptake by the fiber. The dyeing rate can be significantly influenced by the choice of dispersing agent used during the grinding.

2.2 Treatment technologies of dyes

These methods have been discussed under three categories: chemical, physical and biological.

2.2.1 Chemical methods

2.2.1.1 Oxidative processes

This is the most commonly used method of decolourisation by chemical means. This is mainly due to its simplicity of application. The main oxidizing agent is usually hydrogen peroxide (H_2O_2). This agent needs to be activated by some means, for example, ultra violet light. Many methods of chemical decolourisation vary depending on the way in which the H_2O_2 is activated (Slokar and Le Marechal, 1997). Chemical oxidation removes the dye from the dye-containing effluent by oxidation resulting in aromatic ring cleavage of the dye molecules (Raghavacharya, 1997).

2.2.1.2 $H_2O_2 \pm Fe(II)$ salts (Fentons reagent)

Fentons reagent is a suitable chemical means of treating wastewaters which are resistant to biological treatment or is poisonous to live biomass (Slokar and LeMarechal, 1997). Chemical separation uses the action of sorption or bonding to

remove dissolved dyes from wastewater and has been shown to be effective in decolorizing 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 environmentally 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 of poor quality and does not settle well, yielding mediocre results (Raghavacharya, 1997).

2.2.1.3 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 (Lin and Lin, 1993; 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 Gonenc, 1997) and no toxic metabolites (Gahr *et al.*, 1994). Ozonation leaves the effluent with no colour and low COD 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). 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, resulting in reduced colouration (Peralto-Zamora *et al.*, 1999). These smaller molecules may have increased carcinogenic or toxic properties, and so ozonation may be used alongside a physical method to prevent this. Decolouration occurs in a relatively short time.

A disadvantage of ozonation is its short half-life, typically being 20 min. This time 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).

2.2.1.4 Photochemical

This method degrades dye molecules to CO₂ and H₂O (Yang *et al.*, 1998; Peralto-Zamora *et al.*, 1999) by UV treatment in the presence of H₂O₂. Degradation is caused by the production of high concentrations 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-products, such as, halides, metals, inorganic acids, organic aldehydes and organic acids, may be produced (Yang *et al.*, 1998). There are advantages of photochemical treatment of dye-containing effluent; no sludge is produced and foul odours are greatly reduced. UV light activates the destruction of H₂O₂ into two hydroxy radicals.

2.2.1.5 Sodium hypochloride (NaOCl)

This method attacks at the amino group of the dye molecule by the Cl⁺. It initiates and accelerates azobond 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).