BIOSORPTION OF METHYLENE GREEN BY *PYCNOPOROUS SANGUINEUS*: BATCH AND COLUMN STUDIES

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by

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LIST OF ABBREVIATIONS

ANOVA	Analysis of Variance
AOP	Advanced oxidation ptocess
BOD	Biochemical Oxygen Demand
COD	Chemical Oxygen Demand
DO	Dissolved Oxygen
D.O.E.	Department of Environment
FTIR	Fourier Transform Infrared
SEM	Scanning Electron Micrographs
UV	Ultraviolet

LIST OF SYMBOLS

Symbol	**Description**	**Unit**
C_e	Equilibrium concentration	mg/L
C_i	Initial concentration	mg/L
C_o	Highest initial dye concentration as outlined	mg/L
C_f	Final concentration	mg/L
ε	Error	-
ΔH^o	Standard enthalpy	kJ/mol
F	Dye solution flow rate	mL/min
ΔG^o	Gibbs free energy change	kJ/mol
k_1	Rate constant of first-order biosorption	h
k_2	Rate constant of second-order biosorption	g/mg.min
k_{TH}	Thomas rate constant	mL/min.mg
k_{AB}	Kinetic constant	L/mg min
k_{YN}	Rate constant	min^{-1}
K_b	Equilibrium constant	L/mg
K_f	Freundlich constants	-
K_i	Equilibrium constant obtained from equilibrium isotherm	dm^3/mg
λ_{max}	Maximum wavelength	nm
M	Mass of biosorbent	g
n	Freundlich constants	-
N_o	saturation concentration	mg/L
q_e	Amount of dye uptake at equilibrium	mg/g

q_{max}	maximum specific dye uptake corresponding to the site saturation	mg/g
q_t	Amount of dye uptake at time t	mg/g
q_o	biosorption capacity	mg/g
R	Gas law constant	J/mol.K
R_L	Separation factors	-
ΔS^o	Standard entropy	J/mol.K
T	Temperature	Kelvin
τ	Time required for 50% adsorbate breakthrough	min
t	Time	min or hr
U	Superficial velocity	cm/min
V	Volume of solution in the flask	L
V_{ff}	Volume of metal solution passed into the column	L
Y	Response	-
y	Measured response	-
Z	Bed height	cm

BIOERAPAN METILIN HIJAU OLEH *PYCNOPORUS SANGUNEUS*: KAJIAN KELOMPOK DAN TURUS

ABSTRAK

Dalam kajian ini, sejenis kulat pereput putih, *Pycnoporous sanguineus* (*P. sanguineus*), di dalam bentuk sel-sel tersekat gerak telah digunakan sebagai biopenjerap bagi bioerapan larutan metilin hijau. Penjerapan telah dikaji di dalam sistem kelompok dan berterusan dengan menggunakan kelalang goncang dan turus lapisan terpadat masing-masing. Dalam sistem kelompok tersebut, kesan masa sentuh (2-12 jam), kepekatan awal metilin hijau (5 mg/L, 15 mg/L dan 25 mg/L) dan suhu (303 K, 313 K dan 323 K) ke atas penjerapan pencelup menggunakan sel-sel tersekat gerak telah diselidik. Adalah didapati bahawa penjerapan metilin hijau bertambah dengan penambahan masa sentuh, kepekatan awal metilin hijau dan suhu. Keputusan bagi penjerapan metilin hijau menggunakan sel-sel tersekat gerak *P. sanguineus* berpadanan dengan model sesuhu Langmuir dengan nilai $R^2 > 0.99$. Kajian-kajian termodinamik yang berbeza telah juga dijalankan pada suhu berlainan (303 K, 313 K dan 323 K), dan keputusannya menunjukkan bahawa perubahan entalpi (ΔH^O) dan perubahan entropi (ΔS^O) bagi proses bioerapan metilin hijau ke atas miselium tersekat gerak *P. sanguineus* adalah -14.749 kJ/mol dan 0.481 kJ/mol K, masing-masing. Kajian kinetik bagi penjerapan metilin hijau dengan sel-sel tersekat gerak *P. sanguineus* pada 25mg/L, 323 K bagi sistem kelompok berpadanan dengan model tertib pseudo kedua. Keupayaan sel-sel tersekat gerak *P. sanguineus* untuk menjerap pencelup metilin telah juga diselidik dalam sistem turus lapisan terpadat. Kesan ketinggian lapisan (5 cm, 9 cm dan 13 cm), kadar aliran (0.24mL/min, 0.48mL/min dan 0.72 mL/min) dan kepekatan awal metilin hijau (5 mg/L, 15 mg/L dan 25 mg/L) telah dikaji. Keadaan operasi yang optimum telah ditentukan pada ketinggian lapisan 13 cm, kadar aliran sebanyak 0.24 mL/min dan kepekatan awal metilin hijau sebanyak 25 mg/L, sementara masa bulus bagi kajian penjerapan telah ditentukan sebagai 160 min. Eksperimen lengkung bulus telah dibandingkan dengan profil bulus simulasi yang diperolehi dari model-model Thomas, Bohart-Adam dan Yoon-Nelson. Keputusan tersebut menunjukkan bahawa data eksperimen itu telah dijelaskan dengan paling baik dengan menggunakan model Thomas. Penjerapan pencelup metilin hijau telah juga disahkan dengan menggunakan mikrograf imbasan elektron sebelum dan selepas dirawat dengan pencelup. Keputusan menunjukkan spora mengecut dan terlerai daripada miselium akibat jerapan oleh pencelup. Ini menunjukkan bahawa *P. sanguineus* mempunyai potensi sebagai penjerap yang murah dan efektif untuk merawat air sisa tekstil.

BIOSORPTION OF METHYLENE GREEN BY *PYCNOPOROUS SANGUINEUS*: BATCH AND COLUMN STUDIES

ABSTRACT

In this study, a white rot fungus, *Pycnoporous sanguineus* (*P. sanguineus*) in immobilized cells form was used as a biosorbent for the biosorption of methylene green solution. The adsorption was studied in batch and continuous system using shake flask and a packed bed column, respectively. In the batch system, the effect of contact time (2- 12 hour), initial methylene green concentration (5 mg/L, 15 mg/L and 25 mg/L) and temperature (303 K, 313 K and 323 K), on the dye adsoprtion by the immobilized cells were investigated. It was found that methylene green adsorption increased with increasing contact time, initial methylene green concentration and temperature. Results of the methylene green adsorption by immobilized cells of *P. sanguineus* fitted well with the Langmuir isotherm model with $R^2 > 0.99$. Different thermodynamic studies were also carried out at different temperature (303 K, 313 K and 323 K), and the results showed that the enthalpy change (ΔH^o) and entropy change (ΔS^o) for the biosorption process of methylene green onto immobilized mycelium of *P. sanguineus* were -14.749 kJ/mol and 0.481 kJ/mol K, respectively. The kinetic studies for methylene green dye adsorption by immobilized cells of *P. sanguineus* at 25 mg/L, 323 K in a batch system fitted well with the pseudo-second order model. The ability of immobilized cells of *P. sanguineus* to adsorb methylene dye was investigated in a packed bed column system. The effect of bed height (5 cm, 9 cm and 13 cm), flow rate (0.24 mL/min, 0.48 mL/min and 0.72 mL/min) and initial methylene green concentration (5 mg/L, 15 mg/L and 25 mg/L) were studied. Optimum operating conditions were found at the bed height of 13 cm, flow rate of 0.24 mL/ min and initial methylene green concentration of 25 mg/L, while the breakthrough time of the sorption study was determined at 160 min. Experimental breakthrough curves were compared with simulated breakthrough profiles obtained from Thomas, Bohart-Adam and Yoon-Nelson models. The results showed that the experimental data were best described by Thomas model. Biosorption of dye on cell surface was further confirmed by scanning electron micrographs before and after loaded with dye. Results showed the spores shrunk and detached from the mycelium as a result of dye biosorption. This indicate that *P. sanguineus* has a potential to be an effective low cost adsorbent for the treatment of textile wastewater.

CHAPTER 1

INTRODUCTION

1.1 Dye pollution

Dyes are widely used in food, pharmaceutical, cosmetic, textile and leather industries. Over 10,000 commercially available dyes exist and more than 7×10^5 tons of dyestuff produced annually (Kolekar *et al.*, 2008). Water pollution due to the discharge of industrial wastewater that contains dyes is becoming a serious environmental problem on a global scale. Generally most of the developing countries encountered serious water shortage due to severe water pollution as a consequence of their rapid industrialization process.

The dyes significantly affected photosynthetic activity of the aquatic life due to reduce light penetration, and dyes may also be toxic to some aquatic life due to the presence of aromatics, metals, and chlorides (Hafez *et al.*, 1997, Mashitah *et al.*, 1999, Davis *et al.*, 2000, Say *et al.*, 2001, Vijayaraghavan *et al.*, 2005a, Vijayaraghavan *et al.*, 2005b). The chromospheres in anionic and non-ionic dyes are mostly azo or anthraquinone types. Both dyes and pigments appear to be coloured because they absorbed certain wavelengths of light preferentially (Veglio and Beolchini, 1997). In fact, the Ministry of a Natural Resources and Environment of Malaysia has established a National Water Quality Standards for Malaysia. Table 1.1 shows the maximum contaminants levels, their classes and uses according to the mentioned standard. For example the maximum contaminant level for colour is 15 colour units (TUC) for the class 1 wastewater (D.O.E., 2009).

Table 1.1 : Interim Water Quality Standards for Malaysia (D.O.E., 2009)

Parameters	**Unit**	**Classes**					
		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*	µS/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	^{o}C	-	Normal +2 ^{o}C		Normal +2 ^{o}C	-	-
Turbidity	NTU	5	50	50	-	-	-
Faecal Coliform**	Count/ 100mL	10	100	400	5000 (20000)^{a}	5000 (20000)^{a}	-
Total Coliform	Count/ 100mL	100	5000	5000	50000	50000	>50000

Notes

N	No visible flotable materials or debris or objectionable odour, 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

1.2 Treatment technologies for dye removal

The treatment of highly coloured effluent streams from industry has become a great concern for the environmentalists. Dyes removal can be done by physical or chemical methods, such as coagulations, flocculation, biodegradation, adsorption on activated carbon, membrane separation, ion exchange, advance oxidation, selective bioadsorbents and biomass which all of these were commonly used in the industries (Kaushik and Malik, 2009). Currently, adsorption of dye from wastewater via activated carbon has become popular but it is constrained by the high cost, low efficiency and limited versatility (Couto, 2009, Nandi *et al.*, 2009, Tan *et al.*, 2009). Furthermore, newer methods have been extensively researched and tested, particularly those using low cost adsorbents that were able to bind the dye molecules, including specific microorganisms for degradation of the recalcitrant compounds (Yesilada *et al.*, 2003, Li *et al.*, 2008, Won *et al.*, 2008b). Hasan *et al.* (2008) have found that microbial decolourization of industrial dyes was most cost-effective and had much better efficiency. For these reasons, biosorbent has started to receive attention for the treatment of industrial dyes wastewater in recent years. Table 1.2 compares the advantages and disadvantages of existing dye removal technologies.

Table 1.2 : Comparisons of dye removal technologies (Crini, 2006).

	Technology	Advantages	Disadvantages
Conventional treatment process	Coagulation Flocculation	Simple, economically feasible	High sludge, handling and disposal problem
	Biodegradation	Economically attractive, publicly acceptable treatment	Slow treatment and selective to some substance.
	Adsorption on activated carbon	Most effective adsorbent, great, capacity, produce a high-quality treated effluent.	Ineffective against disperse and vat dyes. Expensive cost.
Established recovery process	Membrane separations	Removed all types of dyes and produce high quality treated effluent.	High pressure, expensive and incapable of treating high volume
	Ion exchange	No loss of sorbent on regeneration, effective.	Economic constrain.
	Oxidation	Rapid and efficient process.	High cost and chemical required.
Emerging removal processes	Advance oxidation process	No sludge production, little or no consumption of chemicals.	Requires chemical modification and non-destructive process.
	Selective bioadsorbents	Economically attractive, regenerating not necessary and high selectivity.	Requires chemical modification and non-destructive process.
	Biomass	Low operating cost, good efficiency.	Slow process, performance depends on some external factors (pH, salts)

1.3 Problem statement

The textile industry uses a number of chemicals that have resulted in toxic and harmful effluents impacting the environment negatively and significantly. Due to the cost associated with treating the pollutants, most effluents, especially the dye wastes, were discharged into the environment without any treatment. Such waste discharge constituted 40 % of the total industrial wastewater which is not only voluminous but also much coloured (Kaushik and Malik, 2009). Furthermore, most of the synthetic dyes used in the textile industries are recalcitrant and non-biodegradable. As such, it is imperative to treat coloured effluents for the removal of dyes. To that end, non-conventional, low cost, adsorbing biomass for dyes removal was highly favoured. Also another dye removal method involved using growing cells via bioaccumulation (Won *et al.*, 2008a). In particular, bioaccumulation methods involving fungal decolourization, microbial degradation, adsorption by the microbial biomass and the other similar bioremediation systems are commonly utilized to treat industrial effluents.

Many microorganisms including bacteria, yeasts, algae and fungi are known to be able to accumulate and degrade different pollutants. In particular, interest is the fact that the white rot fungus (WRF) was found suitable for removing dyes. They can produce and secrete ligninolytic enzymes such as laccase (benzenediol: oxygen oxidoreductase; *p*-diphenol oxidase, urishiol oxidase) which presented low specificity with regards to substitute aromatic structures (Vijayaraghavan *et al.*, 2008). Moreover, laccases secreted by *Pycnoporous sanguineus* have previously demonstrated their great ability to decolourize azo, triphenylmethane and anthraquinonic dyes and heavy metal, from wastewater effluent (Trovaslet *et al.*, 2007). Therefore, this particular research was aimed to investigate the potential of removing reactive dyes from the effluent by immobilizing the freely suspended living cells of *Pycnoporous sanguineus* in both shake flask and column bed. Methlyene green a water soluble basic dye, highly toxic to aquatic and the environment organisms was selected as a model dye for this present study. The effect of time, initial concentration, temperature, isotherm and thermodynamic of the sorption processes were evaluated and outlined.

1.4 Research objectives

This study focuses on the biosorption of dye from an aqueous solution by a white rot macro fungus, *Pycnoporous sanguineus*.

The measurable objectives are:

(i) To study the effect of different parameters on the biosorption of methylene green dye by immobilized cells of *Pycnoporous sanguineus* (*P. sanguineus*) in a batch adsorption system.

(ii) To study the equilibrium, kinetics and thermodynamics of the dye biosorption by the immobilized cells of *P. sanguineus*.

(iii) To determine the breakthrough characteristics of dye biosorption on immobilized cells in packed bed column.

(iv) To characterize the immobilized beads using scanning electron micrographs (SEM) and fourier transform infrared analysis (FTIR) before and after the biosorption of dye.

1.5 Scope of study

In this study, biosorbent prepared from of the living *Pycnoporous sanguineus* (*P. sanguineus*) was selected for dye removal. This strain was reported to be a strong biosorbent for metal adsorption. The immobilized cells of *P. sanguineus* were tested for dye biosorption in a batch system. Methylene green, one type of basic dye was used as the tested dye. Theoretical equilibrium models of Langmuir and Freundlich and other kinetics models were utilized and compared. Dye biosorption onto the immobilized *P.sanguineus* was also carried out in a packed bed column. The immobilized cells of this tested fungus were used as biosorbent to study the effect of different variables such as bed height, flow rates and initial dye concentration. In column studies, three models known as Thomas, Bohart- Adam and Yoon-Nelson were used to analyze the experimental data. The biosorbent was then characterized using scanning electron microscopy (SEM) and fourier transform infrared analysis (FTIR) before and after treated with dye.

1.6 Organization of the thesis

The thesis is organized into five chapters and each chapter describes the sequence of this research:

Chapter 1: introduces the scenarios of wastewater pollution in the textile industry, and the treatment technologies commonly used for dye removal from any waste streams. Also this chapter presents the problem statement, research objectives and organization of the thesis.

Chapter 2: covers an overview of dye, the treatment technologies for dye removal and the biosorption process. The impacts of the dye to the environment were also discussed in detail.

Chapter 3: presents the materials and methods of the experimental procedures in the research for batch and packed bed column systems. It also covers the analysis of sample and characterization of biosorbent before and after treatment.

Chapter 4: presents the results and discussion for the biosorption of dye onto the immobilized cells of *P.sanguineus* in batch process either for shake flask or packed bed column. This includes the results of adsorption equilibrium and kinetics modeling for dye removal systems. Langmuir and Freundlich models were tested in the equilibrium studies for dye removal of the immobilized cells of *P.sanguineus*. For kinetic studies, the pseudo first, pseudo second and an intra particle diffusion equations were applied to the experimental data. In column studies, the experimental data were examined using Thomas, Bohart-Adam and Yoon Nelson models. The important parameters that influenced the performance of the packed bed column for each model were also determined.

Chapter 5: covers the overall conclusions that are based on the findings obtained in the results and discussion (Chapter 4). Recommendations for future research of the project are also presented.

CHAPTER 2

LITERATURE REVIEW

2.1 Colourants and dyes

Since prehistoric time, human have used natural colourants in their daily life. However, Perkin’s discovery of mauve marked the start of the modem synthetic dye industry in 1856 (Hunger, 2003). Colourants are characterized by their ability to absorb and emit light in the visible range (400-700 nm). Therefore, this is the reason they appear to be coloured. In term of chemical structure, colourants may be divided into two groups, which are organic and inorganic colourants.

Colourants include both dyes and pigments. Pigments are insoluble materials which have colour, whereas most dyes are soluble. Dyes generally described as coloured substances that have an affinity to the substrate to which it is being applied.

The difference between pigment and dyes is that pigments are used as colourants in the physical form whereas dyes are applied to various substrates (textile materials, leather, paper and hair) from liquid in which they were completely soluble (Zollinger, 1991).

Fu and Viraraghavan (2001) reported that dyes and pigments are highly visible materials. A minor release to the environment can harm aquatic life which is undesirable. Dyes generally are described as coloured substances that have an affinity to the substrate to which it is being applied. In particular, the reduction of residual dyes has become a major issue recently for textile and dyestuff industries, moreover dyes made of aromatic structure tend to be difficult to be treated (Yu *et al.*, 2001).

2.2 Classifications of dyes

Structurally, dyes may be grouped as inorganic or organic compounds. Both groups can be further subdivided into natural and synthetic categories. When classified according to dyeing method, one can distinguish between anionic, direct or disperse dyes, depending on whether these substances are used for dyeing protein, cellulose or polyamide fibres. Sometimes these two classification methods do overlap, since there is hardly a chemical dye class which occurs solely in one colouristic group, and vice versa. Furthermore, some colouristic groups can be applied to two or more substrates, whilst others are specific to a single substrate. Table 2.1 summarizes the classifications of dyes and their chemical types (Hunger, 2003). Table 2.2 shows some typical characteristics of different classes of dyes used in textile dyeing operations as outlined by EPA (1997).

In terms of chemical structure, dyes can be classified as follows: (Hunger, 2003):

- Acetate rayon dyes: developed for cellulose acetate and some synthetic fibres.

- Acid dyes: used for colouring animal fibres via acidified solution (contain sulfuric acid, acetic acid, sodium sulfate, and surfactants) in combination with amphoteric protein.

- Azoic dyes: contain the azo group (and formic acid, caustic soda, metallic compounds, and sodium nitrate); especially for application to cotton. It contains one azo group -N=N-, but contain two (disazo), three (trisazo) or rarely four (tetakisazo) or more (polyazo) azo groups.

- Basic dyes: amino derivatives (and acetic acid and softening agents); used mainly for application on paper.

- Direct dyes: azo dyes, and sodium salts, fixing agents, and metallic (chrome and copper) compounds; used generally on cotton-wool, or cotton-silk combinations.

- Mordant or chrome dyes: metallic salt or lake formed directly on the fiber by the use of aluminum, chromium, or iron salts that caused precipitation in *situ*.

- Lake or pigment dyes: form insoluble compounds with aluminum, barium, or chromium on molybdenum salts; the precipitates are grounded to form pigments used in paint and inks.

- Sulfur or sulfide dyes: contain sulfur or are precipitated from sodium sulfide bath.
- Vat dyes: impregnated into fiber under reducing conditions and reoxidized to an insoluble colour.

Table 2.1 : Classification of dyes according to their usages (Hunger, 2003)

Class	**Principles substrate**	**Method application**	**Chemical classes**
Acid	Nylon, wool, silk, paper and leather	Usually from neutral acidic dyebaths	Azo (including premetallized), anthraquinoe, triphenylmethane, azine, xanthenes, nitro and nitroso
Basic	Paper, Polyacrylonitrile, modified nylon, polyester and inks	Applied for acidic dyebaths	Cyasine, hemicyanie, diazahemicyanine, diphenylmethane, trialrylmethane, azo,azine,xanthenes,acridine, oxazine and anthraquinone azo, phthraquinone, stilbene and oxzine
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, plastics.	Fine aqueous dispersions often applied by high temperature/ pressure or lower temperature carried methods; dye maybe padded on cloth and baked on thermofixed	Azo, anthraquinone, styryl, nitro and benzodifuranone

Table 2.1: continued

Class	Principles substrate	Method application	Chemical classes
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, strains, inks, fats, oils and nylon	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	Intermediate structures
Vat	Cotton, rayon and wool	Water-insoluble dyes solubilized by reducing with sodium hydrogen sulfite then exhausted on fiber and reoxidized	Athraquinone (including polycyclic quinones) and indiqoids

Table 2.2 : Typical characteristics of different class of dyes used in textile dyeing operation (E.P.A., 1997)

Dye Class	**Descriptions**	**Fibers typically applied**	**Typical fixation %**	**Typical pollutants associated with dye**
Acid	Water-soluble anionic compound	Wool, nylon	80-93	Colour, organic acids, unfixed dyes
Basic	Water- soluble, very bright dye	Acrylic, some polyesters	97-98	N/A
Direct	Water-soluble, anionic compound, can be applied directly to cellulosic without mordant	Cotton, rayon, other cellulosic	70-95	Colour, salts, unfixed dyes, cationic fixing agents, surfactant, defoamers, leveling agents, phosophate, lubricants, dispersants, diluents
Disperse	Water- insoluble	Polyesters, acetate, other synthetics	80-92	Colour, organic acids, carriers, defoamers, leveling agents, phosphates, lubricants, dispersants, diluents
Reactive	Water-soluble, anionic compound, largest dye class	Cotton, other cellulosic, wool	60-90	Colour, salts, alkali, unfixed dyes, surfactant, defoamers, diluents
Sulfur	Organic compound containing sulfur or sodium sulfide	Cotton, other cellulosic	60-70	Colour, alkali, oxidizing agents, reducing agents, unfixed dyes

2.3 Cationic (basic) dyes

Cationic dyes carry a positive charge in their molecule, are water soluble and yield coloured cations in solution. The basic dyes are water-soluble and primarily applied for dyeing acrylic fibers (Gupta and Suhas, 2009). Many of these dyes can be converted into water insoluble dye bases by addition of alkali. Generally, the cationic functionality is found in various types of dye, mainly in cationic azo dyes and methane dyes, but also in anthraquinone, di- (diarylmethane) and tri-(triarylmethane) arylcarbenium, phthalocyanine dyes and in various polycarbocyclic and solvent dyes (Hunger, 2003). Cationic dyes were used initially for dyeing of silk, leather, paper and cotton mordant with tannin, as well as for the production of ink and copying paper in the office supplies industry. Basic dyes have high brilliance and colour strength and are partly compensated for their poor light fastness on materials. With the development of synthetic fibers, their most suitable substrates were found and their importance for dyeing textiles increased greatly. Cationic dyes were employed initially for printing of cellulose acetate but had gained much greater importance for dyeing of polyacrylonitrile and acid-modified polyamide fibers. Some of the basic dyes show biological activity and are used in medicine substrates consequently (Hunger, 2003). A cationic dye, methlyene green is selected as a model compound in this study in order to evaluate the adsorption capacity.

2.4 Advanced process involved on dye removal

Advanced processes are the processes involving simultaneous use of more than one oxidation processes, since sometimes a single oxidation system is not sufficient for the total decomposition of dyes. These reactions, all of which involve the accelerated production of the hydroxyl free radical, which is very reactive, are termed advanced oxidation processes and include techniques as Fenton's reagent oxidation, ultra violet (UV) photolysis and sonolysis. They are capable of degrading dyes at ambient temperature and pressure and may also have an advantage over biological treatment for waste streams containing toxic or bioinhibitory contaminants. The central attraction of advanced oxidation processes is that organic contaminants are commonly oxidized to CO_2. A wide variety of advanced oxidation processes are available like chemical oxidation processes using ozone, combined ozone and peroxide, ultra violet enhanced oxidation such as UV/hydrogen peroxide, UV/ozone, UV/air wet air oxidation and catalytic wet air oxidation (Gupta and Suhas, 2009).

All these processes offer powerful water and wastewater treatment solutions for the reduction (removal) of residual organic compounds as measured by COD, BOD or TOC. In particular these advanced oxidation processes are designed to produce hydroxyl radicals with high efficiency to destroy organic compounds (Spartan, 2010).

Nevertheless, in general those processes have the drawback of producing some undesirable by products, complete mineralization is not possible and the process is pH dependent. Also, depending on the process the limitation may vary, e.g., in the process involving colour removal by the UV/H_2O_2 treatment the important factors that influence colour removal are peroxide concentration, time of treatment, intensity of UV radiation, pH, chemical structure of the dye and dye bath additives. Though the advanced processes have proven potential and found technically sound for colour removal they are quite expensive especially for small scale sector of developing countries(Gupta and Suhas, 2009).

2.4.1 Hydrogen Peroxide Treatment

Hydrogen peroxide is a powerful, non-specific oxidant adequate for degradation of pollutants that can be used in combination with a catalyst and or UV light to produce free radical intermediates. The hydroxyl radical is one of the main species that react with non-saturated organic compounds leading to either partial or complete degradation (Lázaro Martínez *et al.*, 2008). It also has been frequently applied to the decolorization of synthetic dyes in water. The major active species involved in the degradation of organic pollutants are hydroxyl radicals which directly attack organic pollutants contained in water due to their high oxidation potential. And the hydrogen peroxide can be effectively decomposed by ultraviolet radiation into hydroxyl radicals to facilitate the wastewater dye treatment. Hydrogen peroxide has been found useful in the treatment of wastewater and is often referred as a friendly oxidant because the oxidation byproducts are water and oxygen (Qiu *et al.*, 2005). The technology using hydrogen peroxide to treat dye wastewater has two different methods, homogeneous and heterogeneous reaction. In the homogeneous reaction, metal ions such as $Fe^{2+}$and Cu^{2+} are used as the catalysts. Hence hydrogen peroxide appears to be dependent on the frequency and intensity of ultrasonic irradiation, the properties of aqueous phase and external factors (Compton *et al.*, 1997, Pétrier and Francony, 1997, Appaw and Adewuyi, 2002, Gogate, 2002, Mason and D. Peters, 2002, Nikitenko *et al.*, 2004, Yazici *et al.*, 2007). The addition of chloride and carbon tetrachloride may improve the effectiveness of ultrasonic treatment.

2.4.2 Ozonation (O_3) Treatment

Ozone can also be used for degradation of dyes pollutants in water. Ozone is a powerful oxidant (electrochemical oxidation potential of 2.07 V versus 2.8 V for hydroxyl radical), which is generally produced by an electric discharge method in the presence of air or oxygen. Two reactions of ozone with dissolved organic substance can be distinguished in water: a highly selective attack of molecular ozone takes place on the organic molecules at low pH, whereas free radicals from ozone decomposition can also react non-selectively with the organic compounds (Hoigné and Bader, 1976, Agustina *et al.*, 2005). Additional free hydroxyl radicals can be produced in the aqueous media from ozone by pH modification or can be introduced by combining ozone either with hydrogen peroxide or UV-irradiation from a high pressure mercury lamp (Chiron *et al.*, 2000). On the other hand, the use of ozone for the destruction of organics in water is also a well known water treatment technique. Unlike photocatalysis, ozonation, due to its capability for selective destruction of recalcitrant organics, is used as a pre-treatment step before ordinary biological techniques, thus being more efficient for highly contaminated wastewater. The simultaneous application of ozonation and photocatalysis has the capability for efficient treatment of textile contaminated wastewaters over a wide range of concentrations (Sánchez *et al.*, 1998).

Generally the ozonation oxidation is still the most basic and yet practical advanced oxidation processes for the treatment of industrial waste streams including textile effluents. Davis *et al.* (1994) and Hitchcock *et al.* (1998) have demonstrated the effect of chemical structure on the decomposition rate of pollutants. In addition to that, the effect of ozonation on the toxicity of wastewater effluents has been also investigated using Nematode *Caenorhabditis elegans*. There were indications that the toxicity was highly dependent on the type of dye to be decomposed. Also influence of operating parameters on the decolourization of a reactive dye by ozone has been studied in detail, thus Wu *et al.* (1998) and Wu and Wang (2001) showed that the decomposition rate increased with increasing pH and temperature. Furthermore, a method employing a combination of membrane filtration with subsequent ozonation of retentates has been developed for the effective purification of colored textile wastewaters. In general it is more effective in using less ozone as compared to conventional ozone treatment. Furthermore, using ozone in presence of a catalyst was found effective in treating large volume of wastewater in terms of colour, biological and chemical oxygen demand due to fats, oils and grease etc. in the waste stream.

2.4.3 UV Treatment

Photocatalytic degradation has proven to be a promising technology for degrading various dye compound including refractory chlorinated aromatics (Calza *et al.*, 1997, Schmelling *et al.*, 1997, Chu, 1999, Davis and Green, 1999, Topalov *et al.*, 1999) and more than 1700 references have been collected on this discipline (Blake, 1999). Compared with other conventional chemical oxidation methods, photocatalysis may be more effective because semiconductors are inexpensive and capable of mineralizing various refractory compounds (Ku *et al.,* 1996). Due to its capability of generating OH• radicals, which is a powerful oxidant species, photocatalysis can be considered as an advanced oxidation process (AOP). Heterogeneous processes employ semiconductor slurries (e.g. TiO_2/UV, ZnO/UV) for catalysis, whereas homogeneous photochemistry (e.g. H_2O_2/UV, Fe^{3+}/UV) is used in a single phase system (Agustina *et al.,* 2005).

Photocatalytic reactions occur when charge separation are induced in large bandgap semiconductor by excitation with ultra bandgap radiations (Rideh *et al.,* 1997). In this way, the absorption of light by the photocatalyst greater than its bandgap energy excites an electron from the valence band of the irradiated particle to its conduction band, producing a positively charged hole in the valence band and an electron in the conduction band (Izumi *et al.*, 1980). The hole in the valence band may react with water absorbed at the surface to form hydroxyl radicals and on the other hand, the conduction band electron can reduce absorbed oxygen to form peroxide radical anion that can further disproportionate to form OH• radical through various pathways. During the photocatalytic process, other oxygen containing radicals are also formed including superoxide radical anion and the hydroperoxide radical (Dionysiou *et al.*, 2000). In addition, the band electron may also react directly with the contaminant via reductive processes (Jones and Watts, 1997). However, although photocatalysis has shown to be adequate for the destruction of a wide variety of compounds, in some cases the complete mineralization is slowly attained and the efficiency of the processes, in terms of energy consumption, is only advantageous for very dilute effluents (Hoffmann *et al.*, 1995).

Photocatalysis is also one of a series of advanced oxidation processes for pollutant degradation (Arslan-Alaton, 2003, Akyol *et al.*, 2004, Aguedach *et al.*, 2005, Behnajady *et al.*, 2006, Ghorai *et al.*, 2007, Gupta *et al.*, 2007). In photocatalysis, light energy from a light source excites an electron from the valence band of the catalyst to the conduction band with a series of reaction which results in the formation of hydroxyl radicals. The hydroxyl radicals have high oxidizing potential and therefore can attack most organic structures causing oxidation. Various chalcogenides (oxides such as TiO_2, ZnO, ZrO_2, CeO_2, etc. or sulfides such as CdS, ZnS, etc.) have been used, as photocatalysts in the photocatalytic process and the process is found suitable for a wide range of dyes including direct, reactive, vat and disperse (Gupta and Suhas, 2009).

UV irradiation for colour removal could be a promising procedure because it does not generate chemical sludge, and the toxicity of wastewater could be reduced as a result. Although information regarding photo decolourization reactions of synthetic aromatic dyes is very limited, it is known that UV decolourization is achieved by the cleavage of conjugated bonds. The bond breaking will shift the wavelength of absorbed light from the visible range to ultraviolet range, which cannot be detected by human eyes. When dye molecules absorb photons, the energy of UV will be transferred to the dye molecules and the electronic structures of dyes are excited to their singlet or triplet states, Dyes in such excited states become unstable and short lived and will either decay back to their ground states losing their excitation energy in some physical ways or undergo chemical reactions and form new species. This self rearrangement of the dye molecule, which varies widely with the dye structure, depends on the photosensitivity and the ease of dye reactivity. The decolourization of dye by UV irradiation mainly depends on the latter dye propensity.

2.4.4 Activated carbon

Adsorption is recognized as an efficient, promising and most widely used technique in the wastewater treatment processes, especially in developing countries which the issue is highly intense and touching, mainly hinges on its simplicity, ease of handling, economically viable, technically feasible and socially acceptable. For this purpose, activated carbon, an adsorbent with its large porous surface area, controllable pore structure, thermo stability and low acid/base reactivity, has been proven to be effective for removal of a wide variety of organic and inorganic pollutants dissolved in aqueous media, or from gaseous environment. Despite its prolific use in adsorption processes, the biggest barrier of its application by the industries is the cost prohibitive adsorbent and difficulties associated with regeneration. This has exerted a growing exploitation to investigate the feasibility and suitability of natural, renewable and low cost materials as alternative adsorbents in the water pollution control, remediation and decontamination processes (bamboo dust, peat, chitosan, lignite, fungi, moss, bark husk, chitin, coir pith, maize cob, pinewood sawdust, rice husk, sugar cane bagasse, tea leaves, and sago waste) (Foo and Hameed, 2009). Activated carbon is the oldest adsorbent known and is usually prepared from coal, coconut shells, lignite, wood etc., using one of the two basic activation methods: physical and chemical (Hassler, 1963, Bansal *et al.*, 1988, Carrott *et al.*, 2003, Phan *et al.*, 2006, Lillo-Ródenas *et al.*, 2007).

It has been found that adsorption on activated carbon is not usually selective as it occurs through van der Waals forces. The ability of charcoal to remove odour and taste was recorded centuries ago. The applicability of activated carbon for water treatment has been demonstrated by various workers (Weber *et al.,* 1970, Stenzel, 1993). Also it is well known that adsorption by activated carbon is an effective and commercially applicable method for removing colour and other pollutants from textile and dye wastes. Porter (1972) suggested that carbon adsorption is a complete treatment for textile water. In order to demonstrate the versatility of activated carbon, different workers (DiGiano and Natter, 1977, Walker and Weatherley, 1999, Al-Degs *et al.*, 2000, Pelekani and Snoeyink, 2000) have used this adsorbent for different types of dyes (Gupta and Suhas, 2009).

McKay (1982) used activated carbon of Filtrasorb type for the removal of acidic, basic, disperse and direct dyes and found it to be excellent for the removal of all except direct dyes. Walker and Weatherley (1999) studied the kinetics of acid dye, tectilon red 2B, on GAC. The adsorption of three reactive dyes used in textile industry on Filtrasorb 400 activated carbon was studied by Al-Degs *et al.* (2000) and same workers (Al-Degs, 2001) further studied various activated carbons for the removal of cationic dye (methylene blue) and anionic dye (reactive black), and reported that there exists a good relationship between performance of activated carbon and methylene blue capacity/surface area.

Studies have shown that activated carbons are good materials for the removal different types of dyes in general but there use is sometimes restricted in view of higher cost. Also, the activated carbons after their use (treatment of wastewater) become exhausted and are no longer capable of further adsorbing the dyes. Once AC has been exhausted, it has to be regenerated for further use in purifying water and a number of methods like thermal, chemical, oxidation, electrochemical (Hemphill *et al.*, 1977, Rollor *et al.*, 1982, Martin and Ng, 1987, Freeman, 1989, Newcombe and Drikas, 1993, Notthakun *et al.*, 1993, Narbaitz and Cen, 1994, Kilduff and King, 1997, Taiwo and Adesina, 2005, Zhou and Lei, 2006) are used for this purpose, the most common being thermal. It is worthwhile noting that regeneration of activated carbon adds cost, furthermore, any regeneration process results in a loss of carbon and the regenerated product may have a slightly lower adsorption capacity in comparison with the virgin activated carbon (Gupta and Suhas, 2009).

2.5 Biosorption process

2.5.1 Conventional treatment technologies and trend towards fungal biosorption

The conventional techniques commonly applied for the removal of dye from wastewater include chemical (precipitation/ neutralization) and physical (ion exchange, membrane separation, electrodialysis and activated carbon adsorption) methods (Beszedits, 1983, Smânia *et al.*, 1995). A number of the above processes, such as coagulation, flocculation, chemical oxidation, reverse osmosis and adsorption have been employed for the treatment of dye bearing wastewater. However, there are several limitations of chemical coagulation-flocculation to produce good quality effluent besides sludge handling problem. In fact, it is not feasible and economical, and possibly produced various detrimental effects such as chemical oxidation. The technical and economical constraints of reverse osmosis due