ADSORPTION OF METHYLENE BLUE ONTO MODIFIED FACTORY TEA WASTE: BATCH AND FIXED BED COLUMN

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by

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF PLATES

LIST OF SYMBOLS

Å	Angstrom unit	-
A_b	Area under breakthrough curve	-
A_C	Constant in the Clark model	-
A	Temperature-independent factor related to Arrhenious equation	-
A_i	Absorbance of component *i*	-
b	Adsorption energy constant of Langmuir adsorption isotherm	L/mg
b_c	Path length of the cell	cm
C_{ad}	Concentration of adsorbate adsorbed in the column	mg/L
C_b	Bulk phenol concentration in the solution in the column	mg/L
C_e, C_{eq}	Equilibrium concentration of liquid phase	mg/L
C_o	Initial concentration of liquid phase	mg/L
C_{break}	Outlet concentration at breakthrough (or limit effluent concentration)	mg/L
E	Activation energy	kJ/mol
ε_λ	Molar absorptivity coefficient of solute at specific wavelength	1/ [(mg/L) cm]
k_c	Standard thermodynamic equilibrium constant	L/g
k_f	Rate constant of pseudo first-order model	1/min
k_s	Rate constant of pseudo second-order adsorption	g / (mg min)
k_i	Intraparticle diffusion rate	mg/g hr$^{1/2}$
k’	Specific rate constant	1/min
K	Mass transfer coefficient Clark	1/min
K_F	Constant in Freundlich isotherm	(mg/g)(L/mg)$^{1/n}$
k_{Th}	Thomas rate constant	mL/(min mg)
k_{YN}	Rate constant	1/min
M	Molarity	mg/L
n	Freundlich exponent	-
τ	Time required for 50% adsorbate breakthrough	min
t_{break}	Time at breakthrough	min
T	Temperature	Kelvin or ºC
Q	Flowrate	mL/min

Q^o	Langmuir constant related to maximum surface coverage of adsorbent	mg/g
q_e	Amount of solute adsorb per unit weight of adsorbent at equilibrium	mg/g
q_o	Constant in Thomas model which refer to the maximum solid-phase concentration of the adsorbate	mg/g
q_t	Amount of solute adsorb per unit weight of adsorbent at time, t	mg/g
R^2	Correlation coefficient	-
R_L	Separation factor	-
R	Gas constant = 8.314	J/(mol K)
ΔG^o	Change in apparent free energy	kJ/mol
ΔH^o	Enthalpy change	kJ/mol
ΔS^o	Entropy change of adsorption	J/(mol K)
V	Volume	L
V_{eff}	Volume of effluent	L
W	Weight of adsorbent	g

LIST OF ABBREVIATIONS

BOD	Biological Oxygen Demand
BET	Brunauer-Emmet-Teller
COD	Chemical Oxygen Demand
FTIR	Fourier transform infrared (FTIR) spectroscopy
IUPAC	International Union of Pure and Applied Chemistry
KOH-TW	KOH-Tea Waste
MB	Methylene Blue
NaOH-TW	NaOH-Tea Waste
rpm	Rotation per Minute
R-TW	Raw Tea Waste
SEM	Scanning Electron Microscopy
TOC	Total Organic Compound

PENJERAPAN METELINA BIRU KE ATAS HASIL BUANGAN KILANG TEH TERMODIFIKASI: PENJERAPAN KELOMPOK DAN TURUS PADATAN TETAP

ABSTRAK

Tujuan penyelidikan ini adalah untuk menyiasat kemungkinan bagi menghasilkan bahan penjerap yang dimodifikasi secara kimia ke atas produk sampingan pertanian, iaitu sisa buangan kilang teh bagi penjerapan metilena biru (MB) daripada larutan akuas. Eksperimen telah membuktikan bahawa, hasil buangan kilang teh termodifikasi daripada larutan sodium hidroksida (NaOH) dan kalium hidroksida (KOH), yang dinamakan NaOH-TW dan KOH-TW, memberi kecekapan tertinggi dalam penjerapan MB dibandingkan dengan modifikasi daripada bahan kimia yang lain. Penjerap R-TW, KOH-TW dan NaOH-TW telah dianalisa penciriannya melalui analisa infra-merah pengubahan fourier, analisa mikroskop elektron imbasan dan analisa isoterma penjerapan/penyahjerapan nitrogen. Kesan konsentrasi awal MB (50 - 500 mg / L), masa sentuh, suhu larutan (30, 40 dan 50 ºC) dan pH larutan (3 - 12) ke atas penjerapan MB telah dinilai melalui kajian penjerapan kelompok. Keputusan menunjukkan, penjerapan MB meningkat dengan peningkatan konsentrasi awal dan masa sentuh. Kecekapan penyingkiran MB adalah tertinggi pada pH 7–10 untuk R-TW, KOH-TW dan NaOH-TW. Isoterma penjerapan MB pada semua bahan penjerap ini adalah terbaik dipadankan oleh model isoterma Langmuir. Keupayaan jerapan MB untuk isoterma Langmuir adalah mengikuti keputusan aliran R-TW < KOH-TW < NaOH-TW. Model kinetik tertib kedua untuk penjerapan MB adalah terbaik dihuraikan ke atas semua adsorbents. Semua proses penjerapan pada semua penjerap menunjukan mekanisme penjerapan fizikal disebabkan tenaga pengaktifannya lebih rendah daripada 40 kJ / mol. Beberapa siri ujian telah dijalankan untuk mengukur perkembangan ciri lengkungan bulus untuk penjerapan MB pada R-TW, KOH-TW dan NaOH-TW dalam lapisan tetap di bawah keadaan pengendalian berbeza termasuk konsentrasi awal (50, 100 dan 200 mg / L), kadar aliran (10, 20 dan 30 mL / min) dan ketinggian lapisan tetap (20, 40 dan 60 mm). Didapati bahawa jumlah MB yang terjerap, q_{eq} (mg / g) meningkat dengan peningkatan konsentrasi awal dan kadar aliran dan berkurangan dengan bertambah ketinggian lapisan tetap. Model Thomas adalah model yang terbaik bagi meramal ciri-ciri perkembangan lengkungan bulus.

ADSORPTION OF METHYLENE BLUE ONTO MODIFIED FACTORY TEA WASTE: BATCH AND FIXED BED COLUMN

ABSTRACT

The aim of this work was to investigate the feasibility of chemically modified agricultural waste, namely factory tea waste (R-TW) for adsorption of methylene blue (MB) from aqueous solutions. The results revealed that modification of R-TW with sodium hydroxide (NaOH) and potassium hydroxide (KOH) which named NaOH-TW and KOH-TW respectively give the highest efficiencies for MB adsorption compared with other modification methods. R-TW, KOH-TW and NaOH-TW were characterized by Fourier transform infrared (FTIR) spectroscopy, scanning electron microscopy (SEM) and nitrogen adsorption/desorption isotherm analyses. The effects of MB initial concentration (50–500 mg/L), contact time, temperature (30, 40 and 50 ºC) and solution pH (3–12), on MB adsorption were investigated in batch process. The results show the MB adsorption uptakes increased with increasing initial concentration and contact time. The highest removal efficiency of MB was at pH 7–10 for R-TW, KOH-TW and NaOH-TW. Adsorption isotherm of MB on all adsorbents was best fitted by Langmuir isotherm model. The maximum monolayer for adsorption capacity MB followed the trend R-TW < KOH-TW < NaOH-TW. The pseudo-second-order kinetic model described well the experimental data of MB adsorption on all adsorbents. The adsorption process for all adsorbents represented physisorption mechanism since activation energy was lower than 40 kJ/mol. A series of experiments were conducted to measure the breakthrough curves for adsorption of MB on R-TW, KOH-TW and NaOH-TW in fixed bed column under different operating conditions including initial concentration (50, 100 and 200 mg/L), bed flow rate (10, 20 and 30 mL/min) and bed height (20, 40 and 60 mm). It was found that the amount of MB adsorbed, q_e (mg/g) increased with increasing initial concentration and flow rate and decreased with increasing height of column bed. A Thomas model was the best model to predict the breakthrough characteristics.

CHAPTER ONE

INTRODUCTION

1.0 Dye pollution in Malaysia

Nowadays environmental research has paid strenuous attention to dye compounds because of the extensive environmental contamination arising from dyeing operations including textiles, cosmetics, printing, paper, plastics, as well as in the food industry. Malaysia had a long history of producing textiles, where colored textiles grow continuously day by day according to the growth of population and exporting demands (Mahmoud, 2008). With exports valued of RM10.6 billion, the industry was the seventh largest contributor to total earnings from manufactured exports in 2006 (Tan, 2008). From the statistics obtained from Malaysia Industrial Development Authority (MIDA), the total number of textile factories in Malaysia is approximately 1500, with 40 % of the textile factories especially the wet processing plants being located in Batu Pahat, Johor (Tan, 2008). As consequences, these industries have contributed to considerable dye wastewater to the many water streams.

The discharge of dye wastewater in the environment is aesthetically undesirable and has serious environmental impact (Demirbas *et al.,* 2008); therefore the Interim National Water Quality Standards for Malaysia (2006) considered the maximum contaminant level for colour is 15 colour units. The colour removal from dyehouse effluent becomes day by day is more than ever. An important objective of wastewater treatment processes to overcome since over the past decades is considered to be most challenging in the environmental fraternity and the industries (Amin, 2009). This goal is pursued not only because legislation requirements become more stringent, but also the quality of water for recycle purpose was taken into account. In fact, if considering both the volume and the effluent composition, dye effluent is rated as the most polluting among all industrial effluents (Khelif *et al*., 2009).

Dyes are the first contaminants to be visually recognized. For some dyes, the dye concentration of less than 1 ppm in receiving water bodies is highly visible, so that even small quantities of dyes can colour large amount of water bodies (Gong *et al*., 2005). Although a great proportion of dyes are not directly or highly toxic for living organisms, high colouration added to the discharge into water courses can suppress photosynthetic processes and generate high chemical and biological oxygen demand (Aksu, 2005). Dyes exhibit considerable structural diversity and are classified by their chemical structure, application to the fiber type and/or solubility (Gupta and Suhas, 2009).

Basic dyes are cationic due to the positive charge delocalized throughout the chromophoric system and have affinity towards materials with negatively charged functional groups (Sachdeva and Kumar, 2009), such as wool, silk, nylon and acrylics, where bright dyeing is the prime consideration. Among basic dyes, methylene blue (MB) is the most common water-soluble dye, widely used including dyeing leather, printing calico, cotton and tannin, coloring paper, hair colorant, for medicinal purposes, etc. Although this dye is not highly toxic to human being, acute exposure to methylene blue can cause increased heart rate, vomiting, shock, Heinz body formation, cynosis, jaundice, quadriplegia and tissue necrosis (Vadivelan and Kumar, 2005).

As a consequence of this, many attempts have been taken seriously for many countries for dye removal from effluent by considering the significance of environmental, technical and commercial aspects. According to Hameed *et al*., 2008, the traditional methods for removing dyes in effluent can be divided into three main categories which are physical, chemical and biological treatment. They include coagulating/flocculating agent (Shi *et al*., 2007, Zhou *et al*., 2008), ion exchange (Bolto *et al*., 2002 and Karim *et al*., 2009), advanced oxidation process (Fenton-like oxidation) (Daud and Hameed, 2010), and biological treatment (Barragan *et al*., 2007). In comparison to other techniques, adsorption is superior in simplicity of design, initial cost, ease of operation and insensitivity to toxic substances (Sismanoglu *et al*., 2010).

1.1 Adsorption Process

Adsorption is the process by which a solid adsorbent can attract a component in water to its surface and form an attachment via a physical or chemical bond, thus removing the component from the fluid phase (Demirbas *et al*., 2008). Adsorption is one of the most effective physical processes for colour removal. This technique uses a large number of suitable adsorbents such as activated carbon (Demirbas *et al*., 2009).

1.1.1 Activated Carbon

In the last few years, activated carbon has been extensively used in dyes removal from textile effluent, which had relatively high adsorption capacity for wide variety of dyes (Deng *et al*., 2009). Activated carbons are known removal of dyes very effective adsorbents due to their high internal surface areas (typically in the range of 500-2500 m^2g^{-1}), well developed internal pore structure and the presence of a wide spectrum of surface functional groups (Chingomombe *et al*., 2005).

In spite of these excellent characteristics, these activated carbons have some weak points. Its use is still limited because of high operating costs (Weng *et al.,* 2009); the higher the quality, the greater the cost (Balci *et al*., 2011). The need for regeneration of activated carbon makes it not valuable since it will add to the cost (Belala *et al.*, 2011). 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 *et al*., 2009). To lower the cost, many researchers have focused on finding non-conventional alternative adsorbents.

1.1.2 Non-conventional adsorbents

Non-conventional adsorbents or so called low-cost adsorbents are generally referred to as non-hazardous wastes produced from industry, agriculture and biosorbents. In particular, the use of agricultural waste in adsorption system has drawn attention from a large number of researches because of the following reasons (Weng *et al*., 2009):

i) it is abundantly available ;
ii) most of agriculture waste are readily available to be used and do not require a complex pretreatment step or activation process before application ;
iii) regeneration of these adsorbents may not be necessary (unlike activated carbon, where regeneration is essential);

iv) less maintenance and supervision are required for the operation of the adsorption process.

Some natural materials not only have excellent adsorbability of dyes, but also have biocompatibility, biodegradability and non-toxicity (Balci *et al*., 2011). Nevertheless, the use of these cheap alternatives for wastewater treatment remains limited due to both insufficient documentation in real wastewater systems and the necessity of post-usage disposal.

1.1.3 Factory tea waste

As far as low-cost adsorbent materials are concerned, tea waste is a tea factory waste material obtained from tea plantation. Tea is largely cultivated in tropical countries, such as China, India, Indonesia, and Malaysia. In Malaysia, an estimated 10,000 tonnes of tea wastes are produced annually.

Normally, tea waste are not used for any purpose and its deposits are only left behind at their plantation since it can be biodegradable (Malkoc *et al*., 2006). In some application, it can be used as a natural compost material or burned on site after the harvest, creating a point source of air pollution. Utilization of this waste for the treatment of wastewater is a win-win strategy because it not only converts the waste into a useful material but it also prevents on-site burning of the waste and save disposal costs. Beside, the exhausted adsorbents can be incinerated (Uddin *et al*., 2009), disposed off by burning and the heat used for steam generation (Gupta *et al*., 2009).

Although it has been used as a potential adsorbent for the removal of metals (Malkoc *et al*., 2006) and methylene blue (Uddin *et al*., 2009) in previous years, however, its capability to improve the adsorb organic substances by physical and chemical means is not much exploited so far.

1.1.4 Modified /treated adsorbents

Some agricultural wastes have directly been used as adsorbent for dye adsorption from wastewater. However, recently the chemical modifications of these materials has enhanced their adsorption capacities it possesses for either positively or negatively charged molecules, but not both (Ong *et al*., 2007) and thus useful in treatment of wastewater. Furthermore, the modification can be carried out to achieve adequate structural durability, enhance their natural ion exchange capability and add value to these materials (Marshall 2001 and O’Connell *et al*., 2008).

Pretreatment methods using different kinds of modifying agents such as base solutions (sodium hydroxide) mineral and organic acid solutions (hydrochloric acid, phosphoric acid), organic compounds (ethylene-diamine, formaldehyde) for the purpose of removing soluble organic compounds, eliminating color of the aqueous solutions and increasing efficiency of metal and dye adsorption have been performed by many researches (Ong *et al*., 2007, Janos, 2009, Han, 2010, Wan Ngah and Hanafiah, 2008).

1.2 Problem Statement

The extensive use of dyes often poses water pollution problems not only high chemical and biological oxygen demands, and content in toxic compounds but also for color which is the first contaminant to be recognized by human eye. Therefore, the dye manufactures, users and government themselves are taking substantial measures to treat the dye containing wastewater (Gupta and Suhas, 2009). Amongst numerous techniques, adsorption process is the most commonly used for the decontamination of the dye-contaminating effluent. Most commercial systems currently use activated carbon as adsorbent because of its excellent adsorption ability (Crini, 2006), but it is expensive and difficult to regenerate (Sakkayawong *et al*., 2005). As such, there is a growing need to search for more economical and effective adsorbent mainly from cheaper and locally available waste materials.

In the past few decades, various agricultural wastes have been explored as low-cost adsorbents. Tea waste is an agricultural wastes which are relatively abundant and accumulates in the agro-industrial yards where it has no significance industrially. One significant problem faced by agricultural industries currently is managing of the by-product and waste produced. The disposal of the waste in large quantity is difficult and expensive to the industries. Utilization of such waste will help to create more income to the tea factories by converting the negative value tea waste to valuable products such as adsorbent. Beside, the use of tea waste as the adsorbent is good to decrease the cost of waste disposal.

Recently, tea waste has been extensively investigated as an adsorbent for removing contaminants from wastewater (Ahluwalia and Goyal, 2005, Malkoc *et al*., 2006, Uddin *et al*., 2009,). However, utilization of these ready-used adsorbents also contributes to several problems such as low adsorption capacity, high chemical oxygen demand (COD) and biological oxygen demand (BOD) as well as total organic carbon (TOC) due to release of soluble organic compounds which contained in the plant wastes (Wan Ngah and Hanafiah, 2008). To circumvent these problems, few researches on modification of adsorbent have been conducted (Batzias *et al*., 2007, Janos *et al*., 2009, Han *et al*., 2010). Findings of these researches proven that removal efficiencies can be improved significantly. However, very less work has been carried out towards this direction. Thus, in this study, the modification of surface factory tea waste as adsorbent to improve dye adsorption capacity is explored. Hence, this study aims to investigate the feasibility of using modified tea waste from alkali solution to remove methylene blue (MB) adsorption in batch and fixed-bed adsorption systems.

1.4 Research Objectives

1. To modify the surface of factory tea waste by chemical treatment and used it as adsorbent for MB removal.
2. To characterize the modified (NaOH-TW and KOH-TW) and unmodified (R-TW) adsorbents in terms of surface area, surface morphology and surface chemistry.
3. To study the adsorption isotherm, kinetics and thermodynamic of MB on modified (NaOH-TW and KOH-TW) and unmodified tea waste (R-TW).
4. To determine the breakthrough characteristics of modified and unmodified adsorbents under varying operating conditions such as inlet initial concentration, feed flow rate and adsorbent bed height.

1.5 Organization of the Thesis

This thesis consists of five chapters, where each chapter represents an important build for general construction of thesis.

Chapter one gives the introductory of this research project. It presents an overview on the dye pollution in Malaysia and dye removal method. The needs of non conventional low-cost adsorbents from agricultural wastes are also included. Problem statement, objectives and the organization of thesis are summarized in the last section of this chapter.

Chapter two presents a literature review which covered the general information of dye including the effect of dye to environmental and health followed by dye removal methods. Information on modification of preparation, adsorption operating condition and characterization are discussed in detail. The last section then consist of the adsorption isotherm, kinetics and thermodynamics for batch adsorption system as well as the breakthrough characteristics of fixed-bed adsorption system with model applied.

Chapter three presents a detailed methodology of this research work in order to achieve the targeted objectives. The experimental procedure consists of adsorbent preparation, characterization, batch and fixed bed adsorption. It is followed with schematic flow diagram showing the overall methodology adopted to carry out this research.

Chapter four displays the results and discussion obtained from the experimental studies. This chapter is divided into five sections. The first section discussed on the effect of modification onto tea waste by several modifying agent. Section two discusses on the characterization of selected modified waste tea. Then, discussion on the batch adsorption studies of methylene blue on modified and unmodified waste tea followed by fixed-bed adsorption studies. Finally, the design of batch adsorption is also included in this section.

Chapter five concludes the findings obtained from this research work. The future works are also recommended in this chapter.

CHAPTER TWO

LITERATURE REVIEW

2.0 Introduction

This chapter provides the general information regarding; i) dyes and their application; (ii) dye pollutants and the method of removal; iii) overview of various low-cost adsorbents and modification of adsorbents; iv) adsorption isotherm, kinetic and as well as thermodynamic of the batch adsorption system; v) fixed-bed column adsorption system.

2.1 Dyes and their applications

Dye molecule comprise of two key components: the chromophores, responsible for producing the colour, and the auxochromes, which can not only supplement the chromophore but also render the molecule soluble in water and give enhanced affinity (to attach) toward the fibers (Gupta and Suhas, 2009). Dyes are formed from ionic complex aromatic organic compounds with structures including aryl rings which delocalized electron systems and other possibilities for dye formation comes from coal tar based hydrocarbons such as benzene, naphthalene, anthrasene, toluene, xylene, etc. (Gong, 2005).

Dyes exhibit considerable structural diversity and are classified in several ways, according to chemical constitution, application and end use (Demirbas, 2009). Dyes may also be classified on the basis of their solubility: soluble dyes which include acid, mordant, metal complex, direct, basic and reactive dyes; and insoluble dyes including azoic, sulfur, vat and disperse dyes. Beside this, either a major azo linkage or the anthraquinone unit also characterizes dyes chemically. The classification and application of dyes are summarized in Table 2.1.

Overall at present, there are more than 100,000 commercial dyes with rough estimated production of $7\text{x}10^5$ –$1\text{x}10^6$ tons per year (Hunger, 2003; Husain, 2006; Christle, 2007). The big consumers of dyes are textile, dyeing, paper and pulp, tannery and paint industries, and hence the effluents of these industries as well as those from plants manufacturing dyes tend to contain dyes in sufficient quantities.

2.1.1 Dye Pollutant

Dyes are considered an objectionable type of pollutant because they are toxic (Bae and Freeman, 2007; Christle, 2007) generally due to oral ingestion and inhalation, skin and eye irritation, and skin sensitization leading to problems like skin irritation and skin sensitization and also due to carcinogenicity (Hatch and Mailbaach, 1999; Rai *et al*., 2005; Christle, 2007). They impart colour to water which is visible to human eye and therefore, highly objectionable on aesthetic grounds. Not only this, they also interfere with the transmission of light and upset the biological metabolism processes which cause the destruction of aquatic communities present in ecosystem (Walsh *et al*.,1980 and Kuo, 1992). Furthermore, the dyes have a tendency to sequester metal and may cause microtoxicity to fish and other organism (Walsh *et al*., 1980).

Table 2.1 Classification and application of dyes (Hunger, 2003; Cristle, 2007; Gupta and Suhas, 2009).

Solubility	Type of Dyes	Application	Principle chemical class
Water Soluble	Acid dyes	Used for nylon, wool, silk, modified acrylics, and also to some extent for paper, leather, ink-jet printing, food, and cosmetics	Azo (including premetallized), anthraquinone, triphenylmethane, azine, xanthene,nitro and nitroso.
	Cationic (Basic) dyes	Used for paper, polyacrylonitrile, modified nylons, modified polyesters, cation dyeable polyethylene terephthalate and to some extent in medicine too. Originally they were used for silk, wool, and tannin-mordanted cotton.	Diazahemicyanine, triarylmethane, cyanine, hemicyanine, thiazine, oxazine and acridine.
	Direct dyes	Used in the dyeing of cotton and rayon, paper, leather, and to some extent to nylon.	Polyazo compounds, along with some stilbenes, phthalocyanines and oxazines.
	Reactive dyes	Generally used for cotton and other cellulosics, but are also used to a small extent on wool and nylon.	Chromophoric groups such as azo, anthraquinone,thiarylmethane, phthalocyanine, formazon, oxazine, etc.
Water insoluble	Disperse dyes	Used mainly on polyster and to some extent on nylon, cellulose, cellulose acetate, and acrylic fibers. Also used for hydrophobic fibers from aqueous dispersion.	Azo, anthraquinone, styryl, nitro, and benzodifuranone groups.
	Solvent dyes	Used for plastics, gasoline, lubricants, oils and waxes.	Predominantly azo and anthraquinone, but phthalocyanine and triarylmethane are also used.
	Sulfur dyes	Used for cotton and rayon and have limited use with polyamide fibers, silk, leather, paper and wood.	Relatively small group of dyes.
	Vat dyes	Used for cotton mainly to cellulose fibers as soluble leuco salts and for rayon and wool.	Anthraquinone (including polycyclic quinines) and indigoids.

In Malaysia, wastewaters containing dyes have been classified as scheduled wastes under Environmental Quality (Scheduled Wastes) Regulation 1989 (EQA, 2002). Therefore, the high volume wastewaters being produced by this polluting industry needs to be properly treated before discharged into the watercourses, as it contains large amount of various dyes which will pose serious environmental problems because of their colour as well as high chemical oxygen demand and toxicity (Kumar *et al*., 2008).

2.1.2 Cationic dyes (basic dyes) pollutant

Cationic dyes are basic dyes with cationic properties originating from positively charged nitrogen or sulfur atoms (El Qada *et al*., 2006).The tinctorial value of cationic dyes is very high; less than 1 mg/L of the dye produces an obvious coloration.

Cationic dyes have been classified as toxic colorants and considered are one of the most problematic classes of dye (El Qada *et al*., 2008), where it can cause allergic dermatitis, skin irritation, cancer and mutations (Karagozoglu *et al*., 2007). Moreover, Hoa *et al*., (2000) reported that cationic dyes were tested as more toxic than anionic dyes. This is because chromium-based dyes can release chromium ions, which are carcinogenic in nature (Anliker *et al.,*1981). Methylene Blue (MB) or tetramethylthionine is one of the most important basic dyes with the structure of heterocyclic aromatic chemical compound. Figure 2.1 shows the example of cationic structure.

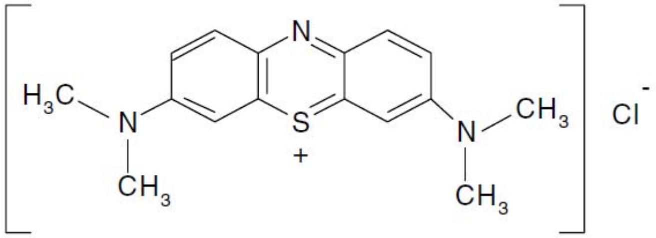

Figure 2.1 Methylene Blue (Cationic dye) structure.

Although MB is not strongly hazardous, it can have various harmful effects (Wang *et al.,* 2008), where acute exposure to MB will cause increased heart rate, shock, Heinz body formation, cyanosis, jaundice, quadriplegia and tissue necrosis in human (Vadivelan and Kumar, 2005). On inhalation, it can give rise to short periods of rapid or difficult breathing while ingestion through mouth produces a burning sensation and may cause nausea, vomiting, profuse sweating, mental confusion and methemoglobinemia (Sethilkumaar *et al.*, 2005 and Tan *et al.,* 2008). Hence, the removal of MB from dye wastewater before discharging into waterways system is extremely important and deserves immediate attention.

2.1.3 Methods of dye removal

Recently, intensive research in new and advanced treatment technologies has been proposed. This is paralleled with increased demand currently being placed on water supply and waste disposal, and thus have necessitated broader concepts in application of wastewater treatment (Qada *et al.,* 2006). Crini (2006) has summarized the various technologies for dyes removal, together with their respective advantages and disadvantages, as listed in Table 2.2.

Table 2.2: Principal existing process for dye removal (Crini, 2006).

	Technology	**Advantages**	**Disadvantages**
Conventional treatment processes	Coagulation and flocculation	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 requirements.
	Adsorption on activated carbons	The most effective adsorbent, great capacity, produce a high quality treated effluent.	High production and regeneration costs.
Established recovery processes	Membrane separation	Removes all dye types, produce a high quality treated effluent	High pressure, expensive, incapable of treating large volume.
	Ion-exchange	No loss of sorbent on regeneration, effective.	Economic constraints
	Oxidation	Rapid and efficient process.	High energy cost, chemicals required.
Emerging removal proceses	Advanced oxidation process	No sludge production, little or no consumption of chemicals, efficient for recalcitrant dyes	Economically unfeasible, formation of by-products, technical constraints.
	Selective bioadsorbents	Economically attractive, regeneration is not necessary, high selectivity	Required 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).

In last few years, a vast number of publications have been dedicated to the removal of basic dyes from wastewater. All these methods have different color removal capacities, capital costs and operating rates (Amin, 2009). Table 2.3 shows recent studies on the removal of basic dyes using various methods.

Table 2.3 Removal of basic dyes using various methods.

Basic Dyes	Methods	Reference
Acid dye-Orange G	Absorption	Luo *et al*., 2011
Methylene blue	Adsorption	Han *et al.,* 2010
Malachite green	Fenton process	Hameed and Lee, 2009
Basic Red 46 and Basic yellow 28	Photocatalytic degradation	Gozmen *et al.,* 2009
Methyl violet 2B	Cation exchange membranes	Wu *et al.,* 2008a
Methyl violet	Biosorption	Ofomaja and Ho, 2008
Methyl Orange	Reverse Osmosis	Al-Bastaki, 2004

Although many methods have been developed, adsorption has been found to be superior to other methods for water re-use in terms of initial cost, flexibility and simplicity of design, ease of operation and insensitivity to toxic pollutants (Rafatullah *et al.,* 2010) and the reuse potentials of adsorbents after long- term application (Acharya *et al.*, 2009). Besides, adsorption does not result in the formation of harmful substances.

2.2 Adsorption process

Adsorption is the separation process by which certain components of a fluid phase are attracted to the surface of a solid adsorbent and form attachments via physical or chemical bonds, thus removing the component from the fluid phase (McCabe, 1985; McKay *et al.,* 1997). In other words, adsorption term also refers to the accumulation of a substance at the interface between two phases such as solid and liquid or solid and gas. The substance that accumulates at the interface is called ‘adsorbate’ and the solid on which adsorption occurs is ‘adsorbent’ (Weber, 1985 and Bhatnagar *et al.,* 2010).

At the surface of the solids, there are unbalanced forces of attraction which are responsible for adsorption. In cases where the forces which are responsible for adsorption is due to weak van der Waals forces, it is called physical adsorption. On the other hand, there may be a chemical bonding between adsorbent and adsorbate molecule and such type of adsorption is referred as chemisorption (Gupta and Suhas, 2009). Table 2.4 shows the general features which distinguish physical adsorption and chemisorption (Ruthven, 1984).

Table 2.4 Typical characteristics of chemisorption and physical adsorption processes (Ruthven, 1984)

Parameter	**Physical Adsorption**	**Chemisorption**
Adsorption enthalpy	Low (< 2 or 3 times latent heat of evaporation)	High (> 2 or 3 times latent heat of evaporation)
Specificity	Non specific	Highly specific
Adsorption site	Monolayer or multilayer	Monolayer only
Nature of adsorption	No dissociation of adsorbed species	May involve dissociation
Temperature range	Only significant at relatively low temperatures	Possible over a wide range of temperature
Kinetics of adsorption	Rapid, non activated, reversible	Activated, may be slow and reversible
Electron transfer	No electron transfer although polarization of sorbate may occur	Electron transfer leading to bond formation between sorbate and solid surface

Meanwhile, the performance of the adsorption process is determined by the high adsorptive capacity and selectivity. In general, the higher the concentration of solute, the higher is the equilibrium adsorbate concentration on the adsorbent (Seader and Henley, 1998). This statement of fact can be achieved by using adsorbents having on their surfaces adsorbents with active centers where the binding forces between the individual atoms of the solid structure are not completely saturated. At these active centers an adsorption of foreign molecules will takes place.

Adsorption methods employing solid sorbents are widely used to remove certain classes of chemical pollutants from wastewater. However, amongst all the sorbent materials proposed, activated carbon has undoubtedly been the most popular and widely used adsorbent in wastewater treatment throughout the world. Activated carbon is produced by a process consisting of raw material dehydration and carbonization followed by activation. Generally, it has a very porous structure with a large surface area ranging from 600 to 2000 m^2/g (Bhatnagar and Silanpaa, 2010). The high performance of activated carbon is not only on its surface area, but they also have excellent internal pore structure, surface characteristic and the presence of functional group on pore surface. Moreover, it has been found to be a versatile adsorbent, which can remove diverse type of pollutants. In spite of abundant uses of activated carbon, their applications are sometime restricted due to its high cost. It is expensive because of the chemicals required for its regeneration after pollutant removal; the higher the quality, the greater the cost (Balci *et al.,* 2011).Due to the problems mentioned above, research interest into the production of alternative adsorbents to replace the costly activated carbon has intensified in recent years.

Attention has been focused on various natural solid supports, which are able to remove pollutants from contaminated water at low cost. According to Bailey *et. al*., (1999), a sorbent can be considered low cost if it requires little processing, is abundant in nature or is a by-product or waste material from another industry.

2.2.1 Future perspectives of Low-Cost Adsorbents (LCAs)

The low-cost adsorbents (LCAs) as reported in literature are usually called substitutes for activated carbons because of their similar wide use; however, in a broad and clearer way they are basically substitutes for all expensive adsorbents. Gupta and Suhas (2009) suggested that LCAs was classified in two ways and presented in Table 2.5.

Table 2.5 Low cost adsorbents (LCAs) classification (Gupta and and Suhas, 2009).

1. Basis of their availability	a) Natural materials b) Industrial/Agricultural/Domestic Waste c) Synthesized product
2. Depending on their nature	a) Inorganic b) Organic

Agricultural waste materials are one of the rich sources of adsorbent. It is economic and eco-friendly due to their unique chemical composition, availability in abundance, renewable nature and low cost are viable option for wastewater. Agricultural materials particularly those containing cellulose shows potential sorption capacity of various pollutants. The basic components of the agricultural waste materials include hemicellulose, lignin, lipids, proteins, simple sugars, water, hydrocarbons and starch, containing variety of functional group (Bhatnagar and Silanpaa, 2010).

In the last several decades, various agricultural wastes have been explored as low cost adsorbent. Table 2.6 shows a list of examples of activated carbon from agricultural wastes used in wastewater treatment.

Table 2.6 Previous studies on the adsorption of various dyes with low cost adsorbents from agricultural solid wastes.

Adsorbents	**Dyes**	**q_m (mg/g)**	**Refferences**
Peanut husk	Methylene Blue	72.13	Song *et al,,* 2011
Date stone	Methylene Blue	43.47	Belala *et al.,* 2011
Palm-trees waste	Methylene Blue	39.47	Belala *et al.,* 2011
Rhizopus arrhizus	Methylene Blue	3770.3	Aksu *et al.,* 2010
Spent coffee ground	Methylene Blue	18.73	Franca *et al.,*2009
Papaya seed	Methylene Blue	555.57	Hameed *et al.,* 2009
Cotton plant waste	Remazol black	35.7-50.9	Tunc *et al.,* 2009
Castor seed shell	Methylene blue	158.73	Oladoja *et al.,* 2008
Wood sawdust	Methyl violet	16.11	Ofomaja, 2008
Wood sawdust	Methylene blue	28.89	Ofomaja, 2008
Hazelnut shell	Acid blue 25	60.2	Ferrero, 2007
Saw dust-walnut	Acid blue 25	36.98	Ferrero, 2007
Lemon peel	Malachite green	51.73	Kumar, 2007
Soy meal hull	Acid blue 92	114.94	Arami *et al.,* 2006
Tree fren	Basic Red 13	408	Ho *et al.,* 2005
Pine sawdust	Acid blue 256	280.3	Ozacar and Sengil, 2005

From the literature survey results, LCAs shows promising results for removal of dye. Thus, the used of LCAs for replacing the activated carbon are possible. In Malaysia, agricultural by-products are the most abundant biomass resources, exceeding 70 million tones annually. The utilization of agricultural waste materials is increasingly becoming a vital concern because these wastes represents unused resources and in many cases present serious disposal problems.

Therefore, to make it beneficial for society, they need to be utilized effectively as they can be considered as valuable products and raw materials to support the industry. Their usage as consequences will contribute to minimize the cost of disposal, hence helping in environmental protection.

2.2.2 Tea waste

Tea is the agricultural product of the leaves, leaf buds, and internodes of various cultivars and sub-varieties of the Camellia sinensis plant, processed and cured using various methods. "Tea" also refers to the aromatic beverage prepared from the cured leaves by combination with hot or boiling water, and is the common name for the Camellia sinensis plant itself. After water, tea is the most widely consumed beverage in the world.

In Malaysia, tea plants are commonly grown in the highland area located at Cameron Highland, Pahang. In the plantation, the harvested tea is only selected from the top leaves of the fresh grown shoots. The harvesting of the tea leaves are done every 15 days, to allow for growth of new leaves. The yield consists of mixed tea harvest and some overgrown woody shoots. This woody overgrown shoots were not treated by tea factory and thus constitute tea waste. Moreover, during the tea planting procedure, tea producers usually trimmed the tea trees to a height of 1.5 to 2 meter after every three years to allow for fresh growth of shoots. These also form part of undesired tea during production and a waste in the plantation. Tea waste accumulates in the agro-industrial yards where it has no significance industrially and are not marketable.

Insoluble cell walls of tea leaves are largely made up of cellulose and hemicellulose, lignin, condensed tannins and structural proteins (Wasewar *et al.,* 2009). The responsible groups in lignin, tannin or other phenolic compounds are mainly carboxylate, aromatic carboxilate, phenolic hydroxyl and oxyl groups (Demirbas, 2008). According to Pagnanelli *et al.,* (2003), these groups have the ability to some extent to bind pollutant component by donation of an electron pair from these groups to form complexes ion in solution.

Tea waste which contains of cellulose irreversibly adsorbs cationic dyes (MB) through coulombic attraction since negative surface charge is acquired by cellulose on contact with water (Bousher *et al.,* 1997). In aqueous solution, the MB molecule will first dissolved, dissociated and then converted to cationic dye ions. Also, in the presence of H^+, the hydroxyl groups of waste tea (-OH) become deprotonated. The adsorption process then proceeds due to the electrostatic attraction between these two oppositely charge ions.

In recent years, tea waste is gaining ground due to its potential to overcome heavy metal and dye pollutants. Very few studies in the literature are available on tea waste as an adsorbent. Table 2.7 shows the listed research works on adsorbent from tea waste for removing various types of pollutants.

Table 2.7 Listed research works of adsorbent from tea waste.

Adsorbent	Adsorbate	Refference
Tea waste	Pb(II)	Panneerselvam, *et al*., 2011
Spent tea	Methylene blue	Hameed, 2009
Tea waste	Methylene Blue	Uddin, *et al.,* 2009
Tea factory waste	Zinc	Wasewar *et al.,* 2009
Waste tea	Cr (IV) and Cu(II)	Razmovski and Šćiban, 2008
Tea waste	Cu and Pb	Amarasinghe and William, 2007
Tea Factory waste	Cromium	Malkoc and Nuhoglu, 2007.
	Nickel	Malkoc and Nuhoglu, 2006
Tea waste	Cu (II) and Cd (II)	Cay *et al.,* 2004

Throughout the study by previous research works, it indicated that tea waste can be used as an effective and environmentally friendly adsorbent for the treatment of wastewater. Furthermore, utilization of such waste will create more income to tea factories. However, one disadvantage about the use of agricultural waste is its low adsorption capacity compared to commercially available activated carbon. Thus, modifications are needed in order to enhance the performance on the adsorption capacity.

2.3 Modification of adsorbents

The application of raw plant wastes as adsorbents can also bring several problems such as low adsorption capacity, high chemical oxygen demand (COD) and biological chemical demand (BOD) as well as total organic compounds (TOC) due to release of soluble organic compounds contained in the plant materials (Gaballah *et al.,*1997). The increase of COD, BOD and TOC can cause depletion of oxygen content in water and can threaten the aquatic life. Therefore, plant wastes need to be modified or treated before being applied for the decontamination of wastewater. In modification, there are different pretreatment methods of modifying agents such as base solutions mineral and organic acid solutions, organic compounds, oxidizing agent, dye etc. The most common chemicals used in the treatment of plant wastes are acids and bases (Wan Ngah and Hanafiah, 2008).

There are few researches done about interaction between functional groups in surface chemistry of modified plant wastes and variety of dyes. From the results, chemically modified adsorbents vary greatly in their ability to adsorb dyes from solution. Chemical modification in general improved the adsorption capacity of adsorbents probably due to higher number of active binding sites after modification, better ion-exchange properties and formation of new functional groups that favours dyes uptake.

Generally, these materials possess high adsorption capacities for either positively or negatively charged dye molecules, but not both. Hence, there is need to have adsorbents capable of removing different types of dyes either singly and simultenously (Ong *et al.,* 2007). From literature, the adsorption properties of the wood-based adsorbents can be modified in a relatively simple way by the pretreatment with the solution of inorganic salts, acids or bases. Although the chemical pre-treatment does not alter substantially the structure of wood, it modifies a surface chemistry of the adsorbent (acid- base properties), and consequently its adsorption ability towards ionic species (Janos *et al.,* 2009). The various types of chemicals used for modifying adsorbents and their maximum adsorption capacities are shown in Table 2.8.