DECOLORIZATION AND COD REDUCTION OF METHYLENE BLUE DYE WASTEWATER THROUGH ADSORPTION USING RAW AND MODIFIED BAGASSE

by

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LIST OF ABBREVIATIONS

A	Fine
AA	Superfine
ANOVA	Analysis of variance
AOX	Absorbable organic halide
B	Blau = Blue
BBD	Box behnken design
BET	Brunauer, Emmet and Teller
BOD	Biological oxygen demand
CA	Citric acid
CCD	Central composite design
COD	Chemical oxygen demand
C.I.	Color index
DR	Dubinin-Radushkevich
FT-IR	Fourier transform infra-red
G	Gelb = Yellow
GDP	Gross domestic product
HNO_3	Nitric acid
KBr	Potassium bromide
MB	Methylene blue
NaOCl	Sodium hypochlorite
NaOH	Sodium hydroxide
OA	Oxalic acid

PVA	Polyvinyl alcohol
R	Rot = Red
RB	Raw bagasse
RSM	Response surface methodology
SEM	Scanning electron microscopy
TA	Tartaric acid
TOC	Total organic carbon

LIST OF SYMBOLS

Symbol	Description	Unit
A_T	Temkin isotherm constant	L/g
B	Mean free energy E	-
b_T	Temkin isotherm constant related to heat of adsorption	J/mol
C	Intraparticle diffusion constant that related to the thickness of boundary layer	mg/g
C_{ad}	Concentration of dye adsorbed	mg/L
C_e	Equilibrium concentration	mg/L
C_o	Initial solute concentration	mg/L
C_t	Solute concentration at respective time, t	mg/L
F	Linear velocity	cm/min
k_1	Rate constant of pseudo-first order model	1/h
k_2	Pseudo-second order rate constant	g/mg.h
k_{AB}	Adam-Bohart rate constant	L/mg.min
k_{ext}	Constant rate of Spahn and Schlunder model	1/min
k_{int}	Intraparticle diffusion rate constant	mg/g.h$^{1/2}$
k_{TH}	Thomas rate constant	mL/min.mg
k_{YN}	Rate velocity constant	1/min
K_L	Langmuir constant related to the affinity of the	L/mg

	binding sites	
K_F	Freundlich isotherm constant	$(m/g)(L/mg)^{1/n}$
M_1	MB stock solution concentration	mg/L
M_2	Final MB concentration	mg/L
n	Freundlich isotherm constant	-
N_o	Saturation concentration	mg/L
q_e	Amount of equilibrium uptake	mg/g
q_{eq}	Maximum capacity of column	mg/g
q_t	Amount of solute adsorbed at any time, t	mg/g
Q	Flow rate	mL/min
Q_{DR}	Dubinin-Radushkevich constant	-
Q_o	Constant rate of Spahn and Schlunder model maximum amount of adsorbed dye per unit mass of adsorbent to form a complete molecular layer on the surface	mg/g
r^2	Determination coefficient	-
R	Universal gas constant = 8.314	J/mol.K
R_L	Separation factor/ Equilibrium parameter	-
S_a	Initial COD concentration	mg/L
S_b	Equilibrium COD concentration	mg/L
t_{total}	Total flow time	min

T	Absolute solution temperature	K
V	Volume of the solution	L
V_1	Required volume of MB stock solution	mL
V_2	Total volume of required final MB concentration	mL
W	Weight of adsorbent	g
x_k	Coded value of k^{th} independent variables	-
x_0	natural value of the *k*th independent variable at the center point	-
y_1	Percentage of color removal	%
y_2	Percentage of COD reduction	%
Z	Bed depth of column	cm
ε	Constant for Dubinin-Radushkevich isotherm	-
τ	Time in required for 50 % adsorbate breakthrough	min
β_0	Offset term	-
β_i	Linear effect	-
β_{ii}	Squared effect	-
β_{ij}	Interaction effect	-
ξ_k	natural variable of the *k*th independent variable	-
δx	value of step change	-

PENYAHWARNAAN DAN PENURUNAN COD BAGI AIR SISA PEWARNA METILEN BIRU MELALUI PENJERAPAN DENGAN MENGGUNAKAN BAGAS MENTAH DAN BAGAS TERUBAHSUAI

ABSTRAK

Dalam kajian ini, penjerapan zat warna biru metilen ke atas bahan lignoselulosa —bagas telah dikaji. Penjerap telah diubahsuai dengan menggunakan pelbagai asid karboksilik seperti asid sitrik (CA), asid osalik (OA), dan asid tartaric (TA). Untuk menyingkirkan sebatian organic yang menyumbang kepada keperluan oksigen kimia (COD), pencucian penjerap dengan penggunaan air suling yang dididih telah dilaksanakan sebagai ganti bagi pencucian biasa dengan menggunakan air suling pada suhu bilik. Beberapa parameter yang memberi kesan terhadap penyahwarnaan dan pengurangan keperluan oksigen kimia bagi zat warna biru metilen seperti pH, dos bahan penjerap, kelajuan pengacauan, tempoh pengacauan, dan suhu telah dikaji dan dioptimumkan dengan menggunakan metodologi permukaan sambutan (RSM) - rekabentuk ujikaji gabungan pusat (CCD). Keputusan menunjukkan bagas yang telah diubahsuai dengan TA adalah lebih berkesan berbanding dengan bagas asli, CA pengubahsuaian bagas dan OA pengubahsuaian bagas dalam penyahwarnaan dan pengurangan keperluan oksigen kimia bagi zat warna biru metilen. Maksimum penyahwarnaan (99.05 %) dan pengurangan COD (98.45 %) untuk TA pengubahsuaian bagas dicapai pada dos bahan penjerap 0.78 g, pH 9.4, kelajuan penjerapan 120 rpm, tempoh pengacauan 34 min, suhu 49 ^{o}C. Model kinetic tertib pseudo-pertama dan pseudo-kedua, model pembauran luar, dan model pembauran antara partikel telah digunakan untuk menganalisis mekanisma proses penjerapan. TA pengubahsuaian bagas menunjukkan nilai korelasi yang baik untuk model kinetik tertib pseudo-kedua. Data isoterm penjerapan telah dikorelasikan dengan model-model isoterm seperti Langmuir, Freundlich, Temkin, Dibinin-Radushkevich (DR). Proses penjerapan didapati mengikuti model Langmuir dan Freundlich. Berdasarkan kajian termodinamik, perubahan entalpi (ΔH^o) yang bernilai 13.178 kJ/mol menunjukkan proses penjerapan menggunakan TA pengubahsuaian bagas adalah bersifat endotermik. Nilai tenaga bebas Gibbs ΔG^o antara -13.714 kJ/mol ke -16.799 kJ/mol menunjukkan proses penjerapan berlaku secara spontan pada suhu tinggi. Dalam eksperimen turus lapisan, data penjerapan disesuaikan pada model Thomas, Adams-Bohart, dan Yoon-Nelson. Beberapa parameter yang memberi kesan terhadap keluk terobos (breakthrough curve) seperti kadar aliran suapan, kepekatan zat warna, dan tinggi lapisan karbon teraktif telah dikaji dan dimaksimakan dengan menggunakan RSM-CCD. TA pengubahsuaian bagas yang telah digunakan boleh diregenerasikan dengan menggunakan 0.1 M NaOH. Keberkesanan sistem jerapan menggunakan TA pengubahsuaian bagas telah dinilai pada sisa tekstil nyata industri dari Penfabric Mill 3, Pulau Pinang. 84.65 % penyahwarnaan, dan 68.13 % pengurangan COD telah diperolehi dengan menggunakan 4.6 g bahan penjerap, pada pH 9.5, 116 rpm kelajuan penjerapan, 256 minit tempoh pengacauan, dan 54 ^oC.

DECOLORIZATION AND COD REDUCTION OF METHYLENE BLUE DYE WASTEWATER THROUGH ADSORPTION USING RAW AND MODIFIED BAGASSE

ABSTRACT

In the present study, batch and column adsorption systems were applied to study the adsorption of methylene blue (MB) from the dye aqueous solution onto a lignocellulosic material —bagasse. The bagasse was modified with various carboxylic acids, namely citric acid (CA), oxalic acid (OA), and tartaric acid (TA). In order to improve chemical oxygen demand (COD) reduction, pretreatment of the bagasse with thorough washing using boiling distilled water was performed instead of conventional washing with distilled water at room temperature only. The effects of pH, adsorbent dosage, shaking speed, contact time, and temperature on decolorization and COD reduction were studied and optimized using response surface methodology (RSM) —central composite design (CCD). The results show that the TA modified bagasse was more effective than raw bagasse (RB), CA modified bagasse, and OA modified bagasse in decolorization and COD reduction of MB dye from the aqueous solution. Maximum decolorization (99.05 %) and COD reduction (98.45 %) for TA modified bagasse were achieved at 0.78 g adsorbent dosage, pH 9.4, shaking speed of 120 rpm, 34 min contact time, and 49 ^{o}C. The adsorption kinetics were analyzed using four kinetic equations, namely, the pseudo-first order, pseudo-second order, the external diffusion model, and the intraparticle diffusion model to examine the adsorption mechanisms and potential rate controlling steps. TA modified bagasse showed good correlations with pseudo-second order kinetic model. Adsorption isotherm data were correlated with Langmuir, Freundlich, Temkin, Dubinin-Radushkevich (DR) isotherm models. The adsorption process followed the Langmuir isotherm as well as Freundlich isotherm. The enthalpy change (ΔH^{o}) of 13.178 kJ/mol showed that adsorption using TA modified bagasse was endothermic in nature. The Gibbs free energy change (ΔG^{o}) of -13.714 kJ/mol to -16.799 kJ/mol showed the feasibility of the process and the spontaneous nature of adsorption with a high preference of MB onto TA modified bagasse. Thomas model, Adams-Bohart model, and Yoon Nelson model were used to study the breakthrough curves for fixed-bed column adsorption. Different parameters, such as feed flow rate, initial dye concentration, and column bed height, affecting the breakthrough curves were studied and optimized using RSM-CCD. Spent TA modified bagasse can be effectively regenerated using 0.1 M NaOH. The efficacy of the adsorption system using TA modified bagasse was evaluated on a real industrial textile wastewater from Penfabric Mill 3, Penang. 84.65 % of color removal and 68.13 % of COD reduction were obtained using 4.6 g adsorbent dosage, at pH 9.5, 116 rpm of shaking speed, 256 min of contact time, and 54 ^{o}C.

CHAPTER ONE

INTRODUCTION

1.1 General

Many industries such as textile, leather, printing, food, pulp and paper, consume large volume of water and chemicals during manufacturing process. As a result, a considerable amount of polluted wastewater was generated (Robinson et al., 2001; Thompson et al., 2001; Pokhrel and Viraraghavan, 2004).

The most polluted wastewater generated among all industrial sectors in terms of both volume and composition of the effluents are wastewater generated from textile industries (Ali and Sreekrishnan, 2001; Anjaneyulu et al., 2005). The major chemical pollutants present in textile wastewater are dyes, carcinogenic amines, toxic heavy metals, pentachlorophenol, chlorine bleaching, halogen carriers, free formaldehyde, biocides, fire retardants, and softeners (Correia et al., 1994). According to Chakrabarti et al. (1988), nearly 40,000 dyes and pigments are listed, which consist of more than 7,000 various chemical formulae.

Discharge of dyes into water resources not only affects their aesthetic nature but destroys aquatic life due to strong color, high biochemical oxygen demand (BOD), chemical oxygen demand (COD), total organic carbon (TOC), and suspended solids (mainly fibers) (Crini and Badot, 2008; Wang et al., 2008). They may also cause formation of toxic carcinogenic metabolites (high concentration of nutrients, presence of chlorinated phenolic compounds, sulfur, and lignin derivatives, etc.). The highest rates of toxicity were found among basic and diazo direct dyes (Robinson et al., 2001).

During the past few decades, a wide range of wastewater treatment techniques have been used. Among them are coagulation and flocculation (Tan et al., 2000; Ho et al., 2010), liquid-liquid extraction (Muthuraman et al., 2009), oxidation (Aleboyeh et al., 2009), advance oxidation (Lim et al., 2009) and others. Most of these other processes suffer from some drawback such as high capital cost, high operational cost, and ineffective to treat wide range of wastewater. Therefore, inexpensive alternative treatment processes are being investigated for possible dye wastewater treatment.

1.2 Dyes and Pigments

Mankind has used dyes for thousands of years (Christie, 2001). About 180,000 years ago, Neanderthal man was believed to be the earliest mankind to use colorant. An organic colorant was used nearly 4,000 years ago, the blue dye indigo was found in the wrappings of mummies in Egyptian tombs (Gordon and Gregory, 1983). Till the late of nineteenth century, all the colorant used were from natural resources such as plants, insects, and mollusks and were prepared on small scale (Venkataraman, 1965; Hunger, 2003). In 1856 William Henry Perkin discovered a synthetic purple dye named Mauveine. The dye was then prepared synthetically on large scale (Christie, 2001).

Synthetic dyes are solely organic compounds. They are use to color the clothes, paints, plastic, articles, and in a wide range of multicolored printed materials. Color is introduced into these materials using substances known as dyes and pigments (Christie, 2001).

Dyes are soluble colored substances which can be applied mainly to textile materials from solution in water, whereas, pigments are insoluble compounds integrated by a dispersion process into products such as paints, printing inks, and plastics (Christie, 2001).

Dye molecules comprise of two main components: the chromophores and the auxochromes. Chromophores are a group of atoms principally responsible for the color of dye, whereas, auxochromes or ‘salt-forming’ groups of atoms are to provide an essential ‘enhancement’ of the color (Christie, 2001). The most important chromophores are the azo (-N = N-), carbonyl (C = O), methine (-CH=), and nitro (NO_2) groups. Common auxochrome groups (hydroxyl (OH) and amino (NR_2) groups) normally increase the intensity of the color and shift the absorption to longer wavelengths of light (Raghavacharya, 1997; Christie, 2001).

Pigments can be classified into two categories, namely, homogenous pigments and mixtures. Homogenous pigments contain similar type of pigments particles, e.g. colorful metal oxides, metallic powders, and etc. Mixtures are obtained either by chemical coating the stain of suitable carrier such as active, highly dispersed silica, precipitated calcium carbonate or by mechanical mixing of intensely staining pigment with a filler (Bogacki et al., 2004).

Dyestuffs may be classified according to either their chemical structure or the method of application (Venkataraman, 1965). Categorization of dyes into native and synthetic dyes is inadequate, since nowadays synthesis of many natural substances is possible (Wesenberg et al., 2003).

Color Index (C.I.), is the most important reference work dealing with the classification of dyes according to their chemical structure (Table A1 in Appendix A) (Christie, 2001). C.I. is also useful in predicting the possible biodegradability of dyes (Wesenberg et al., 2003). Each colorant is given a C.I. generic name determined by its application characteristics, and a C.I. constitution number is assigned based on its chemical structure (Christie, 2001). A listing of dyes based on their most predominant chemical structures is given in Table A2 (Appendix A). The main classes of the chemical structures are azo (-N=N-), carbonyl (C=O) (including anthraquinones), phthalocyanine, arylcarbonium ion (including triphenylmethines), sulfur, polymethine, and nitro chemical classes (Christie, 2001). The two largest groups of commercial dyes are azo and anthraquinone dyes (Lall et al., 2003).

The main dye classes according to their applications can be classified as acid dyes, azo dyes, direct dyes, basic dyes, disperse dyes, mordant dyes, reactive dyes, sulphur dyes, and vat dyes (Christie, 2001).

The commercial name of a dye normally consists of (Giles, 1971):

a) The brand name. This is often an indication of the dye class as well as the manufacturers.

b) Color of the dyes. For example yellow, red, or blue.

c) One or more suffix letters (of German origin) and figures indicating:

  i) Shade of color, referred to as secondary colors. Example, B, G, R (B = Blau = Blue; G = Gelb = Yellow; R = Rot = Red) represent the three secondary colors. A blue color may be described as R (reddish) or 2R (more reddish) or G (yellowish), and so on. Similarly for red or yellow color which may be described in various degrees. For instance, suffix G applied to yellow denotes greenness.

  ii) Special qualities, for example, A = fine; AA = superfine.

  iii) Strength of dye, for example 150, 200 or 250%. This indicates the increased dye strength of a brand, for instance containing less salt or diluents in the proportions given.

1.3 Textile Industry in Malaysia

Textile industry is one of the industry segments that make the largest contribution to Malaysia's Gross Domestic Product (GDP). According to the Environmental Quality Report (2007), there were 366 textile factories operating in the country and this industrial sector was therefore a significant source of water pollution. In general, textile dyes contain high molecular weight compounds and high colored organic substances, mainly synthesized from chemically derived coal tar and petroleum based intermediates (Kang et al., 2002; Sen and Demirer, 2003).

1.3.1 Textile Mill Effluents

In Malaysia, the wet processing operations which include preparation, dyeing and finishing generate the major portion of textile wastewater. The amount of water used depends on the specific process operated at the mill and the equipment used. On average, an approximately 165 liters of water are required to process 1 kilogram of textile (Department of Environment, 2000) due to the wide variety of process steps, diverse and great chemical complexities being generated (Lin and Chen, 1997).

Textile wastewaters are known to contain color, persistent organics, toxicants, surfactants, absorbable organic halide (AOX), and heavy metals (Slokar and Le Marechal, 1998). They are generally characterized by high COD, BOD, suspended solids, conductivity and high intense color (Kim et al., 2002).

Various dyes used in textile industries cause a large difference in the pH of textile wastewater i.e. from pH 2 to 12 (Szpyrkowicz et al., 2001). This has caused some problems to conventional biological and chemical treatment systems which have limited pH tolerance. Therefore, proper pH adjustment is needed for textile dye wastewater treatment (Lin and Lin, 1993).

Generally, textile mill effluent can be categorized into three groups – high, medium, or low strength wastewater, according to their COD concentration and color intensity. High strength wastewater has COD concentration exceeding 1600 mg/L with strong dark color and very low transparency. Medium strength wastewater has COD concentration of 800-1600 mg/L, while the low strength wastewater has COD concentration less than 800 mg/L. The medium or low strength wastewater may also be characterized by strong color in many circumstances (Lin and Lin, 1993).

1.3.2 Laws and Regulations for Textile Dye Wastewater

Owing to harmful effects of dyeing effluents to human being, aquatic life and the environment, permissible limits have been set by environmental authorities for different kinds of waters. In Malaysia, according to the Environmental Quality (Industrial Effluent) Regulations 2009, the effluent discharged from industry must comply with the Fifth Schedule (Environmental Quality Act and Regulation, 2010). Parameter limits of effluent of Standard A and B as stated in the Fifth Schedule is summarized in Table A3.1 (Appendix A). There are a total of 30 parameters of concern that must be monitored when discharging effluent into any receiving water body. Acceptable conditions for discharge of industrial effluent containing COD for specific trade or industry sector have been listed in Seventh Schedule (Table A3.2 in Appendix A). For the textile industry, the discharge limits of COD in standard A, and B are 80 mg/L and 250 mg/L, respectively. Standard A shows the limits that must be complied for effluent that is discharged into any inland waters within the catchment areas while Standard B is the limits for effluent that is discharged into any other inland waters (Environmental Quality Act and Regulation, 2010).

1.4 Types of Wastewater Treatment Methods

In general, wastewater treatment methods comprise of physical, chemical, and biological treatments. These methods can be used either singularly or together in various combinations. Many treatment processes combine two or more treatment technologies to provide a better or more efficient treatment (Crini, 2006).

Physical treatment involves particle separation processes; no gross chemical or biological changes are carried out. Example of physical treatment processes are adsorption, sedimentation, screening, aeration, filtration, floatation and skimming, degasification, and equalization. These processes are particle size dependent (Fitzpatrick and Gregory, 2003).

Chemical treatment involves chemical reactions to improve water quality. Chlorination, ozonation, neutralization, coagulation, adsorption, and ion-exchange are some examples of chemical treatment processes. Generally, chemical treatment processes are economically feasible (but are sometimes costly due to the cost of chemicals). The main drawbacks of the process are large quantities of concentrated sludge, and pH dependence (Kace and Linford, 1975; Lee et al., 2006).

Biological treatment methods use microorganisms, mostly bacteria to decompose organic matters in wastewater. This treatment method is relatively inexpensive, having low running costs and the end products of complete mineralization not being toxic and stable (Gupta and Suhas, 2009). However, their application is often restricted due sensitivity to some chemicals, less feasibility in design and operation (Bhattacharyya and Sarma, 2003). Generally, biological treatment methods can be divided into aerobic (in presence of oxygen) and anaerobic (without oxygen) methods. Example of aerobic treatment methods are activated sludge treatment methods, trickling filtration, oxidation ponds, lagoons, aerobic digestion (Sani and Barnerjee, 1999; Anjaneyulu et al., 2005; Rai et al., 2005). Example of anaerobic treatment methods are anaerobic digestion, septic tanks, and lagoons (Krull and Hemple, 1994; Carliell et al., 1996; Anjaneyulu et al., 2005).

1.5 Adsorption Process

Adsorption process has been widely used in dye wastewater treatment (Freeman, 1989; Danis et al., 1998; Bansal and Goyal, 2005). The term adsorption refers to a process where adhesion of molecules of gas, liquid, or dissolved solids (adsorbate) to a surface (adsorbent) (Cheremisinoff, 2002). Adsorption on porous carbons was described in 1550 B.C. for medical purpose in an ancient Egyptian papyrus and later by Hippocrates and Pliny the Eder (Gupta and Suhas, 2009). In 1773, the phenomenon of adsorption on scientific records was observed by C.W. Scheele (Mantell, 1951; Tien, 1994). This was followed by the observations made by Lowitz in 1785 of the reversible removal of color and odor producing compounds from water by wood charcoal. Larvitz in 1792 and Kehl in 1793 discovered the similar phenomenon with vegetable and animal charcoals, respectively. In 1881, Kayser introduced the term adsorption to differentiate surface accumulation from intermolecular penetration. There are two types of adsorption processes, namely physiosorption and chemisorption. Physiosorption involves the attraction between the solid surface and the adsorbed molecules via van der waals forces and they being weak in nature result in reversible adsorption. Chemisorption involves higher strength chemical bonding which is difficult for the removal of chemisorbed species from the solid surface (Gupta and Suhas, 2009).

Adsorption has been found to be more effective than other wastewater treatment technologies in terms of low cost, flexibility and simplicity of design, ease of operation and insensitivity to toxic pollutants. Moreover, adsorption does not produce harmful end products; the spent adsorbent could be regenerated (Crini, 2006).

1.6 Problem Statement

The adsorption process using activated carbon is one of the most effective and widely used techniques in decolorizing different types of coloring materials (Crini, 2006). However, the usage of commercially available activated carbon has been limited due to high cost. This is because, they are normally made from coal, a non-renewable, and relatively expensive starting material, which is unjustified in pollution control applications (Ahmad and Hameed, 2010). Therefore, inexpensive agro-lignocellulosic material (bagasse) has been used as adsorbents for the removal of methylene blue (MB) dye from aqueous solutions.

MB dye was chosen as synthetic textile dye aqueous solution due to its widely used for printing calico, dyeing, printing cotton and tannin and dyeing leather. MB can cause permanent injury to the eyes of humans and animals, irritation to the gastrointestinal tract with symptoms such as nausea, vomiting and diarrhoea and also cause methemoglobinemia, cyanosis, convulsions, tachycardia, and dyspnea. Contact of MB with the skin causes irritation (Hamdaoui and Chiha, 2007).

Most previous studies only emphasize on the decolorization of dye aqueous solutions. COD should also be taken into consideration because COD is a crucial parameter for evaluating the concentration of organic contaminants in water bodies (Li and Song, 2009). As degradation of organic compounds involves oxygen, their concentrations can be figured by the amount of oxygen needed (Li et al., 2003). COD is the primary index used to evaluate organic pollution in aqueous solutions (Devi and Dahiya, 2006). In the present study, a new method is used to increase the efficiency of adsorbents in COD reduction.

In some previous works, incomplete pretreatment of the lignocellulosic materials has resulted in large differences between percentage of color removal and COD reduction. Sayan (2006) had reported that 99.90 % of color had been removed but only 85.22 % of COD had been reduced for rifacion yellow dye. Belessi et al. (2009) reported 100 % color removal and 81.40 % of COD reduction for Reactive Red 195. The percentage of color removal and COD reduction should be relatively close to each other if not equal.

The adsorption kinetics and thermodynamics were studied under various experimental conditions and the adsorption equilibria were investigated in order to determine which isotherm model fitted well to the experimental data. Therefore, a novel discussion on kinetic data has been carried out.

1.7 Objectives

Specified objectives of present study include:

(a) To determine the efficiencies of color removal and COD reduction of MB dye aqueous solutions and real industrial textile wastewater using various acid modified bagasse.

(b) To determine the factors affecting the color removal and COD reduction using various acid modified bagasse.

(c) To calculate the kinetics and proposed the mass transfer mechanisms involved in adsorption process.

(d) To obtain the optimal conditions of this treatment method in order to achieve best efficiency using various acid modified bagasse.

CHAPTER TWO

LITERATURE REVIEW

2.1 Textile Industries

2.1.1 Textile Manufacturing Processes

The contents of textile effluent are largely dependent on different organic-based compounds, chemicals and dyes applied in the industrial dry and wet processing steps (Dos Santos et al., 2006). Sizing, souring, bleaching, mercerizing, and dyeing processes are the most common textile-processing set up (Department of Environment, 2000; Dos Santos, 2001; Dos Santos et al., 2006)

2.1.1.1 Sizing

Sizing is an important preparation step used to provide strength to the fibres and minimize breakage by adding sizing agents such as starch, polyvinyl alcohol (PVA) and carboxymethyl cellulose (Dos Santos et al., 2007). Little or no wastewater is generated in this process (Department of Environment, 2000). Sizing materials can cause color changes when exposed to sodium hydroxide. Therefore, removing the sizing materials before scouring is necessary (Department of Environment, 2000).

2.1.1.2 Scouring

Scouring is a cleaning process that uses alkali solution (commonly sodium hydroxide) to remove impurities from fibers by breaking down natural oils, fats, and waxes surfactants and to emulsify and suspend impurities in the scouring bath. Scouring procedures, chemicals, temperature and time vary with the type of fiber being processed. Processes of desizing and scouring are always combined (Dos

Santos et al., 2007). The effluent wastewater contains disinfectants and insecticide residues, sodium hydroxide, detergents, fats, oils, pectin, knitting lubricants, spin finishes, and spent solvents (Department of Environment, 2000).

2.1.1.3 Bleaching

Bleaching is a chemical process that is used to remove unwanted color from fibers. This process decolorized colored impurities that are not removed by scouring. The most common bleaching agents being used are hydrogen peroxide, sodium hypochlorite, sodium chlorite, and sulfur dioxide gas (Dos Santos et al., 2007). The effluent wastewater contains hydrogen peroxide, sodium silicate or organic stabilizer, and high pH (Department of Environment, 2000).

2.1.1.4 Mercerising

Mercerising is a continuous chemical process used to increase dye ability, luster, and appearance. During this process, concentrated alkaline solution is applied on the fibers and is neutralized with cold acid solution followed by several rinses to remove acid before the dyeing step (Dos Santos et al., 2007). The wastewater contains high pH, and sodium hydroxide (Department of Environment, 2000).

2.1.1.5 Dyeing

Dyeing is a process of adding color and intricacy to textiles and increases product value. A wide range of dyestuffs, techniques, and equipments are used in this process. Dyeing can be performed using continuous or batch dyeing process. In batch dyeing, a certain amount of textile substrate is loaded into a dyeing machine, with a solution containing dye. In continuous dyeing, textiles are fed continuously into a dye range. Dyeing process requires large volumes of water (Dos Santos et al., 2007). The wastewater contains metals, salts, surfactants, toxins, organic processing assistants, cationic materials, color, BOD, COD, sulfide, acidity, alkalinity, and spent solvents (Department of Environment, 2000).

2.1.2 Textile Dyes

Varieties of dyes are used in the textile dyeing processes. A good dye resists fading by water, light perspiration, and others (Christie, 2001). The dye classes, dye description, types of fibers, and typical pollutants associated with various dyes are listed in Table 2.1 (Kirk, 1993; Department of Environment, 2000; Dos Santos et al., 2007).

Table 2.1: Typical characteristics of dyes used in textile dyeing process (Kirk, 1993; Department of Environment, 2000; Dos Santos et al., 2007).

Dye Class	**Description**	**Type of Fibers**	**Types of Pollutants Associated with Various Dyes**
Acid	Anionic compounds with high water solubility.	Wool, nylon, silk, leather	Color; organic acids; unfixed dyes
Basic	Very bright dyes, water soluble cationic dyes, applied in weakly acidic dyebaths.	Acrylic, polyesters, cotton, silk, nylon	Color; organic acids; unfixed dyes
Direct	Water soluble, anionic compounds, can be applied directly to cellulosics without mordants (a substance that will form a coordination complex with the dye. Useful in setting dyes on fabrics.)	Cotton, rayon, leather, nylon	Color; salt; unfixed dye; cationic fising agents; surfactant; defoamer; leveling and retarding agents; finish; diluents

Table 2.1 (continued)

Disperse	Water insoluble.	Polyester, acetate, acrylic	Color; organic acids; carriers; leveling agents; phosphates; defoamers; lubricants; dispersants; diluents
Mordant	Final color largely dependent on the choice of mordant e.g. of mordant is potassium dichromate.	Wool, leather	Mordants (particularly in heavy metals categories) will cause hazardous to health.
Reactive	Water soluble, anionic compounds, largest dye class.	Cotton, wool, silk, nylon	Color; salt; alkali; unfixed dye; surfactants; defoamer; diluents; finish
Sulfur	Organic compounds containing sulfur or sodium sulfide.	Cotton, rayon	Color; alkali; oxidizing agents; reducing agent; unfixed dye
Vat	Oldest dyes, more chemically complex, water insoluble.	Cotton, rayon, wool	Color; alkali; oxidizing agents; reducing agent

2.2 Technologies Available for Color Removal

Dyes in wastewater can be removed when the cleavage of the -C=C- bonds, the -N=N- bonds and the heterocyclic and aromatic rings occurs. For example, Ghoneim et al. (2011) used Electro-Fenton oxidation process to remove Sunset Yellow FCF azo-dye by breaking -C=C-, -N=N-, and aromatic rings. Molecules which absorb light shift from visible to ultraviolet or infrared region of the electro magnetic spectrum (Slokar and Le Marechal, 1998).

According to Perry et al. (1997) industrial wastewater treatment processes consist of four steps namely pretreatment, primary treatment, secondary treatment, and tertiary treatment. Similar ways are used for dye wastewater treatment (Gupta and Suhas, 2009).

Pretreatment process includes equalization and neutralization. Industrial wastewater streams are pretreated via equalization and neutralization before being discharged to municipal sewerage systems or to a central industrial sewerage system (Gupta and Suhas, 2009).

After undergo pretreatment step, physical or chemical separation techniques (primary treatment) will be applied to remove suspended solids (Gupta and Suhas, 2009).

The wastewater is given a secondary treatment. This treatment process involves microorganisms, also known as biological treatment. The primary bacteria of the microorganism are used to stabilize the waste components prior to tertiary treatment (physical-chemical treatment). The tertiary treatment processes include adsorption, ion-exchange, stripping, chemical oxidation, and membrane separations (Gupta and Suhas, 2009).

The final steps for the wastewater treatment process are the sludge processing and disposal steps (Gupta and Suhas, 2009).

Dyes are non-biodegradable in nature; they are stable to light and oxidation. Therefore, treatments of dye using traditional chemical or biological methods are ineffective (Hasan et al., 2008).

Lin and Lin (1993) classifying the methodologies generally have been used to treat dye wastewater in three categories: i) Physical ii) Chemical and iii) Biological.

Table 2.2 shows the pros and cons of different treatment processes which have been used in dye wastewater treatment process.

Table 2.2 Pros and cons of different treatment processes

Treatment	Pros	Cons
PHYSICAL 1) Ion Exchange	- Able to remove both cationic and anionic dyes from the effluents (Mishra and Tripathy, 1993). - High concentration of acid sites; effective in soluble dye removal (Ali et al., 2007).	- Cannot accommodate a wide range of dyes. - Perform poorly with other additive in wastewater (Anjaneyulu et al., 2005). - High operating cost (Mishra and Tripathy, 1993).
2) Membrane Filtration	- Able to remove and recover dyes, chemicals, and process water (Akbari et al., 2007).	- Flux decline (Goksen et al., 2006).
3) Irradiation	- Effective to remove a wide range of colorants at low volumes. - Effective in eliminating organic contaminants and disinfect harmful microorganisms (Borely et al., 1998).	- Require high dissolved oxygen. - Ineffective for light resistant colorants. (El-Gohary et al., 1995)
4) Adsorption 4.1) Commercial Activated Carbon	- Most popular adsorbent, useful to adsorb high volume of dyes due to its high adsorption capacity (Lin, 1993). - Good color removing capacity when introduced in a	- Expensive. - High regeneration cost because desorption of the dye molecules is not easily achieved.

Table 2.2 (continued)

	separate filtration step. - High removal rate for cationic mordant and acid dyes. (Raghavacharya, 1997)	(McKay et al., 1987)
4.2) Low-Cost Activated Carbon / Adsorbents	- Cheap adsorbent. - Good alternatives for expensive adsorbent (Singh and Tiwari, 2001). - No activation required and cheaper (Dufort and Ruel, 1972), - Good sorbent for dyes and color causing polar organics (Bousher et al., 1997). - Capability of color and dissolved organics removal (Mall et al., 1994). - Biodegradable and non- toxic nature (Chang and Juang, 2004).	- Post treatment disposal (Anjaneyulu et al., 2005). - Due to their hardness, required longer contact time and large amount (Lens et al., 1994). - Different low-cost adsorbent will have different adsorption behavior; therefore need to put more effort to improve their adsorption capabilities (Lin et al., 2008).
CHEMICAL 1) Coagulation and Precipitation	- High color and dissolve organic removal (Tan et al., 2000; Anjaneyulu et al., 2005).	- High cost of chemicals for precipitation and pH adjustment (Anjaneyulu et al., 2005).

Table 2.2 (continued)

2) Oxidative Processes 2.1) Fenton	- Able to decolorize, reduce COD and remove toxic in wide variety of dye wastes (Balchioglu et al., 2001).	- High cost. - High sludge production (Balchioglu et al., 2001).
2.2) Ozonation	- Good oxidizing agent due to its high stability. - High color removal and COD reduction with improved biodegradability (Churchley, 1994). - No residue or sludge formation and no toxic metabolites (Gahr et al., 1994).	- Short half-life (typically being 20 min) demanding continuous application making it a cost intensive process (Xu and Lebrun, 1999).
2.3) Hydrogen Peroxide/ Pyridine/ Copper System	- A pH independent wastewater treatment process. Able to work in a wide range of pH (Ulosoy and Bünyamin, 2005; Lim et al., 2009).	- Only effective on certain dye wastewater (Ulosoy and Bünyamin, 2005).
2.4) Electrochemical Oxidation	- High efficiency for degradation of recalcitrant pollutants. - Lower temperature requirements; do not require any additional chemicals (Kim et al., 2002).	- High processing cost (Kim et al., 2002).

Table 2.2 (continued)

2.5) Sodium Hypochlorite (NaOCl)	- Attacks the amino group of the dye molecule by Cl^+ (Robinson et al., 2001).	- Not suitable for all kinds of dyes. - Release of carcinogenic substances such as aromatic amines (Robinson et al., 2001).
3) Cucurbituril	- Other organic substances which present in the water will not interfere with the formation of complexes (Slokar et al., 2001).	- High cost (Anjaneyulu et al., 2005).
BIOLOGICAL 1) Aerobic	- Effective in color removal and COD reduction (Anjaneyulu et al., 2005).	- Ineffective in treating heavy metals (Anjaneyulu et al., 2005).
2) Anaerobic	- Production of biogas which can be reused to provide heat and power (Bras et al., 2005).	- Longer acclimatization phase (Bras et al., 2005).
3) Single Cell	- Effective for specific colorant removal (Anjaneyulu et al., 2005).	- Cannot cope in large volumes of colored effluents (Anjaneyulu et al., 2005).
4) Enzymatic Treatment	- Able to remove compounds that can interfere with downstream treatment process (Anjaneyulu et al., 2005).	- Tedious method during enzyme isolation and purification (Anjaneyulu et al., 2005).

2.3 Adsorption Process Mechanisms

An adsorption process involves mass transfer of adsorbate (a soluble species) from bulk solution to the surface of the adsorbent (a solid phase). Transformation of adsorbate to the porous media adsorbent will occur through four main steps (Snoeyink and Summers, 1999; Wang et al., 2008). Hence, it is essential to understand the mass transfer mechanisms in order to design a cost effective and efficient adsorption system.

2.3.1 Bulk Solution Transport

This is an adsorption process that involves the transportation of adsorbate form bulk solution to the hydrodynamic boundary layer (liquid-solid interphase) surrounding the adsorbent (Wang et al., 2008).

2.3.2 External (Film) Resistance to Transport (External Diffusion)

The transportation of adsorbate through the hydrodynamic boundary layer surrounding the adsorbent is affected by molecular diffusion. The distance the adsorbate travels is largely depending on the velocity of the bulk solution. The thickness of the boundary layer affects the rate of transportation. For example, the thicker the boundary layer, the lower the rate of transportation (Snoeyink and Summers, 1999; Wang et al., 2008)

2.3.3 Internal (Pore) Transport (Intraparticle Diffusion)

After the adsorbate has passed through the boundary layer to the adsorption site, intraparticle diffusion takes place. There are two types of diffusion that affect the intraparticle transportation, namely pore diffusion and surface diffusion. Pore diffusion takes place when molecules diffuse from the solution into the pores of the adsorbate, whereas surface diffusion occurs in which diffusion takes place along the adsorbent surface (Wang et al., 2008).

2.3.4 Adsorption

Lastly, the adsorbate is attached onto the available active sites on the adsorbent surface. This step occurs very fast; therefore one of the preceding diffusion steps controls the rate of mass transfer (Wang et al., 2008).

In order to investigate the adsorption mechanism and potential rate-controlling step such as the mass transfer and chemical reaction processes, various kinetic models are to be tested on experimental data.

2.4 Kinetic Study

The pseudo-first order, the pseudo-second order, the external diffusion adsorption and the intraparticle diffusion kinetic models have been applied to the experimental data in order to analyze the adsorption processes.

2.4.1 Pseudo-First Order Model

Pseudo-first-order model was proposed by Lagergren and Svenska (1898). The pseudo-first-order equation can be written as:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{2.1}$$

Integrating this for the boundary conditions, t=0 to t=t and q_t=0 to q_t=q_t, Eq. (2.1) becomes

$$\ln(1 - \frac{q_t}{q_e}) = -k_1 t \tag{2.2}$$

where k_1 is the rate constant of pseudo-first order model (h^{-1}), q_e (mg/g) is the amount of equilibrium uptake, q_t (mg/g) is the amount of solute adsorbed at any time t, and is given by Eq. (2.3).

$$q_t = \frac{(C_0 - C_t)V}{W} \tag{2.3}$$

where C_0 (mg/L) is the initial solute concentration, C_t (mg/L) is the solute concentration at respective time, t, V is the volume of the dye solution (L), and W is the weight of the adsorbent (g).

2.4.2 Pseudo-Second Order Model

Pseudo-second-order equation (Ho and McKay, 1998) based on equilibrium adsorption can be expressed as

$$\frac{1}{q_t} = \frac{1}{q_e} + \frac{1}{k_2 q_e^2 t} \tag{2.4}$$

where k_2 (g/mg h) is the pseudo-second order rate constant. This equation can also be written as

$$\frac{1}{q_t} - \frac{1}{q_e} = \frac{1}{k_2 q_e^2 t} \tag{2.5}$$

2.4.3 External Diffusion Model

Spahn and Schlunder model was used to describe the external diffusion on the adsorbent (Spahn and Schlunder, 1975).

$$\ln\left(\frac{C_t}{C_0}\right) = -k_{ext} t \tag{2.6}$$

where k_{ext} is the constant rate of Spahn and Schlunder model (1/min). A linear plot of $\ln C_t$ versus time t will be obtained if this model is applicable.

2.4.4 Intraparticle Diffusion Model

The intraparticle diffusion model was proposed by Weber and Morris (1962), since the pseudo-first-order and pseudo-second-order failed to identify the diffusion mechanism. Intraparticle diffusion model can be expressed as:

$$q_t = k_{\text{int}} t^{1/2} + C \tag{2.7}$$

where k_{int} is the intraparticle diffusion rate constant (mg/g.h$^{1/2}$) and C (mg/g) is a constant that is related to the thickness of boundary layer.

2.5 Equilibrium Study

The adsorption isotherm gives the relationship between mass of adsorbate adsorbed per unit weight of adsorbent in equilibrium and liquid-phase equilibrium concentration of the adsorbate (Lata et al., 2007). It is a basic requirement for the design of adsorption system. A number of isotherms had been proposed and these include Langmuir isotherm, Freundlich isotherm, Temkin isotherm, and Dubinin-Radushkevich (DR) isotherm.

2.5.1 Langmuir Isotherm

Langmuir adsorption model (Langmuir, 1918) is based on the assumption that maximum adsorption takes place at specific homogeneous sites within the adsorbent. Langmuir model is given by the following equation:

$$q_e = \frac{Q_0 K_L C_e}{1 + K_L C_e} \tag{2.8}$$

where C_e is the concentration of adsorbate remaining in the solution at equilibrium (mg/L), Q_0 is the amount of adsorbate adsorbed by unit mass of adsorbent that is required to cover an adsorbent surface completely as a monolayer (mg/g), and