PREPARATION AND CHARACTERIZATION OF MODIFIED OIL PALM (*Elaeis guineensis*) FROND FOR THE REMOVAL OF RHODAMINE B IN WASTEWATER

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by

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LIST OF ABBREVIATIONS

A-EGFF	Phosphoric acid modified *Elaeis guineensis* frond fiber
AC-EGFF	Carbonized phosphoric acid modified EGFF
AC-EGFF-Fe_3O_4	Carbonized phosphoric acid modified EGFF impregnated with iron oxide
ANOVA	Analysis of variance
APHA	American public health association
BBD	Box behnken design
BDDT	Brunauer-Deming-Deming-Teller
BET	Brunauer, Emmett and Teller
BOD	Biochemical oxygen demand
CCD	Central composite design
COD	Chemical oxygen demand
C.I.	Color index
D_{avg}	Average diameter
DOE	Design of experiment
DR	Dubinin-Radushkevich
EDX	Energy dispersive X-ray
EGFF	*Elaeis guineensis* frond fiber
FCCD	Face centered composite design
FTIR	Fourier transform infra red
IUPAC	International union of pure and applied chemistry
RB	Rhodamine B
RSM	Response surface methodology
SEM	Scanning electron microscopy

TEM	Transmission electron microscopy
XRD	X-ray diffraction

LIST OF SYMBOLS

A	Initial solution pH	-
A_1	RB stock solution concentration	mg/L
A_2	Required final RB concentration	mg/L
A_T	Temkin isotherm constant	L/g
Ag_2SO_4	Silver sulphate	-
B	Agitation speed	rpm
b_T	Temkin isotherm constant related to heat of adsorption	J/mol
C	Initial dye concentration	mg/L
C_e	Concentration of dye at equilibrium	mg/L
C_o	Initial dye concentration	mg/L
C_t	Dye concentration at respective time, t	mg/L
-CH=	Methane group	-
C=O	Carbonyl group	-
D	Temperature	^{o}C
E	Contact time	min
F	Adsorbent dosage	g/100 mL
$FeCl_3.6H_2O$	Iron (III) chloride hexahydrate	-
Fe_3O_4	Iron oxide	-
$FeSO_4.7H_2O$	Iron (II) sulphate heptahydrate	-
HCl	Hydrochloric acid	-
$HgSO_4$	Mercury sulphate	-
H_2O_2	Hydrogen peroxide	-
H_3PO_4	Phosphoric acid	-

H_2SO_4	Sulphuric acid	-
KBr	Potassium bromide	-
KCl	Potassium chloride	-
K_2CO_3	Potassium carbonate	-
$K_2Cr_2O_7$	Potassium dichromate	-
KOH	Potassium hydroxide	-
K_F	Freundlich isotherm constant	$mg/g(L/mg)^{1/n}$
K_L	Langmuir isotherm constant related to the affinity of the binding sites	L/mg
k_1	Pseudo-first order rate constant	min^{-1}
k_2	Pseudo-second order rate constant	g/mg.min
M_1	Fe^{2+}:Fe^{3+} ratio	-
M_2	Heating time	min
M_3	Heating temperature	^oC
MnO_4	Permanganate	-
NaOH	Sodium hydroxide	-
NH_4OH	Ammonium hydroxide	-
$-NO_2$	Nitro group	-
-N=N-	Azo group	-
NR_2	Amino group	-
$1/n$	Adsorption intensity	-
OH	Hydroxyl group	-
Q_{DR}	Dubinin-Radushkevich constant	-
Q_o	Amount of adsorbate adsorbed by unit mass of adsorbent that is required to cover an adsorbent surface completely as a monomolecular layer	mg/g

pH_{zpc}	pH point of zero charge	-
q_e	Amount of dye uptake at equilibrium	mg/g
q_t	Amount of dye adsorbed at any time, t	mg/g
R	Universal gas constant	J/mol.K
R_L	Dimensionless constant	-
r^2	Coefficient of determination	-
S_a	Initial COD concentration	mg/L
S_b	Equilibrium COD concentration	mg/L
S_{BET}	BET surface area	-
T	Absolute solution temperature	K
V	Volume of the dye solution	L
V_1	Known volume of RB stock solution	mL
V_2	Total volume of required final RB concentration	mL
V_{micro}	Micropore volume	-
V_{total}	Total volume	-
W	Weight of the adsorbent	g
X_1	Carbonization temperature	^oC
X_2	Carbonization duration	h
X_3	Heating rate	$^oC/min$
X_4	Nitrogen gas flow rate	cm^3/min
x_i	Coded variables	
y_1	color removal or decolorization	%
y_2	COD reduction	%
ΔG^o	Gibbs free energy	kJ/mol
ΔH^o	Standard entalpy	kJ/mol

ΔS^o	Standard entropy	J/mol.K
ε	Constant for Dubinin-Radushkevich isotherm	-
$\beta_o, \beta_i, \beta_{ii}, \beta_{ij}$	Regression coefficients	-
η	Response surface area	-
ξ_i	Natural variable	

PENGHASILAN DAN PENCIRIAN PELEPAH KELAPA SAWIT (*Elaeis guineensis*) TERUBAHSUAI DALAM PENGOLAHAN AIR SISA RHODAMINE B

ABSTRAK

Proses penjerapan telah diaplikasikan dalam pelbagai rawatan air sisa, termasuk air sisa pewarna. Walau bagaimanapun, kajian mengenai penggunaan sisa pertanian seperti pelepah kelapa sawit dan pelepaj kelapa sawit terubahsuai masih tidak dikaji dengan menyeluruh. Dalam kajian ini, penjerapan Rhodamine B (RB) ke atas pelepah kelapa sawit (a) mentah (EGFF), (b) yang diubahsuai dengan asid fosforik (A-EGFF), (c) yang diubahsuai dengan asid fosforik dan dikarbonisasikan (AC-EGFF), (d) yang diubahsuai dengan asid fosforik dan dikarbonisasikan serta dikandungkan dengan oksida ferik (AC-EGFF-Fe_3O_4) telah dikaji. Untuk menyingkirkan sebatian organik yang menyumbang kepada keperluan oksigen kimia (COD), proses pencucian penjerap dengan menggunakan air suling didih telah dilaksanakan sebagai pengganti kepada air suling pada suhu bilik. Proses penyediaan penjerap telah dikaji dan dioptimumkan dengan menggunakan metodologi permukaan sambutan (RSM)- rekabentuk ujikaji gabungan pusat (FCCD). Kesan pH, kelajuan pergaulan, dos penjerap, kepekatan awal pewarna, tempoh pergaulan dan suhu ke atas penyahwarnaan dan penurunan peratus COD telah dikaji dan dioptimumkan. Keputusan menunjukkan AC-EGFF-Fe_3O_4 mempunyai luas permukaan BET yang luas dan lebih berkesan dalam penyahwarnaan dan penurunan COD bagi pewarna RB berbanding dengan EGFF, A-EGFF, dan AC-EGFF. Keadaan penjerapan optimum bagi AC-EGFF-Fe_3O_4 diperolehi pada 550 mg/L kepekatan awal pewarna, pH 8.49, 28.43 ^oC, 27 min dan 0.97 g dos penjerap dengan 98.63 % penyahwarnaan dan 98.06 % penurunan COD. Luas permukaan BET bagi AC-EGFF-Fe_3O_4 ialah 797.68 m^2/g iaitu lebih tinggi daripada EGFF mentah (13.80 m^2/g), A-EGFF (31.67 m^2/g), dan AC-EGFF (555.53 m^2/g). Isoterma penjerap, kinetik, dan termodinamik untuk penjerapan zat warna RB telah dikaji. Data isotherma penjerap pewarna RB dengan menggunakan AC-EGFF-Fe_3O_4 didapati mengikuti model isoterma Langmuir dan Freundlich. Kinetik penjerapan mengikuti model kinetik tertib pseudo-kedua. Kajian termodinamik menunjukkan proses penjerapan adalah proses endotermik. AC-EGFF-Fe_3O_4 yang telah digunakan boleh diregenerasikan dengan menggunakan 0.1 M NaOH. Kajian menunjukkan bahawa sisa agrikultur EGFF terubahsuai adalah bahan penjerap yang sesuai digunakan untuk merawat air sisa berwarna.

PREPARATION AND CHARACTERIZATION OF MODIFIED OIL PALM (*Elaeis guineensis*) FROND FOR THE REMOVAL OF RHODAMINE B IN WASTEWATER

ABSTRACT

The adsorption process has been applied in various wastewater treatments, including dye wastewater. However, research on the use of agricultural waste such as oil palm frond and modified oil palm frond is still not thoroughly investigated. In this research, the adsorption of Rhodamine B (RB) from the aqueous solutions onto (a) raw *Elaeis guineensis* frond fiber (EGFF), (b) phosphoric acid modified EGFF (A-EGFF), (c) carbonized phosphoric acid modified EGFF (AC-EGFF), and (d) carbonized phosphoric acid modified EGFF impregnated with ferric oxide (AC-EGFF-Fe_3O_4) have been investigated. In order to remove organic compounds and to improve the reduction of chemical oxygen demand (COD), the raw EGFF was thoroughly washed with boiling distilled water instead of using room temperature distilled water. The preparation conditions of the adsorbents were optimized using response surface methodology (RSM)-face centered composite design (FCCD). The effects of pH, shaking speed, adsorbent dosage, initial dye concentration, contact time and temperature on color removal and COD reduction were studied and optimized. The results showed that the AC-EGFF-Fe_3O_4 has higher BET surface area and was more effective in terms of color removal and COD reduction of RB dye than the raw EGFF, A-EGFF, and AC-EGFF. The optimal adsorption conditions for AC-EGFF-Fe_3O_4 were obtained at 550 mg/L initial RB dye concentration, pH 8.49, 28.43 ^{o}C, 27 min, and 0.97 g adsorbent with 98.63 % color removal and 98.06 % COD reduction. The BET surface area for AC-EGFF-Fe_3O_4 was 797.68 m^2/g which was higher than that of raw EGFF (13.80 m^2/g), A-EGFF (31.67 m^2/g), and AC-EGFF (555.53 m^2/g). Adsorption isotherms, kinetics and thermodynamics for the adsorption of RB dye were determined. The equilibrium data for the adsorption of RB dye using AC-EGFF-Fe_3O_4 was best represented by Langmuir isotherm model, followed by Freundlich isotherm model. The adsorption kinetics was found to follow the pseudo-second-order kinetic model. The thermodynamic study showed that the adsorption process was endothermic. Spent AC-EGFF-Fe_3O_4 can be effectively regenerated using 0.1 M NaOH. The results indicated that modified agricultural waste EGFF is suitable to be used as adsorbent for the treatment of dye wastewater.

CHAPTER ONE

INTRODUCTION

1.1 Background

The textile industry is one of the most highly-consuming water and energy industries, causing severe pollution. Indeed, the impact of textile effluents on the aquatic medium has been traditionally of immense concern because its high variation in composition with strong color, high chemical oxygen demand (COD), varying pH values and relatively low biodegradability with large amount of dissolved salts and suspended solids (Merouani et al., 2010; Blanco et al., 2014; Pang and Abdullah, 2013a,b). A typical example of the characteristics of textile industry wastewater is given in Table 1.1.

Table1.1 Typical characteristics of textile industry wastewater (Tan et al., 2000; Lim et al., 2010; Pang and Abdullah, 2013a).

Parameters	**Values**
pH	6.9-11.6
Temperature (^oC)	35-58
Color Point (PtCo)	735-8100
Chemical Oxygen Demand (COD) (mg/L)	675-3190
Suspended Solids (mg/L)	530-3000

In addition, these effluents reduce the aesthetic value of the receiving water and pose significant threat to human health and the ecosystem (Sun et al., 2007; Pang and Abdullah, 2013b).

In Malaysia, the Department of Environment under the Ministry of Natural Resources and Environment has established an international water quality standard.

Tables A1 and A2 in Appendix A list the parameter limits of effluent of Standards A and B as stated in the Fifth Schedule of Environmental Quality (industrial effluent) Regulations 2009 (Environmental Quality Act and Regulation, 2010). Standards A and B list the limits that ought to be abided by effluent that is discharged into any inland waters within the catchment areas and any other inland waters, respectively (Environmental Quality Act and Regulation, 2010).

During the past few decades, a wide range of wastewater treatment techniques has been used. The adsorption process is one of the most effective and widely used techniques in decolorizing different types of coloring materials (Crini, 2006; Su et al., 2014; Low et al., 2014). Currently, there are many studies on the development of adsorbents using natural materials, biomass, and agricultural waste materials.

1.2 Oil Palm Biomass (*Elaeis guineensis* Biomass)

Generally, biomass can be defined as compounds or organic matters either produced from marine life, forestry or crops (Awalludin et al., 2015). Biomass can also be defined as a type of hydrocarbon material comprises of oxygen, hydrogen, carbon, and nitrogen, and sometimes sulphur and small proportion of inorganic substances (Yaman, 2004).

Oil palm (*Elaeis guineensis*) is nurtured at an enormous scale as a source of oil in Central and West Africa (where it is originated), and in Thailand, Indonesia and Malaysia (Wan Rosli et al., 2004). In Malaysia, oil palm is one of the most vital commercial crops with world production of 19.22 million tons in year 2013 (MPOB, 2014). The growth of oil palm plantation in Malaysia has generated large amounts of waste, generating problems in replanting operations, and tremendous environmental concerns (Wan Rosli et al., 2004). In the palm oil mill, 10% of the total biomass consists of palm oil, while the remaining 90% is discarded as waste (Abdullah et al., 2013).

The high demand for palm oil is due to its nutritional value and cheaper price as compared with other vegetable oils (Ramli, 2011). Besides food uses, palm oil is also widely applied in non-food applications, such as in cosmetics, pharmaceuticals, lubricants, and various products of the oleo-chemical industries (Nurfahisza et al., 2014).

The oil palm is a lignocellulosic rich material containing cellulose, hemicelluloses, and lignin. Oil palm frond contains a high composition of hemicelluloses (83.13 %), cellulose (47.76 %) and lignin (20.15 %) (Ahmad, et al., 2011) which has made it a suitable precursor as adsorbent in wastewater treatment. The oil palm biomass was found to contain high amount of calcium, silica, aluminina and potassium that can be used to synthesize active compounds that are responsible for adsorption of various pollutants on the surface of the adsorbents (Zainudin et al., 2005; Ghazali et al., 2006; Ahmad et al., 2011).

1.3 Problem Statement

Adsorption process has been widely used in dye wastewater treatment because this process proved 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 (Crini, 2006). However, the use of commercially available activated carbon has been limited due to high cost (1-2

US$/pound) (Babel and Kurniawan, 2004; Tsang et al., 2008). Activated carbons are normally made from petroleum coke, bituminous coal, lignite, wood products, etc. (Drovac and Skipton, 2008). These materials are expensive and non-renewable, which is unjustified in pollution control applications (Ahmad and Hameed, 2010). Therefore, inexpensive agro-lignocellulosic material (*Elaeis guineensis* frond) has been used as adsorbent for the removal of Rhodamine B (RB) dye from aqueous solutions.

In Malaysia, the most vital agro-industry is the palm oil industry (Sumathi et al., 2008). Starting from this decade, replanting of palm oil is likely to increase rapidly. Presently, *Elaeis guineensis* frond, a major lignocellulosic rich, agricultural solid waste are regularly abandoned in the field on pruning and replanting (Hameed and El-Khaiary, 2008) which leads to environmental issues. There are no significant commercial applications for the fronds, unlike trunk, empty fruit bunches (EFB), oil palm fibers and shells; are used as construction materials. Annually, 44.8 million tones of oil palm fronds were generated (Ng et al., 2012). The high chemical compositions of oil palm frond (83.13 % hemicellulose, 47.76 % cellulose, and 20.15 % lignin) have made it suitable to be used as adsorbent in the wastewater treatment. Consequently, economic exploitation of these fibers in wastewater treatment will be favorable and the disposal problem will be solved.

Rhodamine B (RB) is an important water-soluble organic dye. RB has been widely used as a colorant in the textile and food industries as well as a biological stain in biomedical laboratories. RB has been banned to use in the food industry for many years due to its suspected carcinogenic nature. However, with the development of industry and the illegal discharge, RB still has the chances to enter the food chain to hazard human health. RB can cause permanent injury to the humans' eyes, irritation to the gastrointestinal tract with symptoms such as nausea, vomiting and diarrhea and also cause methemoglobinemia, cyanosis, convulsions and skin irritation (Xue et al., 2009; Muthuraman and Teng, 2009). Thereby, the removal of RB from aqueous solutions is of utmost importance prior to their discharge into the receiving water bodies.

Many researchers use raw agricultural waste or acid modified adsorbent for the treatment of dye aqueous solutions (Hameed and Daud, 2008; Jalil et al., 2012; Heibati et al., 2015; Aboua et al., 2015; Elmoubarki et al., 2015) which are unable to achieve high Brunauer, Emmett and Teller (BET) surface area. Adsorbent with high BET surface area gives high adsorption capacity. The present study not only used the conventional carbonization method (only involved two variables, i.e. carbonization temperature and carbonization duration of the process) to increase the BET surface area of the adsorbent (Li et al., 2008; Kim et al., 2012), the influence of heating rate and nitrogen gas flow rate in the carbonization process were also studied. Magnetic nano-composite adsorbent has shown to increase the efficiency of the adsorbent in the adsorption of dye aqueous solutions (Panneerselvam et al., 2011; Konicki et al., 2013).

Although filtration and centrifugation have been used to remove adsorbents from aqueous solutions, magnetic separation provides a promising method to perform solid-liquid separation. For magnetic separation, a magnetic component, such as iron oxide, is added in the composite particles. Then, once dispersed in the water solution during adsorption, an external magnet is used to gather the composite particles that were dispersed in water. When the magnet is removed, these composite particles may redisperse in water without any undesired magnetic aggregation (Zhang et al., 2014).

Most previous studies (Zhang et al., 2012; Lin et al., 2013; Hazzaa and Hussein, 2015; Tan et al., 2015a, b; Maneerung et al., 2016) applied the univariate method (changing one factor at a time and keeping the others constant) in adsorption studies, which might not attain the authentic optimal operational conditions and also energy and time consuming. Response surface methodology (RSM), an amalgamation of mathematical and statistical techniques has been used in the present study to develop, improve, optimize and study the interactions of two or more variables in the adsorption process.

Chemical oxygen demand (COD) is used to measure the capacity of water to consume oxygen during the decomposition of organic matter. COD is the primary index used to evaluate organic pollution in aqueous solutions (Metcalf and Eddy, 2004; Narayanan, 2015). COD has close relation with dye concentration. However, many previous studies (Gil et al., 2011; Madrakian et al., 2012; Pathak et al., 2015) only emphasize on the color removal but no COD measurement was done. In this study, COD is considered as a crucial parameter to be reduced throughout the adsorption process.

1.4 Research Scope and Objectives

Application and reuse of wastes have gained attention and have also been widely applied in various areas by researchers. The present study uses an agricultural waste - *Elaeis guineensis* frond fiber in dye wastewater treatment. Synthesis of effective adsorbents in terms of color removal, COD reduction and BET surface area for the treatment of RB dye aqueous solutions is the primary focus in this study. Various adsorbent modification methods such as phosphoric acid modification method (A-EGFF), carbonized phosphoric acid modification method (AC-EGFF), and impregnation of iron oxide on AC-EGFF through co-precipitation method (AC-EGFF-Fe_3O_4) were carried out and were analyzed using a statistical tool- Response Surface Methodology (RSM)- Faced centered composite design (FCCD). Optimal conditions of the adsorption process using various adsorbents (raw EGFF, A-EGFF, AC-EGFF, AC-EGFF-Fe_3O_4) were determined. To examine the practicability of the prepared adsorbent, the adsorbent was later on used in the treatment of textile industry wastewater.

The objectives of the present study include:

(a) To produce and characterize adsorbents for RB color removal and COD reduction using an agricultural waste- *Elaeis guineensis* frond fiber, through different adsorbent modification methods such as phosphoric acid modification, carbonization, and co-precipitation.

(b) To optimize the adsorbent preparation processes and the adsorption activities using statistical design of experiment (DOE)-Response surface methodology (RSM).

(c) To determine the efficiency of using nano-composite adsorbent for the color removal and COD reduction of Rhodamine B dye aqueous solutions and industrial textile wastewater.

(d) To determine the kinetics and propose the mass transfer mechanisms involved in the adsorption process.

CHAPTER TWO

LITERATURE REVIEW

2.1 Dyes

Textile industry ranks first among other industries such as rubber, paper, cosmetic, plastic, etc. in usage of dyes for fiber coloration (Grag et al., 2003). A dye is a colored, aromatic organic substance that absorbs light in the visible spectrum from 400-800 nm (Rangabhashiyam et al., 2013). The dye molecule contains delocalized electron systems with conjugated double bonds which comprise the chromophore and the auxochrome. The chromophore is a group of atoms principally responsible for the color of dye. The most imperative chromophores are the azo (-N=N-), carbonyl (C=O), methane (-CH=), and nitro (-NO_2) groups (Christie, 2001). The auxochrome intensifies the color of the chromophore by providing solubility of the dye through modification of the overall energy in the electron system. The common auxochrome groups are hydroxyl (OH), and amino (NR_2) groups (Christie, 2001). The distinctive dyes used in textile dyeing process are listed in Table 2.1. From Table 2.1, most of the dyes are water soluble except disperse and vat dyes.

Table 2.1 Distinctive dyes used in textile dyeing process (Demirbas, 2009; Rangabhashiyam et al., 2013).

Dye class	Description
Acid	Anionic compounds; water soluble
Basic	Cationic compounds; water soluble; used in weakly acidic dye baths; very bright color
Direct	Anionic compounds; water soluble; can be used directly to cellulosic without mordant
Disperse	Non-ionic aromatic compounds; Water insoluble
Reactive	Anionic compounds; water soluble; largest dye class
Sulfur	Contain sulfur or sodium sulfide
Vat	Water insoluble; oldest dyes; contain complex chemical structure

2.2 Pollution Due to Dye Wastewater

2.2.1 Color

Colored wastewater is a corollary of batch processes both in the dye manufacturing and dye-consuming industries. According to Easton (1995), 10% of the dyes are lost during textile coloration process due to incomplete exhaustion of dyes onto the fibre. Type of dyestuff, the depth of shade needed, and the application route are the dependent factors that determined the amount of dye lost (Pearce et al., 2003).

Color pollution in aquatic environments is an escalating problem. The toxicity, abnormal coloration and carcinogenic properties of dyes cause severe effects on exposed organisms and hinder the photosynthesis reaction (Slokar and Le Marechal, 1998; Pearce et al., 2003). Moreover, the color of water greatly influences the public perception of water quality, where the presence of colors in water is aesthetically unpleasant and is often associated with contamination (Waters, 1995; Pearce et al., 2003). The recalcitrant nature of dyes causes dyes to be persistent in the water, leading to the imposition of strict environmental regulations.

2.2.2 Chemical Oxygen Demand

In environment chemistry, chemical oxygen demand (COD) is generally used to evaluate the concentration of organic contaminants in water bodies. As degradation of organic compounds involves oxygen, their concentrations can be represented by the amount of oxygen needed (Li et al., 2003). COD concentration in the unit of mg/L is largely dependent on initial dye waste concentration, chemical structure of the dye and treatment duration (Tanja et al., 2003). The COD value indicates the amount of oxygen required for the complete oxidation of a substance in specific volume of aqueous solutions. When organic pollutants are high in a water sample, concentration of COD is high; more oxygen is required to completely oxidize a substance. Therefore, wastewater with high COD concentration denotes high pollution level (Tanja et al., 2003).

2.3 Textile Wastewater Treatment Technologies

High volumes of textile industrial effluent discharge and increasing stringent legislation make the search for appropriate treatment technologies a must. On the whole, textile industrial wastewater treatment encompasses four processes i.e. pretreatment, primary treatment, secondary treatment, and tertiary treatment (Perry et al., 1997). Pretreatment process comprises of equalization and neutralization. In the primary treatment, physical or chemical separation techniques are employed to remove suspended solids in the textile wastewater (Gupta and Suhas, 2009). Secondary treatment, also known as biological treatment, exploits microorganisms to stabilize the dyes components before tertiary treatment (i.e. adsorption, ion-exchange, stripping, chemical oxidation, and membrane separation) takes place. The last steps for the textile wastewater treatment process are the sludge processing and disposal steps (Gupta and Suhas, 2009).

In general, textile wastewater treatment methods include physical, chemical and biological treatments. These methods can be applied either individually or together in various combinations.

Physical treatment involves only particle separation processes and there is no chemical or biological changes carried out (Metcalf and Eddy, 2004). Example of the treatment processes are adsorption (Low et al., 2011; Lin et al., 2013), sedimentation (He et al., 2015; Walker and Narbaitz, 2016), aeration (Wu and He, 2012), filtration (Zuo et al., 2015; Zhao et al., 2016), etc.

Chemical treatment mainly involves the use of oxidizing agents such as ozone (O_3), hydrogen peroxide (H_2O_2), and permanganate (MnO_4) to modify the chemical composition of dyes (Metcalf and Eddy, 2004). The cost of this treatment process is largely dependent on the chemical used. Chemical treatment process has a satisfactory result in removing disperse, sulfur, and vat dyes (Verma et al., 2012). The disadvantages of the treatment process are large quantities of concentrated sludge produced, pH dependent, not effective for highly soluble dyes and not effective in treating acid and basic dyes (Hai et al., 2007). Examples of chemical treatment processes are ozonation (Tehrani-Bagha et al., 2010; Hu et al., 2016), coagulation-flocculation (Yeap et al., 2014; Lau et al., 2014), liquid-liquid extraction (Muthuraman and Teng, 2009, 2010), and sonolysis (Vassilakis et al., 2004; Khataee et al., 2015).

Biological treatment involves the use of microorganisms to decompose organic matters during wastewater treatment. It is the most economical alternative treatment compared to the physical and chemical processes. Examples of biological treatments generally used for the treatment of textile industrial effluents are microbial degradation, adsorption by living or dead microbial biomass and bioremediation systems using microorganisms (McMullan et al., 2001).

The biological process can be aerobic (in the presence of oxygen) (Franca et al., 2015; Liu et al., 2015), anaerobic (without oxygen) (Wong et al., 2009; Hahn and Figueroa, 2015) or combined aerobic-anaerobic (Yang et al., 2016). The main drawbacks of the biological treatment are less feasibility in design and operation, sensitivity to some chemicals, low biodegradability of the COD and dyes, larger land area requirement and longer time required for decolorization-fermentation processes (Dilaver and Kargi, 2009).

The present study focuses on the adsorption of Rhodamine B dye on a locally available biomass.

2.3.1 Adsorption

The process of adsorption involves accumulation of a substance at the interface between two phases such as solid and liquid or solid and gas. It can also be defined as a process that transfers pollutants from the effluent to a solid phase thereby reducing the bioavailability of toxic species to living organisms (Bhatnagar and Sillanpaa, 2009; Ribas et al., 2014). Solids have been widely used for substance removal from either gaseous or liquid phase since biblical times. This process involves the preferential partitioning of substances from the gaseous or liquid phase onto the surface of a solid substrate. Thus, adsorption is different from absorption, a process in which materials are transferred from one phase (liquid phase or gaseous phase) to another interpenetrates the second phase to form a solution (Weber, 1972). Figure 2.1 shows the definitions of adsorbent and adsorbate.

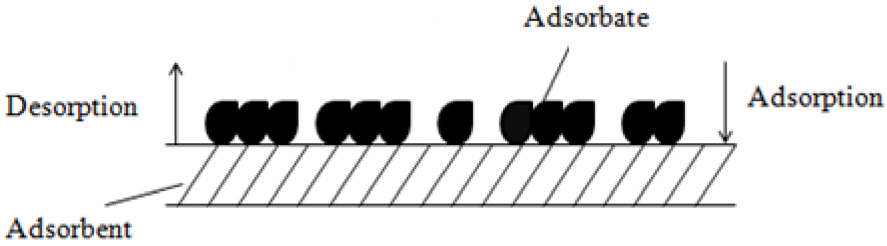

Figure 2.1: Definitions of adsorbent and adsorbate.

The substance to be removed from liquid or gaseous phase at the interface is called adsorbate. Adsorbent can be defined as the solid, liquid, or gas phase onto which the adsorption takes place (Butt et al., 2011).

Generally, transformation of adsorbate to the porous media adsorbent follows four steps, (i) bulk solution transport; i.e. transportation of adsorbate from bulk solution to the hydrodynamic boundary layer (liquid-solid interface) surrounding the adsorbent. (ii) external diffusion; i.e. transportation of the asorbate from the bulk to the external surface of the adsorbent. (iii) intraparticle diffusion. (iv) adsorption; i.e. adsorbate is attached onto the available active sites on the adsorbent surface (Wang et al., 2008).

2.3.2 Classification of Adsorption

On the whole, adsorption process largely depends on the nature of force existing between adsorbate molecules and adsorbent. Adsorption can be categorized into physical adsorption (physisorption) and chemical adsorption (chemisorption).

2.3.2(a) Physisorption

Physisorption involves intermolecular forces such as van der waals and dipole forces between the adsorbent and the adsorbate. This process is completely nonspecific reversible under high temperature and pressure. A physisorption molecule is not attached to a specific site on the solid surface, spontaneously it can leave the surface after a certain time (Sawyer et al., 2003).

2.3.2(b) Chemisorption

Chemisorption occurs as a result of the formation of a chemical linkage (often covalent) between the adsorbent and adsorbate giving a shorter bond length and higher bond energy (Montgomery, 1985). Table 2.2 presents the properties and characteristics of physisorption and chemisorption.

Table 2.2 Properties and characteristics of physisorption and chemisorption (Atkins, 1994).

Properties/ Characteristics	**Physisorption**	**Chemisorption**
Adsorption temperature	Adsorption process decreases with the increase of temperature	Adsorption process increases with the increase of temperature
Adsorption energy	Exothermic or endothermic, 40-200 kJ/mol	Merely exothermic < 40 kJ/mol
Nature of adsorption	Non-dissociative and reversible	Frequently dissociative and irreversible
Adsorption site	Monolayer or multilayer	Monolayer
Adsorption process	Non-activated and fast	Activated and slow
Desorption process	Desorption is possible	Desorption is impossible

For chemisorption, the adsorption process is irreversible and increases with temperature. The adsorption energy is merely exothermic with the value of less than 40 kJ/mol. However, for physisorption, the adsorption process is reversible and decreases with the increases of temperature. The adsorption energy has the value between 40-200 kJ/mol.

2.4 Kinetic Study

Adsorption kinetic study is a vital characteristic in wastewater treatment as it illustrates the adsorbate uptake rate, which in turn controls the residence time of the adsorbate uptake at solid-liquid interface (Dąbrowski, 2001). The pseudo-first order and pseudo-second order models are the most commonly used kinetic models for studying solid-liquid interactions. In pseudo-first order kinetic model, adsorption process is controlled by diffusion and mass transfer of the dye molecules to the adsorption site, whereas in pseudo-second order kinetic model, chemisorption is the rate limiting step (Crini and Badot, 2008; Nair et al., 2014).

2.4.1 Pseudo-First Order Model

Pseudo-first order model was proposed by Lagergren (1898). The pseudo-first-order equation can be written as Equation (2.1):

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

Integrating Equation (2.1) for the boundary conditions, t=0 to t=t and q_t=0 to q_t=q_t, generates Equation (2.2):

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

where k_1 is the rate constant of pseudo-first order model (min^{-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). The value of k_1 can be obtained by plotting $\ln(1-\frac{q_t}{q_e})$ versus *t*.

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

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 Equation (2.4):

$$\frac{1}{q_t} = \frac{1}{q_e} + \frac{1}{k_2 q_e^2 t} \qquad (2.4)$$

where k_2 (g/mg.min) is the pseudo-second order rate constant. This equation can also be written as Equation (2.5):

$$\frac{1}{q_t} - \frac{1}{q_e} = \frac{1}{k_2 q_e^2 t} \qquad (2.5)$$

The value of k_2 can be obtained by plotting $\frac{1}{q_t} - \frac{1}{q_e}$ versus $\frac{1}{t}$.

2.5 Equilibrium Study

The adsorption isotherm gives the relationship between mass of adsorbate adsorbed per unit weight of adsorbent in equilibrium and the concentration of adsorbate at liquid-phase equilibrium (Lata et al., 2007). It is a basic requirement for the design of adsorption system. A number of isotherms have 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 Equation (2.6):

$$q_e = \frac{Q_0 K_L C_e}{1 + K_L C_e} \tag{2.6}$$

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 monomolecular layer (mg/g), and K_L (L/mg) is the Langmuir constant related to the affinity of the binding sites. The values of Q_0 and K_L are determined from intercept and slopes of the linear plots of $\frac{C_e}{q_e}$ versus C_e. The Langmuir model can be represented in the linear form as shown in Equation (2.7):

$$\frac{C_e}{q_e} = \frac{1}{Q_0 K_L} + \frac{C_e}{Q_0} \tag{2.7}$$

A linear plot of $\frac{C_e}{q_e}$ versus C_e suggests the applicability of the Langmuir model for the system.

An essential characteristics of the Langmuir isotherm can be expressed in terms of separation factor or equilibrium parameter, $\mathrm{R_L}$, a dimensionless constant (Weber and Chakkravarti, 1974), which is given by Equation (2.8):

$$R_L = \frac{1}{(1 + K_L C_0)} \tag{2.8}$$

A value of $0 < R_L < 1$ shows unfavourable adsorption conditions;

$R_L < 1$ shows unfavourable adsorption conditions;

$R_L = 1$ shows linear adsorption conditions; and

$R_L = 0$ shows irreversible adsorption conditions.

2.5.2 Freundlich Isotherm

Freundlich model is an empirical equation that assumes heterogenous adsorption due to the diversity of adsorption active sites (Freundlich, 1907). The Freundlich equation is given as Equation (2.9):

$$q_e = K_F C_e^{1/n} \qquad (2.9)$$

where K_F is Freundlich isotherm constant (mg/g $(L/mg)^{1/n}$), an indicator for adsorption capacity and 1/n is the adsorption intensity. A value of $0 < 1/n < 1$ shows adsorption surface homogeneity, as the value gets closer to 0 the adsorption process is heterogeneous (Hameed et al., 2007). A value for $1/n < 1$ shows a normal Langmuir isotherm while $1/n > 1$ indicates cooperative adsorption (Fytianos et al., 2000). The linear form of Freundlich equation is given in Equation (2.10):

$$\ln q_e = \ln K_F + (1/n) \ln C_e \qquad (2.10)$$

The values of K_F and n are calculated from the intercept and slope of the plot of $\ln q_e$ versus $\ln C_e$.

2.5.3 Temkin Isotherm

Temkin isotherm (Temkin and Pyzhev, 1940) discussed on the adsorbent-adsorbate interactions. Based on the isotherm, the heat of adsorption of all the molecules in the layer would decrease linearly with coverage due to adsorbent-adsorbate interactions. The adsorption is described by a consistent distribution of binding energies, up to some maximum binding energy. The Temkin isotherm can be expressed as Equation (2.11):

$$q_e = \frac{RT}{b_T} \ln(A_T C_e) \qquad (2.11)$$

where b_T is Temkin isotherm constant related to heat of adsorption in J/mol, A_T is the Temkin isotherm constant in L/g. R is the universal gas constant with the value of

8.314 J/mol.K and T is the absolute solution temperature in K. The values of $\frac{RT}{b_T}$ and A_T are calculated from the intercept and slope of the plot of q_e versus $ln\ Ce$

2.5.4 Dubinin-Radushkevich (DR) Isotherm

Dubinin-Radushkevich (DR) Isotherm is used for the analysis of isotherms of a high degree of rectangularity (Dubinin and Radushkevich, 1947). DR isotherm can be expressed as Equation (2.12):

$$q_e = Q_{DR} \exp(-B\varepsilon^2) \tag{2.12}$$

where ε can be correlated in Equation (2.13):

$$\varepsilon = RT \ln(1 + \frac{1}{C_e}) \tag{2.13}$$

The constant B establishes the mean free energy E of adsorption per molecule of the adsorbate when it is transferred to the surface of the solid from infinity in the solution. Q_{DR} is the Dubinin-Radushkevich constant. The equation for mean free energy is expressed as Equation (2.14):

$$E = \left[\frac{1}{\sqrt{2B}}\right] \tag{2.14}$$

The values of Q_{DR} and E are calculated from the intercept and slope of $ln\ q_e$ versus ε^2. Table 2.3 presents the compilation of results of the applicability of kinetic and isotherm models for dye adsorption. Most of the dye adsorption studies followed pseudo-second order kinetic model and Langmuir isotherm where chemisorptions is the rate limiting step and maximum adsorption takes place at specific homogeneous sites within the adsorbent.

Table 2.3 Kinetic and isotherm studies of textile dye adsorption.

Adsorbent	**Dye**	**Kinetic model**	**Isotherm model**	**Reference**
Bagasse fly ash	Orange-G	Pseudo-second order	Freundlich	Mall et al., 2006
Chitosan	Remazol black 13	Pseudo-first and second order	Langmuir	Annadurai et al., 2008
Basic oxygen furnace slag	Reactive Blue 19 Reactive Black 5 Reactive Red 120	Pseudo-first order	Langmuir and Redlich–Peterson	Xue et al., 2009
Tunisian olive waste cake	Lanaset grey G	Pseudo-first order	Langmuir	Baccar et al., 2010
Coconut coir	Malachite green	Pseudo-second order	Langmuir and Freundlich	Uma et al., 2013
Rice husk	Methylene blue	Pseudo-second order	Langmuir	Chen et al., 2013
MgO decked multi-layered grapheme	Safranin O	Pseudo-second order	Langmuir	Rotte et al., 2014
Poly(methacrylic acid)/zeolite hydrogel composites	Basic yellow 28	Pseudo-first order	Langmuir and Temkin	Panic and Velickovic, 2014
Spent coal based activated carbon	Methylene blue	Pseudo-second order	Langmuir	Duan et al., 2014
Macore fruit shell	Methylene blue, Methyl orange	Pseudo-second order	Langmuir and Freundlich	Aboua et al., 2015
activated carbon/γ-Fe2O3 nano-composite	Alizarin red S	Pseudo-second order	Langmuir	Fayazi et al., 2015
Ag-doped hydroxyapatite	Congo red	Pseudo-second order	Langmuir	Srilakshmi and Saraf, 2016
Malt bagasse	orange solimax TGL	Pseudo-second order	Langmuir	Fontana et al., 2016
Cerastoderma lamarcki shell	Malachite green	Pseudo-second order	Freundlich	Kazemi et al., 2016

Table 2.3 (continued)

Adsorbent	**Dye**	**Kinetic model**	**Isotherm model**	**Reference**
Bagasse	Methylene blue	Pseudo-second order	Langmuir and Freundlich	Low et al., 2011
Cogongrass	Methylene blue	Pseudo-second order	Langmuir	Su et al., 2014
Raphia hookerie fruit epicarp	Rhodamine B	Pseudo-second order	Freundlich	Inyinbor et al., 2016
MIL-68(In)-NH2/graphite oxide (GO) composites	Rhodamine B	Pseudo-second order	Langmuir	Yang et al., 2016
Aleurites Moluccana seeds	Rhodamine B	Pseudo-second order	Sips isotherm	Postai et al., 2016
Gum Ghatti/Fe_3O_4	Rhodamine B	Pseudo-second order	Langmuir	Mittal and Mishra, 2014
Kaolinite	Rhodamine B	Pseudo-second order	Langmuir	Khan et al., 2012
Carnauba palm leaves	Rhodamine B	Pseudo-second order	Freundlich	Lacerda et al., 2015
Lythrum salicaria L. with pyruvic acid	Rhodamine B	Pseudo-second order	Langmuir	Huang et al., 2016

2.6 Activated Carbon

Activated carbon is a crude form of graphite, which has a highly porous, random or amorphous structure with broad range of pore sizes, from visible cracks, crevices and slits of molecular dimensions (Sun et al., 2013). In the 1940s activated carbon was employed as an adsorbent for wastewater treatment (Gupta and Ali, 2013). Typically, activated carbon includes a broad range of carbonaceous materials, possess high surface area (that can reach 2000 m^2/g), well defined microporous structure (average pore opening is about 1.5 nm), and high degree of surface reactivity (Streat et al., 1995). Commercial activated carbons are mainly prepared from coal and pine wood. However, activated carbon is expensive. This situation compelled scientists toward the development of low cost adsorbents i.e. alternatives of activated carbon (Ali et al., 2012).

2.7 Development of Low-Cost Adsorbents

Currently, there are many studies on the development of low-cost adsorbents using natural materials, biomass, and agricultural waste. In general, an adsorbent can be assumed to be “low-cost” if it requires little processing and is abundant in nature. It could also be waste material from an industry or it's by-products, which have lost economic value even after further processing (Yagub et al., 2014). The use of waste products which have little or no economic value for developing low-cost adsorbents gives advantages in waste minimization, recovery and reuse. In other words, waste treatment by adsorption using low-cost adsorbent is a demanding area as it has benefits in both water treatment and waste management (Yagub et al., 2014).