

**ACTIVATED CARBON PREPARED FROM POMEGRANATE
PEEL MICROWAVE ASSISTED KOH ACTIVATION
FOR DYES ADSORPTION**

by

NUR AZREEN BINTI AHMAD PUAD

**Thesis submitted in partial fulfillment of the requirements
for the degree of
Master of Science**

July 2013

ACKNOWLEDGEMENT

In the name of Allah, the most Compassionate and the Most Merciful;

Alhamdulillah, thanks to Allah S.W.T., with His willing gave me the opportunity to complete this thesis. First of all, I would like to thanks to my supervisor, Assoc. Prof. Dr. Mohd Azmier Ahmad for the guidance, encouragement, continuous support and ideas throughout the completion of this research.

I would like to thanks to the School of Chemical Engineering, Universiti Sains Malaysia for the utilization of the facilities and all staffs for your knowledge, help and advice during the research and class session.

Special gratitude to my parents, Mr. Ahmad Puad Bin Ariffin and Madam Rohana Binti Khalid, for their unconditional love, encourage and support me throughout my study. They have taught me that no matter how hard life has become, determination and hard work will steer me towards my destination. Last but not least, to my entire friends; thanks for your helps and the great moments being with you all.

Nur Azreen Ahmad Puad

July 2013

TABLE OF CONTENTS

	Page
ACKNOWLEDGEMENT	ii
TABLE OF CONTENTS	iii
LIST OF TABLES	vi
LIST OF FIGURES	vii
LIST OF SYMBOLS	ix
LIST OF ABBREVIATIONS	xii
ABSTRAK	xiii
ABSTRACT	xiv
CHAPTER ONE: INTRODUCTION	
1.1 Dyes applications and environmental issues	1
1.2 Dyes removal by adsorption	2
1.3 Problem statements	3
1.4 Research objectives	4
1.5 Scope of research	5
1.6 Thesis organization	5
CHAPTER TWO: LITERATURE REVIEW	
2.1 Dyes applications in textiles industries	6
2.2 Dyes treatment by adsorption	7
2.3 Activated carbon precursor	8
2.4 Microwave technology	9
2.4.1 Microwave assisted preparation of activated carbon	10
2.5 Adsorption Isotherm	11
2.5.1 Langmuir isotherm	12
2.5.2 Freundlich isotherm	13
2.5.3 Temkin isotherm	13
2.5.4 Dubinin-Radushkevich isotherm	14
2.5.5 Sips isotherm	15
2.5.6 Vieth-Sladek isotherm	15
2.5.7 Brouers-Sotolongo isotherm	16
2.5.8 Radke-Prausnitz isotherm	16
2.6 Adsorption kinetics	17
2.6.1 Pseudo-first-order kinetic model	17

2.6.2	Pseudo-second-order kinetic model	18
2.6.3	Elovich kinetic model	18
2.6.4	Avrami kinetic model	19
2.6.5	Validity of kinetic model	20
2.7	Adsorption thermodynamics	20
2.8	Adsorption mechanisms	21
2.8.1	Intraparticle diffusion model	21
2.8.2	Boyd model	22

CHAPTER THREE: MATERIALS AND METHODS

3.1	Materials	24
3.2	General description of equipment	26
3.2.1	PP char and PPAC preparation	26
3.2.2	Batch adsorption and analysis system	28
3.2.3	Characterization systems	29
3.3	Experimental procedures	29
3.3.1	Pomegranate peel preparation	29
3.3.2	Carbonization of pomegranate peel	30
3.3.3	KOH impregnation of char	30
3.3.4	Activation	30
3.3.5	Batch adsorption study	31
3.3.6	Batch kinetic studies	32
3.3.7	Adsorption thermodynamic	33
3.3.8	Adsorption mechanism	33
3.3.9	Experimental activities	34

CHAPTER FOUR: RESULTS AND DISCUSSIONS

4.1	Characterization of PPAC	35
4.1.1	Surface area and pore characteristics	35
4.1.2	Proximate and elemental analysis	36
4.1.3	Surface chemistry	38
4.1.4	Surface morphology	40
4.2	Batch adsorption studies of dyes on PPAC	41
4.2.1	Batch equilibrium studies	41
4.2.1 (a)	Effect of contact time and initial concentration of MG and RBBR	41
4.2.1 (b)	Effect of solution temperature	43
4.2.1 (c)	Effect of initial pH	44
4.2.2	Adsorption isotherm	46
4.2.2 (a)	MG and RBBR adsorption isotherms	46
4.2.3	Batch kinetic studies	52
4.2.4	Adsorption thermodynamic	58
4.2.5	Adsorption mechanism	59

CHAPTER FIVE: CONCLUSIONS AND RECOMMENDATIONS	
5.1 Conclusions	64
5.2 Recommendations	65
REFERENCES	66
APPENDICES	
Appendix A	74
Appendix B	75
Appendix C	76
Appendix D	78
Appendix E	82
Appendix F	86
Appendix G	88

LIST OF TABLES

	page	
Table 2.1	Various group of dyes and its application	6
Table 3.1	List of chemicals	24
Table 3.2	Properties of MG	25
Table 3.3	Properties of RBBR	25
Table 4.1	Surface area and pore characteristics of the samples	36
Table 4.2	Proximate and elemental analysis	38
Table 4.3	FTIR spectrum band assignment for PP, PP char and PPAC	39
Table 4.4	Isotherm values for PPAC-MG and PPAC-RBBR at 30°C	50
Table 4.5	Kinetic model constant values for PPAC-MG adsorption at 30°C	56
Table 4.6	Kinetic model constant values for PPAC-RBBR adsorption at 30°C	57
Table 4.7	Thermodynamic parameters for MG and RBBR adsorption onto PPAC	59
Table 4.8	Intraparticle diffusion model constant for adsorption of MG and RBBR onto PPAC at 30°C	62
Table C.1	Isotherm values for PPAC-MG and PPAC-RBBR at 45°C	76
Table C.2	Isotherm values for PPAC-MG and PPAC-RBBR at 60°C	77
Table E.1	Kinetic model constant values for PPAC-MG adsorption at 45°C	82
Table E.2	Kinetic model constant values for PPAC-MG adsorption at 60°C	83
Table E.3	Kinetic model constant values for PPAC-RBBR adsorption at 45°C	84
Table E.4	Kinetic model constant values for PPAC-RBBR adsorption at 60°C	85
Table G.1	Intraparticle diffusion model constant for adsorption of MG and RBBR onto PPAC at 45°C	88
Table G.2	Intraparticle diffusion model constant for adsorption of MG and RBBR onto PPAC at 60°C	89

LIST OF FIGURES

	page
Figure 3.1	Schematic diagram of the experimental setup for PP char production 26
Figure 3.2	Schematic diagram of the experimental setup for PPAC production 27
Figure 3.3	Schematic flow diagrams of experimental activities 34
Figure 4.1	FTIR spectrums; (a) PP; (b) PP char; and (c) PPAC 39
Figure 4.2	SEM micrographs of (a) PP (x6000); (b) PPAC (x6000) 40
Figure 4.3	Adsorption uptakes versus adsorption time at various initial concentrations at 30°C for a) MG and b) RBBR 41
Figure 4.4	Effect of solution temperature on MG and RBBR adsorption capacity of PPAC 43
Figure 4.5	Effect of initial pH on MG and RBBR removal on PPAC 44
Figure 4.6	Plots of (a) Langmuir, (b) Freundlich, (c) Temkin, (d) Dubinin-Radushkevich, e) Radke-Prausnite, (f) Sips, (g) Vieth-Sladek, (h) Brouers-Sotolongo isotherms for MG adsorption on PPAC 48
Figure 4.7	Plots of (a) Langmuir, (b) Freundlich, (c) Temkin, (d) Dubinin-Radushkevich, e) Radke-Prausnite, (f) Sips, (g) Vieth-Sladek, (h) Brouers-Sotolongo isotherms for RBBR adsorption on PPAC 49
Figure 4.8	Plots of separation factor versus dyes initial concentration of a) MG and b) RBBR for adsorption of PPAC at 30°C, 45°C and 60°C 51
Figure 4.9	Linearized plots of (a) pseudo-first-order; (b) pseudo-second-order; (c) Avrami, and (d) Elovich kinetic model for MG adsorption on PPAC at 30°C 53
Figure 4.10	Linearized plots of (a) pseudo-first-order; (b) pseudo-second-order; (c) Avrami, and (d) Elovich kinetic model for RBBR adsorption on PPAC at 30°C 54
Figure 4.11	Plots of intraparticle diffusion model for (a) MG adsorption and (b) RBBR adsorption on PPAC at 30°C 60
Figure 4.12	Boyd plots for adsorption of (a) MG and (b) RBBR on PPAC at 30°C 63
Figure A.1	Adsorption uptake versus adsorption time at various initial concentrations at 45°C for a) MG and b) RBBR 74

Figure A.2	Adsorption uptake versus adsorption time at various initial concentrations at 60°C for a) MG and b) RBBR	74
Figure B.1	Percentage removal versus time for a)MG at 30°C, b)MG at 45°C, c)MG at 60°C d) RBBR at 30°C, e)RBBR at 45°C and f)RBBR at 60°C	75
Figure D.1	Linearized plots of (a) pseudo-first-order; (b) pseudo-second-order; (c) Avrami, and (d) Elovich kinetic model for MG adsorption on PPAC at 45°C	78
Figure D.2	Linearized plots of (a) pseudo-first-order; (b) pseudo-second-order; (c) Avrami, and (d) Elovich kinetic model for MG adsorption on PPAC at 60°C	79
Figure D.3	Linearized plots of (a) pseudo-first-order; (b) pseudo-second-order; (c) Avrami, and (d) Elovich kinetic model for RBBR adsorption on PPAC at 45°C	80
Figure D.4	Linearized plots of (a) pseudo-first-order; (b) pseudo-second-order; (c) Avrami, and (d) Elovich kinetic model for RBBR adsorption on PPAC at 60°C	81
Figure F.1	Plots of intraparticle diffusion model for (a) MG adsorption and (b) RBBR adsorption on PPAC at 45°C	86
Figure F.2	Plots of intraparticle diffusion model for (a) MG adsorption and (b) RBBR adsorption on PPAC at 60°C	87

LIST OF SYMBOLS

		Unit
A	Arrhenius factor	-
A_i	Measured absorbance for component i	-
A_T	Constant for Temkin isotherm	L/g
b_c	Path length of the cell	-
b_T	Constant for Temkin isotherm	mg/g h
B_t	Constant for Boyd model	-
C	Solute/outlet concentration	mg/L
C_e	Concentration of adsorbate at equilibrium	mg/L
C_i	Constant for Intraparticle diffusion model	mg/g
C_t	Concentration of adsorbate at time, t	mg/L
C_o	Initial/inlet adsorbate concentration	mg/L
D_p	Average pore diameter	nm
E_a	Arrhenius activation energy of adsorption	kJ/mol
F	Fraction of solute adsorbed for Boyd model	-
K_F	Adsorption or distribution coefficient for Freundlich isotherm	mg/g (L/mg) ^{1/n}
K_L	Rate of adsorption for Langmuir isotherm	L/mg
k_{Av}	Avrami kinetic constant	-
k_{pi}	Adsorption rate constant for intraparticle diffusion model	mg/g h ^{1/2}
k_1	Adsorption rate constant for pseudo-first-order	1/h
k_2	Adsorption rate constant for pseudo-second-order	g/mg h
k_s	Sips isotherm model constant	L/mg
K_{BS}	Brouwers Sotolongo constant	-
K_{RP}	Radke-Prausnitz model constant	-
k_{VS}	Vieth-Sladek constant	-
m_{RP}	Radke-Prausnitz model exponent	-
m_s	Sips isotherm model exponent	-

N	Total number of experiments required/data point	-
n_{Av}	Avrami kinetic constant	-
n_F	Constant for Freundlich isotherm	-
Q_o	Adsorption capacity for Langmuir isotherm	mg/g
Q_m	Maximum adsorption capacity of adsorbent	mg/g
q_e	Amount of adsorbate adsorbed per unit mass of adsorbent at equilibrium	mg/g
q_t	Amount of adsorbate adsorbed per unit mass of adsorbent at time, t	mg/g
$q_{t, cal}$	Calculated adsorption uptake at time, t	mg/g
$q_{t, exp}$	Experimental adsorption uptake at time, t	mg/g
R	Universal gas constant	8.314 J/mol K
R_L	Separation factor	-
R^2	Correlation coefficient	-
S_{BET}	BET surface area	m ² /g
T	Absolute temperature	K
T	Time	h
V	Volume of the solution	L
V_{meso}	Mesopore volume	cm ³ /g
V_T	Total pore volume	cm ³ /g
W	Mass of adsorbent	g
w_c	Dry weight of prepared activated carbon	g
w_o	Dry weight of precursor	g
X	Activated carbon preparation variable	-
Y	Predicted response	-

Greek letters

ΔG°	Changes in standard free energy	kJ/mol
ΔH°	Changes in standard enthalpy	kJ/mol
Δq_t	Normalized standard deviation	%
ΔS°	Changes in standard entropy	J/mol K
α_{BS}	Brouwers-Sotolongo constant	-
α_{El}	Initial desorption rate for Elovich kinetic model	mg/(g min)
α_t	Adsorption fraction of time of Avrami kinetic model	-
ε_{λ}	Molar absorptivity coefficient of solute at wavelength	-
β_{El}	Desorption constant for Elovich kinetic model	g/mg
β_{VS}	Vieth-Sladek constant	-
λ	Wavelength	nm

LIST OF ABBREVIATIONS

AC	Activated carbon
BET	Brunauer-Emmett-Teller
FTIR	Fourier Transform Infrared
IR	Impregnation ratio
IUPAC	International Union of Pure and Applied Chemistry
MG	Malachite green
MSDS	Material Safety Data Sheet
PP	Pomegranate peel
PPAC	Pomegranate peel based activated carbon
RBBR	Remazol brilliant blue R
SEM	Scanning electron microscopy
STA	Simultaneous thermogravimetric analyser

**PENYEDIAAN KARBON TERAKTIF DARIPADA KULIT DELIMA MELALUI
PENGAKTIFAN KOH BERBANTUKAN GELOMBANG UNTUK
PENJERAPAN PEWARNA**

ABSTRAK

Penghasilan karbon teraktif berasaskan kulit buah delima (KTKBD) melalui pengaktifan KOH berbantuan gelombang mikro telah berjaya dikaji. KTKBD yang terhasil telah digunakan untuk penyingkiran pewarna malacit hijau (MH) dan remazol brilliant biru reaktif (RBBR) daripada larutan akuas. KTKBD mempunyai luas permukaan yang tinggi $941.02 \text{ m}^2/\text{g}$ dan menunjukkan struktur liang meso tidak seragam serta terdapat pelbagai kumpulan berfungsi pada permukaan KTKBD. Kesan kepekatan awal pewarna (50-500 mg/L), masa sentuh (0-24 h), suhu larutan ($30\text{-}60^\circ\text{C}$) dan pH larutan (2-12) telah dinilai melalui kajian penjerapan berkelompok. Jumlah penjerapan pewarna meningkat dengan peningkatan suhu, kepekatan awal pewarna dan masa sentuh. Penjerapan pewarna MH dan pewarna RBBR ke atas KTKBD adalah terbaik dipadankan oleh model Freundlich. Penjerapan kinetik MH dan RBBR ke atas KTKBD terbaik dipadankan oleh model kinetik pseudo-tertib kedua. Melalui kajian termodinamik, penjerapan pewarna MH dan RBBR ke atas KTKBD adalah berlaku secara jerapan fizikal, spontan dan endotermik. Melalui kajian mekanisma, kadar penjerapan dikawal oleh mekanisma serapan-filem.

**ACTIVATED CARBON PREPARED FROM POMEGRANATE
PEEL MICROWAVE ASSISTED KOH ACTIVATION
FOR DYES ADSORPTION**

ABSTRACT

The production of pomegranate peel based activated carbon (PPAC) through microwave assisted KOH activation has been successfully investigated. PPAC produced was used for removal of malachite green (MG) and remazol brilliant blue reactive (RBBR) dyes from aqueous solution. The PPAC has high surface area of 941.02 m²/g and demonstrated heterogeneous mesoporous type of pore structure with a presence of various functional groups on the PPAC's surface. The effects of adsorbate initial concentration (50-500 mg/L), contact time (0-24 h), solution temperature (30-60°C) and solution pH (2-12) were evaluated through batch adsorption test. All dyes adsorption uptakes increased with increasing temperature, initial dyes concentration and contact time. Adsorption of MG and RBBR dyes onto PPAC were best fitted by Freundlich model. Adsorption kinetic of MG and RBBR dyes onto PPAC were best fitted by pseudo-second-order kinetic model. From the thermodynamic study, the MG and RBBR adsorption onto PPAC were physically controlled type, spontaneous and endothermic in nature. From the mechanism study, the adsorption rate was governed by film diffusion mechanism.

CHAPTER ONE

INTRODUCTION

1.1 Dyes applications and environmental issues

Water pollution becomes among the major pollution contribution in the country. Approximately 0.02% amount of water are in the form of rivers, lake and streams. It is available to be used by the living organisms and attentions are needs to prevent any water pollution to occur (Olugbenga *et al.*, 2012). The major sources of wastewater that leads to the water pollution are produced from the textile and dyestuff industries compared to the cosmetic, paper, leather, pharmaceutical and food industries. Large proportions of dyes have been consumed by the textile industry to fulfill the demand for the production of cotton fabrics with brilliant colors (Sen and Demirer, 2003). This industry uses variety types of dyes such as reactive dyes and basic dyes as their main raw material (Olugbenga *et al.*, 2012).

Reactive dye is widely used for cotton dyeing. It has been characterized by nitrogen to nitrogen double bonds (N=N). Example of reactive azo dye is remazol brilliant blue reactive (RBBR) which normally used for polymeric dyes starting materials. The azo bond and associated chromophores describe the azo dyes color (Olugbenga *et al.*, 2011). For basic dye, malachite green (MG) is commonly used to color silk, wool, paper, cotton and leather (Mendez *et al.*, 2007). However, wastewaters containing reactive and basic dyes are complicated to treat because it consists of complex molecular structures. Both dyes are easily lost directly into water stream during washed off in textile dyeing process. Thus wastewaters containing both dyes need to be treated before released to the environment. The presence of these dyes could restrict the

downstream use of the wastewater, effect from the highly visible of the dyes, give some toxic effect on receiving bodies and aesthetically displeasing even in low dye concentration (Olugbenga *et al.*, 2012).

1.2 Dye removal by adsorption

There are several methods for dyes removal from wastewater includes coagulation, flocculation, adsorption, ozonation, membrane separation, ultrafiltration, photocatalytic degradation, electrochemical and fungal decolonization. Somehow, due to the high operation cost and sludge production, most of the methods are not widely used in dyes wastewater treatment. For example, on large scale industries, the chemical, electrochemical oxidation and coagulation methods were not feasible. However, the adsorption technique has been widely used due to the high efficiency in removing wide range of dyes from wastewater either in terms of low initial cost, easy to operate and simplicity of design (Theivarasu and Mylsamy, 2011).

Recently, many researchers have focused on the usage of activated carbon (AC) for dyes removal from aqueous solution. The high adsorption capacity, large surface area and large mesoporous structure of AC suitable for dyes adsorption (Theivarasu and Mylsamy, 2011). The initial pH, temperature, initial concentrations, and contact time are among the other factors that influenced the adsorption process (Shanti and Mahalakshmi, 2012). The utilization of the agro wastes for the AC production are widely evolved because it can decrease these waste disposal by converting them to products. Agro wastes such as mangosteen peel, oil palm fibre, date stones, palm shell, durian shell and tamarind wood, pearl millet husk, date pits, olive stone, and coconut shell were used as AC's precursor for removal dyes application.

Pomegranate fruit has the total annual production of about 1 million tonnes worldwide (Suat *et al.*, 2009). The pomegranates fruit is widely consumed fresh or in forms of juice, jams and wine. However, pomegranate peel has become a by-product of the pomegranate juice industry. In this work, pomegranate peel was used for AC's production.

1.3 Problem statements

The major problem faced by the textiles industries is the dyes removal from wastewater. This colored wastewater has been discharged to the water streams and and cause harm to the aquatic life and environment (Shanti and Mahalakshmi, 2012). Dyes contain acidic or caustic dissolved solids, toxic compounds, heavy metals, ammonia, alkali, salts and large amounts of pigments (Olugbenga *et al.*, 2012). Examples of the dyes discharged to the waste streams are MG, a basic dye, and RBBR, a reactive dye which are widely used in coloring cotton fabrics, color silk, wool, paper, cotton and leather (Mendez *et al.*, 2007).

The MG and RBBR dyes have complex chemical structures which are hard to be removed from the wastewater by using conventional methods such as biological treatment, chemical precipitation, membrane separation, and ultrafiltration (Mi-Hwa *et al.*, 2010). Therefore, the removals of MG and RBBR dyes from wastewater are necessary and adsorption via AC adsorbent was the most preferred process (Sarawut *et al.*, 2009). However, the usage of the commercial coal based AC is limited due to the nonrenewable and expensive precursor (Nazri *et al.*, 2011). This lead to the investigation of producing AC from renewable and cheap precursor particularly agrowastes.

The production of AC from agro wastes such as mangosteen peel, durian peel (Sarawut *et al.*, 2009), durian seed (Amri *et al.*, 2010), oil palm fibre, degreased coffee bean (Mi-Hwa *et al.*, 2010), rice husk (Rahman *et al.*, 2005), date stones, cocoa shell (Theivarasu and Mylsamy, 2011), rubber seed coat (Nazri *et al.*, 2011), palm shell, and Tamarind wood (Arivoli, 2009) have been reported previously. In this work, pomegranate peel was used for AC production via microwave assisted KOH activation for the removal of MG and RBBR dyes from aqueous solution. Previous study has been carried out by Ay *et al.*, (2012) and Moghadam *et al.*, (2013), for PPAC prepared by conventional activation step. The conversion of pomegranate peel into value added adsorbent as an alternative to commercial AC can reduced the cost for waste disposal and also potentially to solve the problem of dyes removal in wastewater treatment.

1.4 Research objectives

The objectives of the present study are:

- (i) To produce pomegranate peel activated carbon (PPAC) using microwave assisted KOH activation for the removal of malachite green (MG) and remazol brilliant blue reactive (RBBR) dyes from aqueous solution and
- (ii) To characterize the PPAC in terms of surface area, surface morphology, surface chemistry, proximate and element content.
- (iii) To study the effects of initial pH solution, contact time, initial dyes concentrations and temperature on the batch adsorption performance of MG and RBBR adsorption.
- (iv) To study the adsorption isotherm, kinetic, thermodynamic and mechanism of dyes onto PPAC.

1.5 Scope of research

The aim of the present study was to investigate the effect of the initial dyes concentrations, contact time, initial pH, and temperature on the adsorption of MG and RBBR onto PPAC. The PPAC preparation was done by using microwave assisted KOH activation. The PPAC was characterized in terms of surface area, surface morphology, proximate and element content, and surface chemistry. The MG and RBBR were used in the adsorption equilibrium, kinetic, thermodynamic and mechanism studies onto PPAC. The effect of dyes initial concentration (50-500 mg/L), contact time (0-24 h), solution temperature (30-60°C) and solution pH (2-12) for dyes adsorption onto PPAC were carried out using batch adsorption study.

1.6 Thesis organization

This thesis is arranged into five chapters starting with Chapter One which discusses the problem statement and objectives of the study. Chapter Two focus on the recent research related to present study. It covers on dyes applications in textiles industry, dyes treatment by adsorption, AC's precursor, AC preparation, microwave technology, batch adsorption study, AC characterization, adsorption isotherms, adsorption kinetics, adsorption thermodynamics and adsorption mechanisms. Chapter Three covers all the materials, equipment and methodology used in the present research, the batch adsorption test, batch kinetics studies, adsorption thermodynamics, adsorption mechanism and the flow diagram of the overall experiment that carried out. Chapter Four discusses about all the results and findings that have been obtained from the research. Lastly, the conclusions and recommendations are includes in Chapter Five.

CHAPTER TWO

LITERATURE REVIEW

2.1 Dyes applications in textiles industries

Large proportions of dyes have been consumed by the textile industry to fulfill the demand for the production of cotton fabrics with brilliant colors (Sen and Demirer, 2003). Variety types of dyes such as reactive dyes, basic dyes, solvent dyes, disperse dyes, sulfur dyes and direct dyes are used to color the cloths or fabrics (Olugbenga *et al.*, 2012). Dyes are normally obtained from coal tar and petroleum based intermediate, which are largely synthetic. Table 2.1 shows various groups of dyes and its applications in textile industries.

Table 2.1: Various group of dyes and its application (Gupta and Suhas, 2009)

Dyes	Applications
Direct	Cotton, rayon, cellulosic and blends
Vat dyes	Cotton, cellulosic fibers and blends
Sulfur	Cotton, cellulosic fibers
Organic pigments	Cotton, cellulosic, blended fabrics, paper
Reactive	Cellulosic fibers and fabric
Dispersed dyes	Synthetic fibers
Acid Dyes	Wool, nylon, silk, synthetic fibers, leather
Azoic	Printing inks and pigments
Basic	Silk, wool, tannin-mordanted cotton
Oxidation dyes	Hair
Developed Dyes	Cellulosic fibers and fabric
Mordant dyes	Cellulosic fibers and fabric, silk, wool
Optical or Fluorescent Brighteners	Synthetic fibers, leather, cotton, sports goods
Solvent dyes	Wood staining, solvent inks, waxes, colouring oils

2.2 Dyes treatment by adsorption

Adsorption is a mass transfer process which involved the displacement of the substance from the liquid phase onto a solid surface and attached by the physical or chemical interactions. There are two terms that important in the adsorption process which is adsorbent and adsorbate. The adsorbent is the solid phase and adsorbate is the molecule that adsorbed on the adsorbent. The adsorption using AC progressively performed and was increasingly recognized. The AC which has a high surface area is considered as one of the most effective adsorbent to be used in the dyes wastewater treatment (Theivarasu and Mysamy, 2011).

The adsorption capacity of AC depends on several factors such as textural properties of the AC surface (pore structure, surface characteristics, ash content and presence of the functional group), and also the solution conditions (pH and adsorbate concentration). The adsorption process in the dyes removal by using AC is a resulted of the interaction between the AC's surface and adsorbate. There are two types of adsorption process known as physical adsorption and chemisorption. Basically, in the physical adsorption process, the weak Van Der Waals forces resulted from the intermolecular attraction hold the molecules on the carbon surface, thus make the carbon and adsorbate unchanged chemically (Salleh *et al.*, 2011).

During the physical adsorption process, the adsorbed molecules are free to move about the surface of the adsorbent, which not affixed to the adsorbent surface. In chemisorption process, the much stronger forces that are chemical bond hold and react chemically between molecules with the carbon surface. During the

chemisorption process, the adsorbed molecules not freely move from one to another surface site and a layer over the surface also developed (Rahman *et al.*, 2005).

2.3 Activated carbon precursor

Commercially available AC is usually derived from coal and petroleum residue. This AC is expensive due to the use of non-renewable and relatively expensive starting material (Demirbas, 2009). There is a need to produce AC from alternative material that is cheaper, renewable and readily available. Typically, the preparation of the AC from agrowastes such as rambutan peel (Ahmad and Alrozi, 2011), date stone (Theydan and Ahmed, 2012), corn cobs and soya stalks (Ioannidou *et al.*, 2010), and pine cone (Mahmoodi *et al.*, 2011) have been done recently. Ay *et al.*, (2012) and Moghadam *et al.*, (2013) have studied on the preparation of PPAC by conventional heating for the removal of lead (II) ions and Acid Blue 40, and Fe (II) from aqueous solution, respectively.

The BET surface area of pomegranate peels reported by Ay *et al.*, (2012) was 10 m²/g and the chemical composition of carbon, hydrogen, nitrogen and sulfur were 43.94, 4.73, 1.23 and 0.55%, respectively. There are various functional groups present on the pomegranate peels which are the amino, carboxylic, hydroxyl and carbonyl. The maximum adsorption capacities obtained in this work are 193.9 mg/g and 138.1 mg/g for lead (II) ions and Acid Blue 40, respectively. In other study, the PPAC prepared via conventional heating has the porosity of 60%, moisture content of 6.79 wt%, and ash content of 9.98 w%. The maximum adsorption capacity of Fe (II) onto PPAC prepared was 18.52 mg/g (Moghadam *et al.*, 2013).

2.4 Microwave technology

Microwave is an electromagnetic energy, where the mutual interaction between media converts the applied energy into heat (Zhao and Chen, 2008). Electromagnetic radiation in the microwave frequency range from 300 MHz to 300 GHz ($\lambda=1$ mm to 100 cm) is known as microwave radiation. Generally, domestic and industrial microwave ovens operate at frequency of 2.45 GHz ($\lambda= 12.2$ cm) and energy of 1.02×10^{-5} eV, or frequency around 900 MHz ($\lambda=37.2$ cm) which can provide up to 100 kW in larger heating applications. The potential ability of the microwaves has been proved with the used of microwave oven which providing rapid and energy-efficient heating applications (Foo and Hameed, 2011a).

The materials that interact with microwave can be classified into three main groups which are conductor, insulator and absorber. The conductor is the material which microwaves are reflected and cannot penetrates such as metals and alloys. The insulators are low loss materials such as glasses, ceramics and Teflon, which are substantially transparent to the microwaves and has property to partially reflect and transmit the incident waves travelling through the material. While the absorbers are high loss materials such as aqueous solution or polar solvent, which absorb microwave radiation, direct energy transfer, and effectively heated at room temperature (Ji *et al.*, 2007).

Materials that absorb microwave radiation called as dielectrics, which usually characterized with very few free charge carriers and exhibit dipole movement. The dipoles within materials will attempt to realign themselves and flip around the applied field when microwaves are applied to the dielectric materials

with an oscillating electric field. The friction inside dielectric materials generates by the dipole movement and the internal energy is dissipated as heat (Foo and Hameed, 2011a).

2.4.1 Microwave assisted preparation of activated carbon

Recently, the preparation of AC by microwave irradiation has received wide concern among the researchers. Examples of environmental applications that involved the use of microwaves include phase separation and extraction processes, pyrolysis, soil remediation, coal desulphurization and chemical catalysis. There are some of the advantages that owned by microwave heating compared to the conventional heating. In conventional heating, the heat is transferred from the surface towards the center core by convection, conduction and radiation.

In contrast, microwave heating involved the transfer of electromagnetic energy to thermal energy. The heat in the microwave can be regenerated throughout the volume of material, rather than from external source (volumetric heating). Hence, both heating systems possess opposite thermal gradients and temperature distribution. The other potential advantages of microwave heating over conventional heating are (i) the treatment time can be considerably reduced, (ii) rapid heating, (iii) uniform heating, (iv) higher heating rate, (v) cleaner energy sources, (vi) no direct contact between the heating source and heated materials, (vii) reduced the equipment size, (viii) rapid temperature rise which about 26.7K/min, and (ix) energy saving. Microwave energy is derived from electrical energy with a conversion efficiency of approximately 50% for 2450 MHz and 85% for 915 MHz. Other than