

SYNTHESIS AND CHARACTERIZATION OF RENEWABLE CARBON
CRYOGEL BEADS FROM EMPTY FRUIT BUNCH FOR ADSORPTION OF
ETHYL ORANGE

DILAELEYANA BINTI ABU BAKAR SIDIK

UNIVERSITI TEKNOLOGI MALAYSIA

SYNTHESIS AND CHARACTERIZATION OF RENEWABLE CARBON
CRYOGEL BEADS FROM EMPTY FRUIT BUNCH FOR ADSORPTION OF
ETHYL ORANGE

DILAELEYANA BINTI ABU BAKAR SIDIK

A thesis submitted in fulfilment of the
requirements for the award of the degree of
Master of Engineering (Chemical)

Faculty of Chemical Engineering
Universiti Teknologi Malaysia

JULY 2013

*To my beloved husband, Kamarizan Jawahir and daughter Damia Khaisara
Kamarizan for their constant encouragement and motivation and also to my
supportive family members for their Love, Prayer and Support*

ACKNOWLEDGEMENT

This thesis has been accomplished by the accumulation of successes and failures of my Master research. Thanks to ALLAH S.W.T because of HIS guidance and blessing, finally I can fulfill my Master research successfully. In general, my deepest thanks and appreciations to those who are giving me a lot of supports and ideas to make my research targets accomplished.

In preparing this thesis, I was in contact with many people, academicians and practitioners. They have contributed towards my understanding and thoughts. In particular, I wish to express my sincere appreciation to my main supervisor, Dr Norzita Ngadi for her continuous encourage, guidance and support throughout this research work. Her critical comments and deep thoughts have encouraged me to look deep insights into my research and brushed up my experimental results. My deep pleasure also to my co-supervisor, Prof. Dr. Nor Aishah Saidina Amin for her guidance and advices related to this project. Without their continued support and interest, this thesis would not have been the same as presented here.

Besides, I wish to express my appreciation to Chemical Reaction Engineering Group (CREG, UTM) for their co-operation, support and pleasant friendship. Last but not least, I would also like to gratefully acknowledge the financial support by Zamalah Universiti Teknologi Malaysia (UTM). Thanks a lot to my beloved family and friends for their support, love and prayer.

ABSTRACT

Liquefaction of empty palm fruit bunch (EFB) to lignin was carried out by using ionic liquid [BMIM]Cl. Response surface methodology (RSM) was employed to identify the optimum condition for lignin yield. The liquefied product (i.e. lignin EFB) was reacted with furfural to synthesize resin. The resin was washed, freeze-dried and carbonized to obtain carbon cryogel beads (CCBs). The CCBs were then chemically activated with potassium hydroxide (KOH) to produce activated CCBs (A-CCBs). Both CCBs and A-CCBs were characterized for their morphology and physical properties using Fourier Transform Infrared Spectroscopy, Scan Electron Microscope, X-Ray Diffraction, Breuner, Emmer and Teller (BET) and Thermogravimetric Analysis. The performance of A-CCBs towards the removal of ethyl orange dye via adsorption process was performed. The adsorption mechanism was revealed through adsorption kinetic, isotherm and thermodynamic properties. The results indicate that the optimum lignin yield of 26.6% was produced at temperature of 150.5°C, time of 151 minutes, ionic liquid to EFB weight ratio of 3:1, and sulfuric acid concentration of 4.73 %. The results obtained reveal that chemical activation with KOH increased the BET surface area to 58 m²g⁻¹ and 1068 m²g⁻¹ for CCBs and A-CCBs, respectively. The experimental data were appropriately described by the Langmuir model with correlation coefficient of 0.997. The adsorption kinetics followed the pseudo-second order. The negative values of the free energy change indicated the adsorption is spontaneous. The positive value of enthalpy change (414.36 J/mol) and entropy change (191.97 J/K.mol) confirmed the endothermic nature and showed the increment of structural changes at solid-solution interface during adsorption process, respectively. It can be concluded that the prepared A-CCBs derived from lignin EFB provide reasonable ethyl orange dye removal capability by up to 83% removal capacity.

ABSTRAK

Pencairan tandan kosong sawit (EFB) kepada lignin telah dijalankan dengan menggunakan cecair ionik [BMIM]Cl. Kaedah respon permukaan (RSM) telah digunakan untuk menentukan keadaan optimum bagi penghasilan lignin. Produk cecair (iaitu lignin EFB) telah bertindak balas dengan furfural untuk mensintesis resin. Resin dibasuh, dibeku-kering dan dibakar untuk mendapatkan manik karbon kryogel (CCBs). CCBs kemudiannya diaktifkan secara kimia dengan kalium hidroksida (KOH) untuk menghasilkan aktif karbon kryogel (A-CCBs). Kedua-dua CCBs dan A-CCBs telah dicirikan untuk morfologi dan sifat fizikal menggunakan Transformasi Fourier Inframerah Spektroskopi, Mikroskopi Pengimbas Electron, Pembelauan sinar-X, Breuner, Emmer dan Teller (BET) dan Analisis Termogravimetri. Prestasi A-CCBs terhadap penyingkiran pewarna etil oren melalui proses penjerapan telah dilaksanakan. Mekanisma penjerapan telah dinyatakan melalui kinetik penjerapan, isoterma dan sifat termodinamik. Keputusan menunjukkan bahawa hasil optimum lignin sebanyak 26.6% telah dihasilkan pada suhu 150.5°C, masa 151 minit, nisbah berat cecair ionik kepada EFB 3:1, dan kepekatan asid sulfurik 4.73%. Keputusan yang diperolehi menunjukkan bahawa pengaktifan kimia dengan KOH meningkatkan luas permukaan BET kepada 58 m²g⁻¹ dan 1068 m²g⁻¹ untuk CCBs dan A-CCBs, masing-masing. Data ujikaji adalah sesuai dijelaskan dengan model Langmuir dengan nilai pekali korelasi 0.997. Kinetik penjerapan mengikut tertib pseudo-kedua. Nilai negatif perubahan tenaga bebas menunjukkan penjerapan adalah spontan. Nilai positif perubahan entalpi (414.36 J/mol) dan perubahan entropi (19.97 J/K.mol) mengesahkan sifat endotermik dan menunjukkan pertambahan perubahan struktur di permukaan larutan pepejal semasa proses penjerapan. Kesimpulannya, A-CCBs yang dihasilkan daripada lignin EFB berupaya menyingkirkan pewarna etil oren sehingga 83% keupayaan penyingkiran.

TABLE OF CONTENTS

CHAPTER	TITLE	PAGE
	TITLE	i
	DECLARATION	ii
	DEDICATION	iii
	ACKNOWLEDGMENTS	iv
	ABSTRACT	v
	ABSTRAK	vi
	TABLE OF CONTENTS	vii
	LIST OF TABLES	xi
	LIST OF FIGURES	xiii
	LIST OF SYMBOLS	xvii
	LIST OF ABBREVIATIONS	xix
	LIST OF APPENDICES	xxi
1	INTRODUCTION	1
	1.1 Research Background	1
	1.2 Statement of Problem	4
	1.3 Objectives of Study	6
	1.4 Scope of Study	7
	1.5 Significance of study	9
2	LITERATURE REVIEW	10
	2.1 Lignocellulosic	10
	2.1.1 Palm Oil Empty Fruit Bunch	12

2.1.2	Lignin	13
2.1.3	Lignin Extraction	15
2.2	Thermal Chemical Conversion of Biomass	16
2.2.1	Liquefaction	17
2.2.2	Pretreatment with Ionic Liquid	18
2.2.3	Regeneration of Ionic Liquid	19
2.3	Carbon Gel	20
2.3.1	Carbon Cryogel	22
2.3.2	Carbon Aerogel	24
2.3.3	Carbon Xerogel	24
2.4	Modification of the textural properties of carbon gel	25
2.4.1	Impregnation with Metal	25
2.4.2	Physical or chemical activation	27
2.4.3	Synthesis condition	28
2.5	Textile Industrial Waste	30
2.5.1	Ethyl orange	31
2.5.2	Method of dye removal	32
2.5.3	Effects of various parameters on adsorption process	33
2.5.4	Adsorption Isotherms	35
2.5.4.1	Langmuir Isotherm	35
2.5.4.2	Freundlich Isotherm	37
2.5.4.3	Temkin Isotherm	37
2.5.5	Adsorption Kinetics	38
2.5.5.1	Pseudo-First Order	38
2.5.5.2	Pseudo-Second Order	39
2.5.5.3	The Intraparticle Diffusion Model	40
2.5.6	Thermodynamic adsorption	41
2.6	Optimization Studies	42
2.6.1	Response Surface Methodology	42
3	RESEARCH METHODOLOGY	44
3.1	Introduction	44

3.2	Materials	47
3.3	Sample preparation	47
3.4	Composition of untreated EFB	48
3.5	Production of lignin from EFB via liquefaction process	49
3.5.1	Regeneration of Ionic Liquid (IL)	50
3.5.2	Design of Experiment	51
3.5.3	Analyses	51
3.5.3.1	UV analyses	51
3.5.3.2	FTIR Measurements	52
3.6	Synthesis and Characterization of CCB	52
3.6.1	Synthesis of CCBs	52
3.6.2	Chemical activation of CCBs	53
3.6.3	Characterization of gels	54
3.7	Adsorption studies to test performance of A-CCBs	55
4	PRODUCTION OF LIGNIN FROM EFB VIA LIQUEFACTION	57
4.1	Introduction	57
4.2	Response Surface Methodology (RSM)	58
4.3	Statistical Analysis of Lignin EFB yield	61
4.4	Interaction effects of temperature and time on the lignin yield	66
4.5	Interaction effects of IL/EFB and catalyst concentration on the lignin yield	69
4.6	Optimization of lignin yield	71
4.7	UV-Vis Spectra	73
4.8	FTIR Analysis	74
4.9	Regeneration of Ionic Liquid (BMIM[Cl])	76
5	SYNTHESIS AND CHARACTERIZATION OF CCBs AND A-CCBs	78

5.1	Introduction	78
5.2	Effect of activation of CCBs with KOH	79
5.3	Effect of activation on the porous structure	81
5.4	Analysis of physical properties	84
5.5	Analysis of thermal characteristic	88
6	PART C: ADSORPTION OF ETHYLORANGE ON MODIFIED A-CCBs	91
6.1	Introduction	91
6.2	Investigation of effect of adsorption parameters towards removal of ethyl orange dye	92
6.2.1	Effect of contact time	92
6.2.2	Effect of initial concentration of dye	93
6.2.3	Effect of pH	95
6.2.4	Effect of dosage	96
6.3	Surface functional group of adsorbent	97
6.4	Adsorption Isotherms	99
6.5	Adsorption Kinetics	101
6.6	Adsorption Mechanism	105
6.7	Thermodynamic study	105
7	CONCLUSIONS AND RECOMMENDATIONS	108
7.1	Conclusions	108
7.2	Recommendations	110
	REFERENCES	112
	Appendices A-E	129-137

LIST OF FIGURES

FIGURE NO.	TITLE	PAGE
2.1	Empty Fruit bunch	13
2.2	Four main monolignols in lignin	14
2.3	Network structure formed in carbon cryogel (Yamamoto, <i>et al.</i> , 2009)	22
2.4	Structure of ethyl orange dye	31
3.1	Research flow chart	46
3.2	Liquefaction process	50
4.1	Predicted values versus experimental values of lignin yield (Unreduced Model)	65
4.2	Predicted values versus experimental values of lignin yield (Reduced Model)	65
4.3	The response surface plot of the combine temperature and time on yield of liquefied product	67

4.4	The response contour plot of the combine temperature and time on yield of liquefied product	68
4.5	The response surface plot of the combine IL/EFB and catalyst concentration on yield of liquefied product	70
4.6	The response contour plot of the combine IL/EFB and catalyst concentration on yield of liquefied product	71
4.7	UV spectra of lignin-EFB and commercial lignin alkali	74
4.8	FTIR spectra of lignin alkali and liquefied product with wave number: 4000-600 cm^{-1}	76
4.9	The regeneration performance of IL [BMIM]Cl on the lignin yield	77
5.1	Adsorption and desorption isotherm of Nitrogen on a) CCBs and b) A-CCB at 77K	82
5.2	Pore size distribution of a) CCB and b) A-CCB	84
5.3	X-Ray diffractogram of CCB and A-CCB samples	85
5.4	FTIR spectrogram of CCB and A-CCB samples	86
5.5	SEM images of a) CCB 50 μm ; b) A-CCB 50 μm	88
5.6	TG and DTG thermogram of (a) CCB and (b) A-CCB synthesized from lignin EFB	90

6.1	Effect of contact time on the removal of ethyl orange dye by A-CCB. Conditions: $C_o = 10\text{mg/L}$ of ethyl orange dye solution; Mass of A-CCB = 20mg; pH = 10; Temperature = 30°C	93
6.2	Effect of initial concentration on the removal of ethyl orange dye by A-CCB. Conditions: Mass of A-CCB = 20mg; pH = 10; Temperature = 30°C	94
6.3	Effect of pH on the removal of ethyl orange dye by A-CCB. Conditions: $C_o = 10\text{mg/L}$ of ethyl orange dye solution; Mass of A-CCB = 20mg; Temperature = 30°C	96
6.4	Effect of adsorbent dosage on the removal of ethyl orange dye by A-CCB. $C_o = 10\text{mg/L}$ of ethyl orange dye solution; pH = 10; Temperature = 30°C	97
6.5	FTIR spectra of the A-CCB adsorbent before and after adsorption	98
6.6	Langmuir Isotherm for adsorption of ethyl orange dye onto A-CCB at different temperature	99
6.7	Freundlich Isotherm for adsorption of ethyl orange dye onto A-CCB at different temperature	100
6.8	Kinetic pattern of pseudo-first order model of ethyl orange adsorption onto A-CCB at temperature 30°C	102
6.9	Kinetic pattern of pseudo-second order model of ethyl orange adsorption onto A-CCB at temperature 30°C	102

6.10	Intraparticle diffusion model of ethyl orange adsorption onto A-CCB at temperature 30°C	104
6.11	Plot of $\ln K_L$ versus $1/T$ for estimation of thermodynamic parameters for the adsorption of ethyl orange dye onto A-CCB	106

LIST OF SYMBOLS

A	-	Amount of adsorbate to form a complete monolayer
\AA	-	Armstrong
B	-	Empirical formula
C_e	-	Equilibrium concentration
C_o	-	Initial concentration
Hr	-	Hours
K	-	Kelvin
K_1	-	Equilibrium rate constant
K_f	-	Freundlich coefficient factor
L	-	Liter
M	-	Meter
mg	-	Mili-gram
Min	-	Minutes
mL	-	Mili-liter
mm	-	Mili-meter
N	-	Amount of gases adsorbed by solid
Nm	-	Nano-meter
P	-	Gas pressure at time
P_o	-	Initial equilibrium gas pressure at time
q_e	-	Amount of adsorbent at equilibrium
q_t	-	Equilibrium rate constant
R^2	-	Correlation Coefficient
R_L	-	Langmuir constant
V	-	Volume of solution
wt%	-	Weight percent

wt/wt	-	Weight per weight
β	-	Beta
$^{\circ}\text{C}$	-	Degree Celcius
%	-	Percent
$\frac{1}{n}$	-	Freundlich intensity parameter
n_m	-	Monolayer capacity
ΔG	-	Free Energy Change
ΔH	-	Enthalpy Change
ΔS	-	Entropy Change
μm	-	Micro-meter

LIST OF ABBREVIATIONS

A-CCB	-	Activated-Carbon Cryogel Bead
ANOVA	-	Analysis of Variance
ASTM	-	American Society for Testing and Materials
BET	-	Breuner, Emmer and Teller
CCB	-	Carbon Cryogel Bead
CCD	-	Central Composite Design
CO ₂	-	Carbon dioxide
DOE	-	Design of experiment
EFB	-	Empty Fruit Bunches
FTIR	-	Fourier Transform Infrared Spectroscopy
H ₂ SO ₄	-	Sulfuric acid
HCl	-	Hydrochloric Acid
HPLC	-	High Performance Liquid Chromatography
IL	-	Ionic Liquid
IUPAC	-	International of Pure and Applied Chemistry
KOH	-	Potassium Hydroxide
LAP	-	Laboratory analytical procedures
L-EFB	-	Lignin-Empty Fruit Bunches
Na ₂ CO ₃	-	Sodium carbonate
NaOH	-	Sodium hydroxide
OH	-	Hydroxyl
PF	-	phenol–formaldehyde
RSM	-	Response Surface Methodology
SEM	-	Scan Electron Microscope
TCC	-	Thermal Chemical Conversions

TG	-	Termogravimetric
TGA	-	Thermogravimetric Analysis
USA	-	United States America
UV	-	Ultraviolet
UV-vis	-	Ultra Violet – viscometer
XRD	-	X-Ray Diffraction
[AMI]Cl	-	Allyl-methylimidazolium chloride
[BMIM]Cl	-	1-Butyl-3-Methylimidazolium Methyl Chloride

LIST OF APPENDICES

APPENDIX	TITLE	PAGE
A	Example Calculation of Lignin Yields	128
B	Response Surface Methodology	129
C	Calibration Curves of Ethyl Orange Concentration	132
D	Example Calculation of Adsorption Capacity and Removal Percentage	133
E	Publications	135

CHAPTER 1

INTRODUCTION

1.1 Research Background

Water quality is becoming a significant problem in many areas around the world due to non-effective treatment of wastewater discharge from industrial factories; food industries, textile, cosmetics, pharmaceutical, paper and etc. Wastewater usually consists of synthetic organic compound such as dye, phenol and some heavy metals which are highly toxic substance that will harm human health and consequently to aquatic life. Therefore, development of an efficient wastewater treatment system is still being sought to ensure natural water resources always under control with good quality. There are three main categories of conventional wastewater treatments methods such as biodegradation, physical and chemical process available for removal of organic compounds such as dyes in effluent. Adsorption has proven to be one of the superior techniques for wastewater treatment among various physicochemical treatment due to the capability of efficiency adsorbing a broad range of adsorbates and its simplicity of design (Tan *et al.*, 2008; Wang *et al.*, 2010).

Recently, carbon cryogel beads (CCBs) have been found as a potential adsorbent due to the ease of mass transfer. CCBs is a kind of porous carbon material with unique microstructure which have desirable characteristic such as high surface area (400-700m²/g), ultrafine particle and large pores size (6-25nm), adjustability and high mesopores (1.3-2.5cm³/g) synthesized by sol-gel polymerization (Yamamoto *et al.*, 2009). These novel carbon materials with highly cross-linked and transparent gels offering attractive potential applications for preparation of nano-composite electrocatalyst, as adsorbents for separation process and as support material for catalyst industry. Moreover, the porous structure of carbon cryogel is potentially advantageous as an adsorbent for treating wastewater. Most of the published works extensively focus on the synthesis condition by varying the amounts of reactant, catalyst and water used in sol-gel process in order to tailoring the texture structure of porous carbon (Babic *et al.*, 2004; Chaichanawong *et al.*, 2009; Yamamoto *et al.*, 2002). The properties of carbon gel also can be engineered through carbonization and activation condition (Mirzaeian and Hall, 2009). The ability of tailoring the internal structure of this CCB makes them particularly well suited for a variety application.

However, CCBs are costly when synthesized from conventional combination of alcohols such as resorcinol and phenol with formaldehydes. Besides, the production of CCBs involves the usage of phenol and resorcinol which are categorized as harmful substances. Therefore, substitution for phenolic compound which is low in cost and yet effective is vigorously been sought. There have been reported on the usage of oil palm empty palm fruit bunch (EPFB) (Ahmadzadeh *et al.*, 2009), grapevine cane (*Vitisvinisera*L.) (Alma and Basturk, 2006), and lodgepole pine barks (*Pinuscontorta*Dougl.) (Zhao *et al.*, 2010) for phenolic substitution in the production of phenol-formaldehyde resin which usually used as raw material to produce carbon gel. Liquefaction is one of the promising methods to convert lignocellulosic wastes to phenolic compounds. The liquefaction efficiency of wood, its viscosity, and the reactivity of resulting resin were remarkably dependent on some parameters such as type of catalyst, temperature and reaction time (Broséus *et al.*, 2009).

Lignin derived from EFB for example, has high potential to be a substitute for the expensive petroleum-derived phenolic compounds due to its amorphous polymer composed of phenylpropane. Lignin is highly cross-linking aromatic polymer which consist of three major phenylpropanoid monomers which are syringyl alcohol, guaiacyl alcohol and p-coumaric alcohol. It has been reported that the EFB fiber contains about 25.2% lignin (Ya'aini *et al.*, 2012). At present, the EFB is burned in boiler and left at the landfill. However, this practice essentially make the EFB become a subject of environmental concern, subsequent consumes unproductive cost and energy. Hence, to overcome these problems, the abundant, inexpensive, and renewable resources generated from palm oil industries which is EFB has been chosen as the potentially feedstock in this study among other biomass produced in Malaysia.

1.2 Statement of Problem

Agriculture residues such as EFB are one of the enormous amounts of biomass generated every day in Malaysia. Goh *et al.*, (2010) reported that the quantity of empty fruit bunch produce in year 2007 was around 18, 022 ktons per year. Lack of efficient method in handling the waste leads to environmental pollutions problems. Some plantation companies disposed this solid biomass by burning it in the boiler to produce bunch ash to be distributed back to the landfill as fertilizer. By optimizing the utilization of EFB will rapidly decrease the environmental problems. EFB contains about 54.3% holocellulose (which consist of 41.0 and 13.3% α -cellulose and hemicelluloses respectively) and 25.2% lignin (Ya'aini, *et al.*, 2012). Therefore, there is huge potential for EFB to be exploited in the production of high value-added products, which not only complies with zero-waste strategy but also generated additional profits for the palm oil industry. Lignin derived from EFB shows a potential features to substitute an expensive petroleum-derived phenolic compounds as a chemical feed stocks or fuels.

Massive usage of phenol will cause environmental pollution problem and harmful to human health. Therefore, substitution for phenolic compound is vigorously been sought. Many researchers had developed various studies involving lignin derived from biomass as a phenol substitute in the synthesis of lignin modified resins. Direct use of lignin as a substitute for phenol in phenol–formaldehyde (PF) resins is limited because lignin has a lower reactivity due to its complex chemical and physical structure. Reactivity of lignin has been found to vary according to the process by which it was extracted (Mansouri and Salvadó, 2006). Lignin reactivity can be improved through phenolation process. Lignin-modified resins, with up to 35% phenol replacement by lignin, have been widely used in the USA to bond fibreboard and plywood. Work is continuing to find ways to produce adhesive resins with 50% or greater replacement of petroleum-derived phenol with bio-mass-derived phenolic compounds (Peng and Riedl, 1994).

Therefore, in this study, it is aimed to synthesis and characterizes CCBs from a renewable source which is empty palm fruit bunch (EPFB). This work proposes a new study on the production of CCB from EFB without addition of phenol which is harmful to human health and environment. The ability of lignin EFB to substitute phenolic compounds in phenol-furfural resin and the behaviour of CCB after activation process with KOH was investigated. Next the performances of the activated CCBs as a potential adsorbent to remove dye from wastewater through adsorption, kinetics and thermodynamic study were employed. Successive utilizing EFB as a renewable resource which leading to sustainable development can help palm oil industry complies with zero-waste strategy and generated additional profits for the palm oil industry.

1.3 Objectives of Study

The objectives of this study are:

- 1 To produce carbon cyrogel beads (CCBs) from empty fruit bunch (EFB).
- 2 To perform an optimization study on lignin extraction using response surface methodology (RSM).
- 3 To produce porous properties of A-CCBs via chemical activation with potasium hydroxide (KOH).
- 4 To study the performance of synthesized A-CCBs as potential adsorbents for removal of ethyl orange dye.

1.4 Scope of Study

In order to achieve the above objective, this research was extended into more specialized scope. This study approaches liquefaction of EFB with ionic liquid in the presence of catalyst to produce lignin. There are four variables which are temperature (130-170°C), time (90-180min), catalyst concentration (3-5%) and ratio of IL to EFB (2:1-4:1) that were manipulated to get the optimum lignin yield. The relationships of four variables were analyzed using STATISTICA Statsoft software to obtain optimum condition for lignin yield. The presence of lignin liquefied product was confirmed by UV-Vis and FTIR analysis. In addition, the performance of regenerated ionic liquid on lignin yield was investigated.

Formation of CCBs employed sol gel polycondensation of Lignin-EFB with furfural, followed by freeze drying and subsequent pyrolyze under inert gas. The synthesis condition of CCBs were fixed and the physical properties of CCBs were characterized using SEM, XRD, FTIR, TGA and BET. The CCBs then were further impregnated with KOH to study the effect on porous properties of CCBs after chemically activate. Similar characterizations with CCBs were employed for A-CCBs to evaluate the modified structure of porous carbon.

The performance of modified A-CCBs was tested towards removal of dye which is ethyl orange. The adsorption capacity was determined by employing adsorption and kinetic study. The experimental condition for adsorption test were including temperature (30-60°C), time (60-480 minutes), pH (2-10), initial concentration of adsorbates (10-100mg/L) and weight of carbon adsorbent (20-100 mg). The carbon adsorbent (before and after dye adsorption) were analyzed using FTIR.

Kinetic studies of pseudo first- order and second- order was applied for determination of mechanism of adsorption rate of ethyl orange dye adsorptions. Meanwhile, adsorption isotherm was determined through Freundlich and Langmuir equations. Finally, the effect of temperature on the adsorption of dye was determined based on the adsorption thermodynamic.

1.5 Significance of study

This research enable CCBs synthesized from EFB to be further developed based on the optimum condition in order to reduce the cost of production with high quality. The developed mathematical models can be used for detailed description of the interactions between the corresponding variables in production of lignin from EFB.

Besides that, the production of CCBs normally involves the presence of phenol or resorcinol substance. However, in this study, the usage of phenol in the formation of CCBs was avoided by substituting phenol with lignin-EFB (i.e. the novelty of this research) completely. In order to tailoring the texture structure of porous CCB, modification with chemical activation was employed. The performance of final product ACCB was tested on the potentiality to remove dye.

In this present study, it is expected that by utilizing EFB it will help palm oil industry to comply with zero-waste strategy and at the same time could reduce the production cost for production of CCBs. Moreover, production of CCBs from EFB has not yet been ventured in. Thus, findings from this study would be beneficial for palm oil industry and wastewater treatment industry.

REFERENCES

- Abdullah, N. and Gerhauser, H. (2008). Bio-Oil Derived from Empty Fruit Bunches. *Fuel*. 87(12): 2606-2613.
- Abdullah, N., Gerhauser, H. and Sulaiman, F. (2010). Fast Pyrolysis of Empty Fruit Bunches. *Fuel*. 89(8): 2166-2199.
- Ahmadzadeh, A. And Zakaria, S. (2009). Preparation of Novolak Resin by Liquefaction of Oil Palm Empty Fruit Bunchs (EFB) and Characterization of EFB Residue. *Polymer Plastics Technology and Engineering*. 48(1): 10-16.
- Ahmadzadeh, A., Zakaria, S. and Rashid, R. (2009). Liquefaction of Oil Palm Empty Fruit Bunch (EFB) into Phenol and Characterization of Phenolated EFB Resin. *Industrial Crops and Products*. 30(1): 54-58.
- Akhtar, J., Kuang, S. K. and Amin, N. S. (2010). Liquefaction of Empty Palm Fruit Bunch (EPFB) in Alkaline Hot Compressed Water. *Renewable Energy*. 35(6): 1220-1227.
- Aksakal, O. and Uzun, H. (2010). Equilibrium, Kinetic and Thermodynamic Studies oo The Biosorption of Textile Dye (Reactive Red 195) onto Pinus Sylvestris L. *Journal of Hazardous Materials*. 181(1-3): 666-672.
- Alam, M. Z., Muyibi, S. A., Mansor, M. F. and Wahid, R. (2007). Activated Carbon Derived from Oil Palm Empty-Fruit Bunches: Application to Environmental Problems. *Journal of Environmental Sciences*. 19(0): 103-108.

- Alam, M.Z., Mamun, A.A., Qudsieh, I.Y., Muyibi, S.A., Salleh, H.M. and Omar, N.M. (2009). Solid State Bioconversion of Oil Palm Empty Fruit Bunches for Cellulase Enzyme Production using a Rotary Drum Bioreactor. *Biochemical Engineering Journal*. 46(1): 61-64.
- Alim, M. A., Lee, J. H., Akoh, C. C., Choi, M. S., Jeon, M. S., Shin, J. A., et al. (2008). Enzymatic Transesterification of Fractionated Rice Bran Oil with Conjugated Linoleic Acid: Optimization by Response Surface Methodology. *LWT - Food Science and Technology*. 41(5): 764-770.
- Alma, M. H. and Basturk, M. A. (2006). Liquefaction of Grapevine Cane (*Vitis Vinisera* L.) Waste and its Application to Phenol-Formaldehyde Type Adhesive. *Industrial Crops and Products*. 24(2): 171-176.
- Amin, N. A. S., Ya'aini, N., Misson, M., Haron, R., and Mohamed, M. (2010). Enzymed Pretreated Empty Palm Fruit Bunch for Biodiesel Production. *Journal of Applied Sciences*. 10(12): 1181-1186.
- Amin, N. K. (2008). Removal of Reactive Dye from Aqueous Solutions by Adsorption onto Activated Carbons Prepared from Sugarcane Bagasse Pith. *Desalination*. 223(1-3): 152-161.
- Annadurai, G., Ling, L. Y. and Lee, J. F. (2008). Adsorption of Reactive Dye from an Aqueous Solution by Chitosan: Isotherm, Kinetic and Thermodynamic Analysis. *Journal of Hazardous Materials*. 152(1): 337-346.
- Asgher, M. and Bhatti, H. N. (2010). Mechanistic and Kinetic Evaluation of Biosorption of Reactive Azo Dyes by Free, Immobilized and Chemically Treated Citrus Sinensis Waste Biomass. *Ecological Engineering*. 36(12): 1660-1665.
- Astimar, A. B., Wan Hasamudin, W. H., Zawawi, I., Rosnah, M. S., Ropandi, M. and Anis, M. (2009). A Pyro-Ligno Binder from Oil Palm Empty Fruit Bunch. *MPOB Information*. ISSN 1511-7871.

- Babic, B., Kaluđerovic, B., Vracar, L. and Krstajic, N. (2004). Characterization of Carbon Cryogel Synthesized by Sol-Gel Polycondensation and Freeze-Drying. *Carbon*. 42(12-13): 2617-2624.
- Basta, A. H., Fierro, V., El-Saied, H. and Celzard, A. (2009). 2-Steps KOH Activation of Rice Straw: An Efficient Method for Preparing High-Performance Activated Carbons. *Bioresource Technology*. 100(17): 3941-3947.
- Broséus, R., Vincent, S., Aboulfadl, K., Daneshvar, A., Sauvé, S., Barbeau, B., et al. (2009). Ozone Oxidation of Pharmaceuticals, Endocrine Disruptors and Pesticides during Drinking Water Treatment. *Water Research*. 43(18): 4707-4717.
- Çetin, N. S. and Özmen, N. (2002). Use of Organosolv Lignin in Phenol-Formaldehyde Resins for Particleboard Production: II. Particleboard Production and Properties. *International Journal of Adhesion and Adhesives*. 22(6): 481-486.
- Chai, L. L., Zakaria, S., Chia, C.-H., Nabihah, S. and Rasid, R. (2009). Physico-Mechanical Properties of PF Composite Board from EFB Fibres using Liquefaction Technique. *Iranian Polymer Journal*. 18(11): 917-923.
- Chaichanawong, J., Yamamoto, T., Kim, S. I. and Ohmori, T. (2009). Preparation and Characterization of Nickel-Modified Carbon Cryogel Beads with Uniform Particle Size. *Journal of Non-Crystalline Solids*. 355(31-33): 1605-1612.
- Chaichanawong, J., Yamamoto, T. and Ohmori, T. (2010). Enhancement Effect of Carbon Adsorbent on Ozonation of Aqueous Phenol. *Journal of Hazardous Materials*. 175(1-3): 673-679.

- Chao, Y. J., Yuan, X. and Ma, Z. F. (2008). Preparation and Characterization of Carbon Cryogel (CC) and CC-Sio Composite as Anode Material for Lithium-Ion Battery. *Electrochimica Acta*. 53(9): 3468-3473.
- Choi, J.S., Kim, T. H., Choo, K. Y., Sung, J. S., Saidutta, M. B., Ryu, S. O., et al. (2005). Direct Synthesis of Phenol from Benzene on Iron-Impregnated Activated Carbon Catalysts. *Applied Catalysis A: General*. 290(1-2): 1-8.
- Contreras, M. S., Páez, C. A., Zubizarreta, L., Léonard, A., Blacher, S., Olivera-Fuentes, C. G., et al. (2010). A Comparison of Physical Activation of Carbon Xerogels with Carbon Dioxide with Chemical Activation using Hydroxides. *Carbon*. 48(11): 3157-3168.
- Crini, G. (2006). Non-Conventional Low-Cost Adsorbents for Dye Removal: A Review. *Bioresource Technology*. 97(9): 1061-1085.
- Demirbas, A. (1998). Yields of Oil Products from Thermochemical Biomass Conversion Processes. *Energy Conversion and Management*. 39(7): 685-690.
- Elkhatat, A. M. and Al-Muhtaseb, S. A. (2011). Advances in Tailoring Resorcinol-Formaldehyde Organic and Carbon Gels. *Advanced Materials*. 23(26): 2887-2903.
- Elsayed, K. and Lacor, C. (2011). Modeling, Analysis and Optimization of Aircyclones using Artificial Neural Network, Response Surface Methodology and CFD Simulation Approaches. *Powder Technology*. 212(1): 115-133.
- Ferreira, S., Duarte, A. P., Ribeiro, M. H. L., Queiroz, J. A. and Domingues, F. C. (2009). Response Surface Optimization of Enzymatic Hydrolysis of Cistus Ladanifer and Cytisus Striatus for Bioethanol Production. *Biochemical Engineering Journal*. 45(3): 192-200.

- Foo, K. Y. and Hameed, B. H. (2011). Preparation of Oil Palm (*Elaeis*) Empty Fruit Bunch Activated Carbon by Microwave-Assisted KOH Activation for the Adsorption of Methylene Blue. *Desalination*. 275(1–3): 302-305.
- Foo, K. Y. and Hameed, B. H. (2012a). Preparation of Activated Carbon by Microwave Heating of Langsat (*Lansium Domesticum*) Empty Fruit Bunch Waste. *Bioresource Technology*. 116(0): 522-525.
- Foo, K. Y. and Hameed, B. H. (2012b). Microwave-Assisted Preparation and Adsorption Performance of Activated Carbon from Biodiesel Industry Solid Residue: Influence of Operational Parameters. *Bioresource Technology*. 103(1): 398-404.
- Fu, D. and Mazza, G. (2011). Aqueous Ionic Liquid Pretreatment of Straw. *Bioresource Technology*. 102(13): 7008-7011.
- Fu, D., Mazza, G. and Tamaki, Y. (2010). Lignin Extraction from Straw by Ionic Liquids and Enzymatic Hydrolysis of the Cellulosic Residues. *Journal of Agricultural and Food Chemistry*. 58(5): 2915-2922.
- Gellerstedt, G. and Lindfora, E. L. (1984). Structure Changes in Lignin during Kraft Pulping. *Holzfoorschung*. 38(3), 151-158.
- Girgis, B. S., Attia, A. A. and Fathy, N. A. (2011). Potential of Nano-Carbon Xerogels in the Remediation of Dye-Contaminated Water Discharges. *Desalination*. 265(1-3): 169-176.
- Girisuta, B., Janssen, L. P. B. M. and Heeres, H. J. (2006). Green Chemicals: A Kinetic Study on the Conversion of Glucose to Levulinic Acid. *Chemical Engineering Research and Design*. 84(5): 339-349.
- Goh, C.S., Tan, K.T., Lee, K.T. and Subhash Bhatia. (2010). Bioethanol from Lignocellulose: Status, Perspectives and Challenges in Malaysia. *Bioresource Technology*. 101(13): 4834-4841.

- Hameed, B. H., Tan, I. A. W. and Ahmad, A. L. (2008). Adsorption Isotherm, Kinetic Modeling and Mechanism of 2,4,6-Trichlorophenol on Coconut Husk-Based Activated Carbon. *Chemical Engineering Journal*. 144(2): 235-244.
- Hamzah, F., Idris, A. and Shuan, T. K. (2011). Preliminary Study on Enzymatic Hydrolysis of Treated Oil Palm (Elaeis) Empty Fruit Bunches Fibre (EFB) by using Combination of Cellulase and B 1-4 Glucosidase. *Biomass and Bioenergy*. 35(3): 1055-1059.
- Jaafar, N. F., Abdul Jalil, A., Triwahyono, S., Muhd Muhid, M. N., Sapawe, N., Satar, M. A. H., et al. (2012). Photodecolorization of Methyl Orange over α -Fe₂O₃-Supported HY Catalysts: The Effects of Catalyst Preparation and Dealumination. *Chemical Engineering Journal*. 191(0): 112-122.
- Jarvis, K. L., Barnes, T. J. and Prestidge, C. A. (2011). Surface Chemical Modification to Control Molecular Interactions with Porous Silicon. *Journal of Colloid and Interface Science*. 363(1): 327-333.
- Jung, K.W., Kim, D.H., Kim, H.W. and Shin, H.S. (2011). Optimization of Combined (Acid + Thermal) Pretreatment for Fermentative Hydrogen Production From Laminaria Japonica using Response Surface Methodology (RSM). *International Journal of Hydrogen Energy*. 36(16): 9626-9631.
- Kamboh, M. A., Solangi, I. B., Sherazi, S. T. H. and Memon, S. (2011). A Highly Efficient Calix[4]Arene based Resin for the Removal of Azo Dyes. *Desalination*. 268(1-3): 83-89.
- Katinonkul, W., Lee, J. S., Ha, S. H. and Park, J. Y. (2012). Enhancement of Enzymatic Digestibility of Oil Palm Empty Fruit Bunch by Ionic-Liquid Pretreatment. *Energy*. 47(1): 11-16.

- Kim, S. I., Yamamoto, T., Endo, A., Ohmori, T. and Nakaiwa, M. (2006). Adsorption of Phenol and Reactive Dyes from Aqueous Solution on Carbon Cryogel Microspheres with Controlled Porous Structure. *Microporous and Mesoporous Materials*. 96(1-3): 191-196.
- Kincl, M., Turk, S. and Vrečer, F. (2005). Application of Experimental Design Methodology in Development and Optimization of Drug Release Method. *International Journal of Pharmaceutics*. 291(1-2): 39-49.
- Kirali, E. G. and Laçin, O. (2006). Statistical Modelling of Acid Activation on Cotton Oil Bleaching by Turkish Bentonite. *Journal of Food Engineering*. 75(1): 137-141.
- Kraiwattanawong, K., Mukai, S. R., Tamon, H. and Lothongkum, A. W. (2007). Preparation of Carbon Cryogels from Wattle Tannin and Furfural. *Microporous and Mesoporous Materials*. 98(1-3): 258-266.
- Lee, W. J. and Chen, Y. C. (2008). Novolak PF Resins Prepared from Phenol Liquefied *Cryptomeria Japonica* and used in Manufacturing Moldings. *Bioresource Technology*. 99(15): 7247-7254.
- Lee, S. H., Doherty, T. V., Linhardt, R. J. and Dordick, J. S. (2009). Ionic Liquid-Mediated Selective Extraction of Lignin From Wood Leading To Enhanced Enzymatic Cellulose Hydrolysis. *Biotechnology and Bioengineering*. 102(5): 1368-1376.
- Li, B., Asikkala, J., Filpponen, I. and Argyropoulos, D. S. (2010a). Factors Affecting Wood Dissolution and Regeneration of Ionic Liquids. *Industrial and Engineering Chemistry Research*. 49(5): 2477-2484.
- Li, C., Knierim, B., Manisseri, C., Arora, R., Scheller, H. V., Auer, M., et al. (2010b). Comparison of Dilute Acid and Ionic Liquid Pretreatment of Switchgrass: Biomass Recalcitrance, Delignification and Enzymatic Saccharification. *Bioresource Technology*. 101(13): 4900-4906.

- Li, M. F., Fan, Y. M., Sun, R. C. and Xu, F. (2010). Characterization of Extracted Lignin of Bamboo (*Neosinocalamusaffinis*) Pretreated with Sodium Hydroxide/Urea Solution at Low Temperature. *Bioresources*. 5(3): 1762-1778.
- Li, Q., He, Y. C., Xian, M., Jun, G., Xu, X., Yang, J. M., et al. (2009). Improving Enzymatic Hydrolysis of Wheat Straw using Ionic Liquid 1-Ethyl-3-Methyl Imidazolium Diethyl Phosphate Pretreatment. *Bioresource Technology*. 100(14): 3570-3575.
- Li, W. C., Lu, A. H. and Guo, S. C. (2001). Characterization of the Microstructures of Organic and Carbon Aerogels based upon Mixed Cresol-Formaldehyde. *Carbon*. 39(13): 1989-1994.
- Liang, L., Zhihuai, M., Yebo, L., Caixia, W., Tipeng, W., Lianhui, Z., et al. (2006). Liquefaction of Crop Residue for Polyol Production. *Bioresource. Peer-Reviewed Article*. (1).
- Lin, C. and Ritter, J. A. (1997). Effect of Synthesis pH on the Structure of Carbon Xerogels. *Carbon*. 35(9): 1271-1278.
- Liu, H., Liu, W., Zhang, J., Zhang, C., Ren, L. and Li, Y. (2011). Removal of Cephalixin from Aqueous Solutions by Original and Cu(II)/Fe(III) Impregnated Activated Carbons Developed from Lotus Stalks Kinetics and Equilibrium Studies. *Journal of Hazardous Materials*. 185(2-3): 1528-1535.
- Liu, Q. S., Zheng, T., Wang, P., Jiang, J. P. and Li, N. (2010). Adsorption Isotherm, Kinetic and Mechanism Studies of some Substituted Phenols on Activated Carbon Fibers. *Chemical Engineering Journal*. 157(2-3): 348-356.
- Lu, C. Y. and Wey, M. Y. (2007). Simultaneous Removal of VOC and NO by Activated Carbon Impregnated with Transition Metal Catalysts in Combustion Flue Gas. *Fuel Processing Technology*. 88(6): 557-567.

- Machado, F. M., Bergmann, C. P., Fernandes, T. H. M., Lima, E. C., Royer, B., Calvete, T., et al. (2011). Adsorption of Reactive Red M-2BE Dye from Water Solutions by Multi-Walled Carbon Nanotubes and Activated Carbon. *Journal of Hazardous Materials*. 192(3): 1122-1131.
- Maldas, D. and Shiraishi, N. (1997). Liquefaction of Biomass in the Presence of Phenol and H₂O using Alkalies and Salts as the Catalyst. *Biomass and Bioenergy*. 12(4): 273-279.
- Mansouri, N. E. E. and Salvadó, J. (2006). Structural Characterization of Technical Lignins for the Production of Adhesives: Application to Lignosulfonate, Kraft, Soda-Anthraquinone, Organosolv and Ethanol Process Lignins. *Industrial Crops and Products*. 24(1): 8-16.
- Mazaheri, H., Lee, K. T., Bhatia, S. and Mohamed, A. R. (2010). Subcritical Water Liquefaction of Oil Palm Fruit Press Fiber in the Presence of Sodium Hydroxide: An Optimisation Study Using Response Surface Methodology. *Bioresource Technology*. 101(23): 9335-9341.
- Mirzaeian, M. and Hall, P. (2009). The Control of Porosity at Nano Scale in Resorcinol Formaldehyde Carbon Aerogels. *Journal of Materials Science*. 44(10): 2705-2713.
- Misson, M., Haron, R., Kamaroddin, M. F. A. and Amin, N. A. S. (2009). Pretreatment of Empty Palm Fruit Bunch for Production of Chemicals Via Catalytic Pyrolysis. *Bioresource Technology*. 100(11): 2867-2873.
- Mohamad Ibrahim, M. N., Mohamad Yusof, N. N. and Hashim, A. (2007). Comparison Studies on Soda Lignin and Soda-Anthraquinone Lignin. *The Malaysian Journal of Analytical Science*. 11(1): 206-212.

- Mohamad Ibrahim, M. N., Zakaria, N., Sipaut, C. S., Sulaiman, O. and Hashim, R. (2011). Chemical and Thermal Properties of Lignins from Oil Palm Biomass as a Substitute for Phenol in a Phenol Formaldehyde Resin Production. *Carbohydrate Polymers*. 86(0): 112-119
- Mohan, D., Pittman, C. U. and Steele, P. H. (2006). Pyrolysis of Wood/Biomass for Bio-Oil: A Critical Review. *Energy and Fuels*. 20(3): 848-889.
- Moussavi, G. and Mahmoudi, M. (2009). Removal of Azo and Anthraquinone Reactive Dyes from Industrial Wastewaters using MgO Nanoparticles. *Journal of Hazardous Materials*. 168(2-3): 806-812.
- Mukai, S. R., Tamitsuji, C., Nishihara, H. and Tamon, H. (2005). Preparation of Mesoporous Carbon Gels from an Inexpensive Combination of Phenol and Formaldehyde. *Carbon*. 43(12): 2628-2630.
- Nada, A. A. M. A., El-Sakhawy, M. and Kamel, S. M. (1998). Infra-Red Spectroscopic Study of Lignins. *Polymer Degradation And Stability*. 60(2-3): 247-251.
- Ngah, W. S. W. and Fatinathan, S. (2010). Adsorption Characterization of Pb(II) and Cu(II) Ions onto Chitosan-Tripolyphosphate Beads: Kinetic, Equilibrium and Thermodynamic Studies. *Journal of Environmental Management*. 91(4): 958-969.
- Nishihara, H., Mukai, S. R. and Tamon, H. (2004). Preparation of Resorcinol-Formaldehyde Carbon Cryogel Microhoneycombs. *Carbon*. 42(4): 899-901.
- NREL (1996). Standard Biomass Analytical Procedures, Department of Energy, National Renewable Energy Laboratory, U.S.
- Olivier-Bourbigou, H., Magna, L. and Morvan, D. (2010). Ionic Liquids and Catalysis: Recent Progress from Knowledge to Applications. *Applied Catalysis A: General*. 373(1-2): 1-56.

- Órfão, J. J. M., Silva, A. I. M., Pereira, J. C. V., Barata, S. A., Fonseca, I. M., Faria, P. C. C., et al. (2006). Adsorption of a Reactive Dye on Chemically Modified Activated Carbons - Influence of pH. *Journal of Colloid and Interface Science*. 296(2): 480-489.
- Özcan, A., Özcan, A. S., Tunali, S., Akar, T. and Kiran, I. (2005). Determination of the Equilibrium, Kinetic and Thermodynamic Parameters of Adsorption of Copper(II) Ions onto Seeds of Capsicum Annuum. *Journal of Hazardous Materials*. 124(1-3): 200-208.
- Pekala, R. W. (1989). Organic Aerogels from the Polycondensation of Resorcinol with Formaldehyde. *Journal of Materials Science*. 24(9): 3221-3227.
- Peng, W. and Riedl, B. (1994). The Chemorheology of Phenol-Formaldehyde Thermoset Resin and Mixtures of the Resin with Lignin Fillers. *Polymer*. 35(6): 1280-1286.
- Petit, C., Karwacki, C., Peterson, G. and Bandosz, T. J. (2007). Interactions of Ammonia with the Surface of Microporous Carbon Impregnated with Transition Metal Chlorides. *The Journal of Physical Chemistry C*. 111(34): 12705-12714.
- Prins, M. J., Ptasiński, K. J. and Janssen, F. J. J. G. (2005). Exergetic Optimisation of a Production Process of Fischer-Tropsch Fuels From Biomass. *Fuel Processing Technology*. 86(4): 375-389.
- Sajab, M. S., Chia, C. H., Zakaria, S. and Khiew, P. S. (2013). Cationic and Anionic Modifications of Oil Palm Empty Fruit Bunch Fibers for the Removal of Dyes from Aqueous Solutions. *Bioresource Technology*. 128(0): 571-577.
- Scalbert, A. and Monties, B. (1986). Comparison of Wheat Straw Lignin Preparations, II Straw Lignin Solubilisation in Alkali. *Holzforschung*. 40(4): 249-254.

- Schuchardt, U., Rodrigues, J. A. R., Cotrim, A. and Costa, J. L. M. (1993). Liquefaction of Hydrolytic Eucalyptus Lignin with Formate in Water, using Batch and Continuous-Flow Reactors. *Bioresource Technology*. 44(2): 123-129.
- Sharma, C. S., Upadhyay, D. K. and Sharma, A. (2009). Controlling the Morphology of Resorcinol-Formaldehyde-based Carbon Xerogels by Sol Concentration, Shearing, and Surfactants. *Industrial and Engineering Chemistry Research*. 48(17): 8030-8036.
- She, D., Xu, F., Geng, Z., Sun, R., Jones, G. L. and Baird, M. S. (2010). Physicochemical Characterization of Extracted Lignin from Sweet Sorghum Stem. *Industrial Crops and Products*. 32(1): 21-28.
- Shlyakhtin, O. and Oh, Y. J. (2009). Inorganic Cryogels for Energy Saving and Conversion. *Journal of Electroceramics*. 23(2): 452-461.
- Sidik, D. A. B., Ngadi, N. and Amin, N. A. S. Optimization of Lignin Production from Empty Fruit Bunch via Liquefaction with Ionic Liquid. *Bioresource Technology*. (0). In Press [Http://Dx.Doi.Org/10.1016/J.Biortech.2012.09.041](http://dx.doi.org/10.1016/j.biortech.2012.09.041).
- Sun, F. and Chen, H. (2008). Enhanced Enzymatic Hydrolysis of Wheat Straw by Aqueous Glycerol Pretreatment. *Bioresource Technology*. 99(14): 6156-6161.
- Sun, N., Rahman, M., Qin, Y., Maxim, M. L., Rodriguez, H. and Rogers, R. D. (2009). Complete Dissolution and Partial Delignification of Wood in the Ionic Liquid 1-Ethyl-3-Methylimidazolium Acetate. *Green Chemistry*. 11(5): 646-655.
- Sun, R., Tomkinson, J. and Bolton, J. (1999). Effects of Precipitation pH on the Physico-Chemical Properties of the Lignins Isolated from the Black Liquor of Oil Palm Empty Fruit Bunch Fibre Pulping. *Polymer Degradation and Stability*. 63(2): 195-200.

- Sun, Y., Liu, J. and Kennedy, J. F. (2010). Application of Response Surface Methodology for Optimization of Polysaccharides Production Parameters from the Roots of *Codonopsis Pilosula* by a Central Composite Design. *Carbohydrate Polymers*. 80(3): 949-953.
- Szczurek, A., Jurewicz, K., Amaral-Labat, G., Fierro, V., Pizzi, A. and Celzard, A. (2010). Structure and Electrochemical Capacitance of Carbon Cryogels Derived from Phenol-Formaldehyde Resins. *Carbon*. 48(13): 3874-3883.
- Tamon, H., Ishizaka, H., Mikami, M. and Okazaki, M. (1997). Porous Structure of Organic and Carbon Aerogels Synthesized by Sol-gel Polycondensation of Resorcinol with Formaldehyde. *Carbon*. 35(6): 791-796.
- Tamon, H., Ishizaka, H., Yamamoto, T. and Suzuki, T. (1999). Preparation of Mesoporous Carbon by Freeze Drying. *Carbon*. 37(12): 2049-2055.
- Tan, H. T., Lee, K. T. and Mohamed, A. R. (2011). Pretreatment of Lignocellulosic Palm Biomass using A Solvent Ionic Liquid [BMIM]Cl for Glucose Recovery: An Optimisation Study using Response Surface Methodology. *Carbohydrate Polymers*. 83(4): 1862-1868.
- Tan, I. A. W., Ahmad, A. L. and Hameed, B. H. (2008). Adsorption of Basic Dye on High Surface Area Activated Carbon Prepared from Coconut Husk: Equilibrium, Kinetic and Thermodynamic Studies. *Journal of Hazardous Materials*. 154(1-3): 337-346.
- Tan, S. S. Y., Macfarlane, D. R., Upfal, J., Edye, L. A., Doherty, W. O. S., Patti, A. F., et al. (2009). Extraction of Lignin from Lignocellulose at Atmospheric Pressure using Alkylbenzenesulfonate Ionic Liquid. *Green Chemistry*. 11(3): 339-345.
- Tansel, B. (2008). New Technologies for Water and Wastewater Treatment: A Survey of Recent Patents. 17-26. *Recent Patents on Chemical Engineering*. 1(1).

- Teramoto, Y., Lee, S. H. and Endo, T. (2009). Cost Reduction and Feedstock Diversity for Sulfuric Acid Free Ethanol Cooking of Lignocellulosic Biomass as a Pretreatment to Enzymatic Saccharification. *Bioresource Technology*. 100(20): 4783-4789.
- Toor, S. S., Rosendahl, L. and Rudolf, A. (2011). Hydrothermal Liquefaction of Biomass: A Review of Subcritical Water Technologies. *Energy*. 36(5): 2328-2342.
- Tymchyshyn, M. and Xu, C. (2010). Liquefaction of Biomass in Hot Compressed Water for the Production of Phenolic Compounds. *Bioresource Technology*. 101(7): 2483-2490.
- Tzong-Horng, L. (2010). Development of Mesoporous Structure and High Adsorption Capacity of Biomass based Activated Carbon by Phosphoric Acid and Zinc Chloride Activation. *Chemical Engineering Journal*. 158(2): 129-142.
- Wan Omar, W. N. N. and Saidina Amin, N. A. (2011). Optimization of Heterogeneous Biodiesel Production from Waste Cooking Palm Oil via Response Surface Methodology. *Biomass and Bioenergy*. 35(3): 1329-1338.
- Wang, L. (2012). Application of Activated Carbon Derived from 'Waste' Bamboo Culms for the Adsorption of Azo Disperse Dye: Kinetic, Equilibrium and Thermodynamic Studies. *Journal of Environmental Management*. 102(0): 79-87.
- Wang, G., Li, W., Li, B., Chen, H. and Bai, J. (2007). Direct Liquefaction of Sawdust under Syngas with and without Catalyst. *Chemical Engineering and Processing*. 46(3): 187-192.

- Wang, H. and Chen, H. Z. (2007). A Novel Method of Utilizing the Biomass Resource: Rapid Liquefaction of Wheat Straw and Preparation of Biodegradable Polyurethane Foam (PUF). *Journal of the Chinese Institute of Chemical Engineers*. 38(2): 95-102.
- Wang, H., Shu, Y., Wang, A., Wang, J., Zheng, M., Wang, X., et al. (2008). One Pot Synthesis and Characterization of Metal Phosphide doped Carbon Xerogels. *Carbon*. 46(15): 2076-2082.
- Wang, L., Zhang, J., Zhao, R., Li, C., Li, Y. and Zhang, C. (2010). Adsorption of Basic Dyes on Activated Carbon Prepared from Polygonum Orientale Linn: Equilibrium, Kinetic and Thermodynamic Studies. *Desalination*. 254(1-3): 68-74.
- Wang, M., Leitch, M. and Xu, C. (2009). Synthesis of Phenol-Formaldehyde Resol Resins using Organosolv Pine Lignins. *European Polymer Journal*. 45(12): 3380-3388.
- Wu, D. and Fu, R. (2006). Synthesis of Organic and Carbon Aerogels from Phenol-Furfural by Two-Step Polymerization. *Microporous and Mesoporous Materials*. 96(1-3): 115-120.
- Wu, S. and Argyropoulos, D. S. (2003). An Improved Method for Isolating Lignin in High Yield and Purity. . *Journal of Pulp and Paper Science*. 29(7): 235-240.
- Xiao, J., Li, Z., Liu, B., Xia, Q. and Yu, M. (2008). Adsorption of Benzothiophene and Dibenzothiophene on Ion Impregnated Activated Carbons and Ion-Exchanged Y Zeolites. *Energy and Fuels*. 22(6): 3858-3863.
- Ya'aini, N., Amin, N. A. S. and Asmadi, M. (2012). Optimization of Levulinic Acid from Lignocellulosic Biomass using a New Hybrid Catalyst. *Bioresource Technology*. 116(0): 58-65.

- Yamada, T., Aratani, M., Kubo, S. and Ono, H. (2007). Chemical Analysis of the Product in Acid-Catalyzed Solvolysis of Cellulose using Polyethylene Glycol and Ethylene Carbonate. *Journal of Wood Science*. 53(6): 487-493.
- Yamamoto, T., Kim, S.-I., Chaichanawong, J., Apiluck, E.-U. and Ohmori, T. (2009). Removal of Aqueous Organic Pollutants by Adsorption-Catalytic Process using Mesoporous Carbon Beads Loaded with Metal Oxides. *Applied Catalysis B: Environmental*. 88(3-4): 455-461.
- Yamamoto, T., Ohmori, T. and Young, H. K. (2008). Preparation and Characterization of Monodisperse Carbon Cryogel Microspheres. *Microporous and Mesoporous Materials*. 112(1-3): 211-218.
- Yamamoto, T., Sugimoto, T., Suzuki, T., Mukai, S. R. and Tamon, H. (2002). Preparation and Characterization of Carbon Cryogel Microspheres. *Carbon*. 40(8): 1345-1351.
- Yamashita, J., Ojima, T., Shioya, M., Hatori, H. and Yamada, Y. (2003). Organic and Carbon Aerogels Derived from Poly(Vinyl Chloride). *Carbon*. 41(2): 285-294.
- Yang, K., Peng, J., C. Srinivasakannan, Zhang, L., Xia, H. and Duan, X. (2010). Preparation of High Surface Area Activated Carbon from Coconut Shells using Microwave Heating. *Bioresource Technology*. 101(15): 6163–6169.
- Zhang, Y., Ikeda, A., Hori, N., Takemura, A., Ono, H. and Yamada, T. (2006). Characterization of Liquefied Product from Cellulose with Phenol in the Presence of Sulfuric Acid. *Bioresource Technology*. 97(2): 313-321.
- Zhao, Y., Yan, N. and Feng, M. (2010). Characterization of Phenol-Formaldehyde Resins Derived from Liquefied Lodgepole Pine Barks. *International Journal of Adhesion and Adhesives*. 30(8): 689-695.

Zubizarreta, L., Arenillas, A., Pirard, J. P., Pis, J. J. and Job, N. (2008). Tailoring the Textural Properties of Activated Carbon Xerogels by Chemical Activation with KOH. *Microporous and Mesoporous Materials*. 115(3): 480-490.