KINETIC DEGRADATION OF OIL PALM MESOCARP FIBRE PYROLYSIS AND APPLICATION OF BIOCHAR FOR REMOVAL OF METHYLENE BLUE

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ABSTRACT

Malaysia is currently having a big problem on agricultural waste such as residues from palm oil industry and extra attention is required to handle this issue. The waste from oil palm mills is a renewable resource that potentially can be used to produce chemical feedstocks, fuels, and adsorbents through a process called pyrolysis. This study used oil palm mesocarp fibre (OPMF) from Kulai Palm Oil Mill located in Johor, Malaysia as sample. The sample was characterized (proximate, ultimate, lignin content, pore size, functional group, surface morphology) and kinetic properties was investigated using thermogravimetric analyser. Three non-isothermal methods namely Kissinger, Ozawa-Flynn-Wall (OFW) and Kissinger-Akahira-Sunose (KAS) were used to analyse the solid-state kinetics, and data obtained were compared. The sample was heated using different heating rates of 5, 10, 15, 20, and 30 Kmin^{-1} ranging from 298 K to 1173 K. The thermal decomposition process revealed that three main stages existed; dehydration, active, and passive pyrolysis. The activation energy (E_a) and pre-exponential factor achieved from Kissinger, KAS and OFW methods were 159.74 kJ/mol, 161.90 kJ/mol, 163.29 kJ/mol and 1.02E+10 min^{-1}, 1.90E+13 min^{-1}, 3.79E+17 min^{-1}, respectively. A variance of E_a with conversion was noticed when both KAS and OFW models were employed. This revealed that the pyrolysis of OPMF progresses through more complex and multi-step kinetics. The results achieved from Kissinger method represents the actual values of kinetic parameters which were the same for the whole pyrolysis process. KAS and OFW methods represented the apparent values of kinetic parameters. All devolatilization processes were described by first order single reaction and the results showed that values of kinetic parameters using three different methods were in good agreement. However, OFW and KAS methods were more efficient in describing the degradation mechanism of the solid-state reactions. Further pyrolysis of OPMF with certain conditions was also carried out to obtain char product for adsorption study. The dye removal performance of one selected char was investigated using methylene blue (MB) with some parameters; initial concentration of MB, biochar dosage (adsorbent), temperature, and pH. Results showed that the rate of removal of methylene blue depends on concentration of solute (MB), pH value, MB concentration and adsorbent dosage. However, temperature of surrounding did not significantly affect the adsorption efficiency. Highest adsorption capacity were recorded at 400 mg/L with 42.53 mg/g removal, at pH 12 with 97.81 % removal, and at 0.5 g adsorbent dosage with 19 mg/g at shortest time of 240 minutes. The equilibrium isotherm study for adsorption of MB showed that Temkin isotherm model was best fit amongst all isotherm models. Langmuir and Freundlich models indicate that the the heat of adsorption of all molecules in the layer linearly decreases with coverage because of adsorbent-adsorbate interactions. Lastly, pseudo-second order was found as the best fit kinetics to the MB removal by OPMF-C followed by Elovich, pseudo-first order kinetic and Weber-Morris.

ABSTRAK

Malaysia kini mempunyai masalah besar berkaitan sisa pertanian seperti sisa-sisa industri kelapa sawit dan lebih perhatian diperlukan untuk menangani masalah ini. Sisa dari kilang kelapa sawit adalah sumber boleh diperbaharui yang berpotensi digunakan untuk menghasilkan bahan mentah kimia, bahan bakar dan bahan penjerap melalui proses yang dipanggil pirolisis. Kajian ini menggunakan serat mesokarp kelapa sawit (OPMF) dari Kilang Sawit Kulai yang terletak di Johor, Malaysia sebagai sampel. Sampel dicirikan (kandungan proksimat, ultimat, lignin, saiz liang, kumpulan berfungsi, morfologi permukaan) dan sifat-sifat kinetik yang kemudian diuji menggunakan penganalisis termogravimetrik. Perbandingan daripada beberapa kaedah bukan isotermal seperti Kissinger, Ozawa-Flynn-Wall (OFW) dan Kissinger-Akahira-Sunose (KAS), digunakan untuk menganalisa data kinetik keadaan pepejal dan data yang diperolehi dibandingkan. Sampel dipanaskan menggunakan kadar pemanasan yang berbeza 5, 10, 15, 20, dan 30 Kmin^{-1} dari 298 K hingga 1173 K. Proses penguraian terma menunjukkan bahawa terdapat tiga peringkat utama iaitu dehidrasi, pirolisis aktif, dan pirolisis pasif. Tenaga pengaktifan (E_a) dan faktor pra eksponen yang diperoleh dari kaedah Kissinger, KAS dan OFW masing-masing adalah 159.74 kJ/mol, 161.90 kJ/mol, 163.29 kJ/mol dan 1.02E+10 min^{-1}, 1.90E+13 min^{-1}, 3.79E+17 min^{-1}. Satu variasi E_a dengan penukaran telah diperoleh apabila kedua-dua model KAS dan OFW digunakan. Ini menunjukkan bahawa pirolisis OPMF berlangsung melalui kinetik yang lebih kompleks dan pelbagai langkah. Hasil yang dicapai dari kaedah Kissinger mewakili nilai sebenar parameter kinetik yang sama untuk keseluruhan proses pirolisis. Kaedah KAS dan OFW mewakili nilai sebenar parameter kinetik. Semua proses pemeruapan digambarkan oleh tindak balas tunggal tertib pertama dan hasilnya menunjukkan bahawa nilai parameter kinetik menggunakan tiga kaedah yang berbeza adalah sama. Walau bagaimanapun, kaedah OFW dan KAS lebih cekap dalam menerangkan mekanisma degradasi tindak balas keadaan pepejal. Pirolisis OPMF dengan syarat-syarat tertentu juga dilakukan untuk mendapatkan produk arang untuk kajian penjerapan. Prestasi penyingkiran pencelup oleh arang terpilih diuji menggunakan metilena biru (MB) dengan beberapa parameter; kepekatan awal MB, dos bioarang (penjerap), suhu dan pH. Keputusan menunjukkan bahawa kadar penyingkiran metilena biru bergantung kepada kepekatan bahan larut (MB), nilai pH, kepekatan MB, dan dos penjerap. Walau bagaimanapun, suhu sekitar tidak menjejaskan kecekapan penjerapan. Muatan penjerapan tertinggi dicatatkan pada 400 mg/L iaitu penyingkiran 42.53 mg/g, pH 12 dengan penyingkiran sebanyak 97.81 %, dan dos penjerap 0.5 g iaitu 19 mg/g pada masa terawal 240 minit. Kajian isoterma keseimbangan untuk penjerapan MB menyatakan bahawa model isoterma Temkin adalah paling sesuai di antara semua model isoterma. Model Langmuir dan Freundlich menunjukkan bahawa haba penjerapan semua molekul dalam lapisan berkurangan secara linear disebabkan liputan hasil dari interaksi penjerap-bahan terjerap. Akhir sekali, kinetik pseudo tertib-kedua didapati sebagai kinetik terbaik bagi penyingkiran MB oleh OPMF-C, diikuti oleh Elovich, kinetik pseudo tertib-pertama dan Weber-Morris.

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LIST OF ABBREVIATIONS

ASTM	-	American Society for Testing and Materials
C_2H_4	-	Acetylene
C_2H_6	-	Ethane
CH_4	-	Methane
CO_2	-	Carbon dioxide
DSC	-	Differential scanning calorimetry
DTA	-	Derivative thermogravimetry
EFB	-	Empty fruit bunch
N_2	-	Nitrogen
H_2SO_4	-	Sulfuric acid
HPLC	-	High-performance liquid chromatography
I.D	-	Internal diameter
LAP	-	Laboratory Analytical Procedure
MF	-	Mesocarp fibre
MPOB	-	Malaysia Palm Oil Board
NREL	-	National Renewable Energy Laboratory
OPMF	-	Oil palm mesocarp fibre
OPT	-	Oil palm trunk
PKS	-	Palm kernel shell
POME	-	Palm oil mill effluent
PV	-	Photovoltaic
RBO	-	Raw bio-oil
S.D	-	Standard deviation
TGA	-	Thermogravimetric analysis
U.K	-	United Kingdom

LIST OF SYMBOLS

cm^3	-	Centimeter cube
E	-	Activation energy
e	-	Exponential
α	-	Conversion rate
°C	-	Degree Celcius
°F	-	Degree Fahrenheit
GHz	-	Gigahertz
g	-	Gram
>	-	Greater than
h	-	hour
K	-	Kelvin
K/s	-	Kelvin per second
kW	-	Kilowatt
f(α)	-	Kinetic equation
<	-	Lower than
MHz	-	Megahertz
MW	-	Megawatt
m	-	Meter
m_0	-	Initial weight
m	-	Actual weight
m_∞	-	Final weight
µm	-	Micrometer
mg	-	Milligram
ml	-	Milliliter
mm	-	Millimeter
min	-	minute
%	-	Percent
±	-	plus-minus

A	-	Pre-exponential factor
n	-	Reaction order
k	-	Reaction rate
s	-	Second
T	-	Temperature
R	-	Universal gas constant
W	-	Watt
wt%	-	Weight percent

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CHAPTER 1

INTRODUCTION

1.0 Introduction

Malaysia is well-known as a developing country and resource-wealthy. One of them is agricultural resource to be specific, oil palm biomass. Oil palm biomass industry has become a major contributor to the country's economy making Malaysia as a giant palm oil producer (ranked second) in the world after Indonesia. Malaysia's palm oil plantation area was summed up 5.74 million hectares in 2016, 1.7% increased from previous year, 2015 which is 5.64 million hectares. According to that statistic, Sabah ranked first with the largest state with palm oil plantation area of 1.55 million hectares, and Sarawak goes second with 1.51 million hectares of total palm oil plantation area. Another 11 states in peninsular Malaysia totalled up 2.68 million hectares (MPOB, 2017).

Biomass is defined as renewable energy came from plant or animal material used for production of energy (fuel, electricity and power), heat, or in diverse industrial processes to produce value-added products. There are three main components in lignocellulosic biomass namely cellulose, hemicellulose and lignin. Other minor constituents include protein, pectin, extractives, and ashes. This study used oil palm mesocarp fibre biomass to produce biochar. The background, problem statement, objective, scope, and significance of study were further explained in this chapter.

1.1 Background of Research

Nowadays, oil palm industry has become the largest economic contributors in Malaysia and plays an essential role in maintaining good socio-economy and well-being of this country. There are various types of biomass available and being used for various application including energy and power generation. It is known as renewable energy that provides clean and green source and could improve environment, economy and energy security. The biomass from oil palm crops in Malaysia generated wastes such as oil mesocarp fibre (OPMF), empty fruits bunches (EFB), palm kernel shell (PKS), and oil palm fronds (OPF) from oil palm mills every year with an annual increment of 5%.

There are many researches who reported on waste conversion to value-added products for example chemicals, absorbents, and fuels. However, the commercial utilization is not applied in large scale yet. Biomass conversion technologies include pyrolysis, gasification and liquefaction. Pyrolysis is the thermal degradation of organic material with high temperature in an inert environment. It is one of the most promising technologies and the most widely used method of biomass utilization. The process will produce three categories of products namely solid, liquid, and gas product (Sadaka and Boateng, 2009). Biochar is a solid product come from pyrolysis process in low temperature, low rate of heating, and longer residence time condition (Demirbas, 2004b). Increase in temperature will increase the devolatilisation thus resulting in higher pore volume. In turn, the surface area becomes greater (Onay, 2007). Char also can be directly used as dye removal agent, solid fuel in boiler, produce hydrogen rich gas through gasification process (Onay, 2007, Lua et al., 2004), and can be used in soil improvement (Sohi et al., 2010).

Biochar and activated carbon can be used to remove dyes due to their adsorptive properties. The using of synthetic dyes is widespread in clothing industries for example cotton, silk, fabrics and manufacturing inks. However, it poses problems to the environment if it were not properly treated because most of dyes used today are of synthetic origin. The contamination of dyes would lead to visible pollution in water as it reduces the light penetrating water. Microorganisms in water need light to survive and maintain the ecosystem of other water-based organisms such as plants and fishes. Overall water ecosystem could be disrupted if dyes contamination in water uncontrolled (Ong et al., 2012, Prahas et al., 2008, Kumar et al., 2011). Study by Padhi (2012) on human cells has shown that dyes are also mutagenic and carcinogenic which can lead to chromosomal breakage, newly formed micronuclei, and aneuploidy. The decision to use methylene blue (MB) as dyes for this research is because it was widely used in textile industry. Moreover, it was easier to compare with existing precursors of biochar for adsorption of MB (Hossain et al., 2017a, Li et al., 2016, Tripathi et al., 2016).

1.2 Problem Statement

The process of producing oil palm has created oil palm wastes such as palm oil mill effluent (POME), oil palm trunks (OPT), empty fruit bunch (EFB), palm kernel shell (PKS), and oil palm mesocarp fibre (OPMF) (Hossain et al., 2017a). Nevertheless, these wastes have generated a major waste disposal problem and pose a threat to the environment if not properly treated due to its large volume. The main purposes of waste management are to minimise, recycle, and recover the energy contained in the wastes before disposing them. In addition of that, current uses and disposal measures of palm mill residues must be considered in order to recover the potential energy.

Kinetic parameters of pyrolysis process are very important because it includes the initial step in combustion and gasification processes. The knowledge of kinetics for thermal decomposition of lignocellulosic materials are necessarily important for the design and optimization of reactors. Thus, useful parameters such as activation energy, Ea, pre-exponential factor, k, and reaction order, n, are required for further use in designing of reactor, product features, and establishment of process conditions. Thus, this study used Thermogravimetic Analysis (TGA) to determine the kinetic parameters. This technique allows measurement of mass change versus temperature and the results are expressed in the form of curves of weight loss (TGA) and derivative mass loss (DTG).

Dyes are vastly used in textile, printing and paper industries as they used more than 90,000 commercial dyes and produced over 70,000 tonnes of dye-stuff annually (Tan et al., 2007). Since most of those are used synthetic dyes, it contributed to potential source of pollution that ends up in waste water. Moreover, the contaminated dyes in water will give bad impacts such as visible pollution, limiting light penetration into water (Kumar et al., 2011), and could lead to serious potential mutagenic and carcinogenic effects (Padhi, 2012). Some conventional techniques for dye removal are membrane filtration, irradiation, and photochemical could lead to other pollution such as spent catalyst and fouled membrane. MB dye was selected as sample dye for adsorption studies in this project.

Oil palm fibre waste is one of the most abundant waste in agricultural sector. In example, the mesocarp fibre will be disposed as waste after extracting oil for further product. Some of other waste such as palm kernel shell and fibre itself are usually burned down as fuel in power stations. The potential use of OPMF waste to produce alternative adsorbent which is low cost and wider availability in Malaysia offers good choice for dye removal (Mahamad et al., 2015) instead of using activated carbon. Thus, oil palm mesocarp fibre (OPMF) waste biomass was selected to be used in this study to convert into biochar and further used to remove MB from water.

1.3 Objectives of Study

The objectives of this study are to investigate the potential of biochar produced from the microwave-assisted pyrolysis of oil palm mesocarp fibre to remove dyes from solution. Specific objectives of this study are as follows:

i. To determine the kinetic degradation profile of oil palm mesocarp fibre (OPMF) during microwave-assisted pyrolysis process
ii. To identify and evaluate the biochar produced from oil palm mesocarp fibre (OPMF) via pyrolysis.
iii. To investigate the kinetics and adsorptive capabilities of biochar produced from pyrolysis to remove MB.

1.4 Scope of Study

First, the sample of OPMF was collected from two local oil palm processing facilities located at Kulai and Simpang Waha. It was then ground and sieved to a size of 100µm to 300µm before went through some processes to determine its physical and chemical properties. Thermogravimetric analyser was used to pyrolyse raw OPMF with some different heating rates (5-30K/min). In order to determine kinetic degradation profile of OPMF during pyrolysis, kinetic parameters such as activation energy and pre-exponential factor of degradation of raw OPMF was calculated using Kissinger, Ozawa-Flynn-Wall (OFW), and Kissinger-Akahira-Sunose (KAS) methods.

A modified microwave was used to prepare the biochar using some varied parameters; microwave power (600-800W), MWA loading ratio (1:0.5 to 1:1) and nitrogen flow (2-6 LPM) from preliminary study. The biochar produced was then identified and evaluated for its physical and chemical properties such as surface area (Brunauer Emmet Teller Analysis, BET) moisture and ash content, surface functional group (Fourier Transform Infrared Spectroscopy, FTIR) surface morphology (Scanning Electron Microscopy, SEM) and point zero charge (pH_{pzc}).

The highest surface area from biochar products was further investigated for its adsorptive properties to remove dye (MB) based on some factors; initial concentration and contact time, adsorbent dosage, temperature, and pH. Equilibrium isotherm study was carried out by using three models; Langmuir, Freundlich, and Temkin isotherm models. Kinetic study of adsorption was also carried out by using three different adsorbent dosage; 0.25g, 0.50g, and 0.75g, and three different initial MB concentrations of 50, 100, and 150mg L^{-1}. The pseudo-first order, pseudo-second order, Elovich, and Weber-Morris intra-particle diffusion models were used to analyse kinetic of adsorptive capacity of biochar.

1.5 Significance of Study

The outcome of this study is expected to directly benefit the oil palm industry from the development of proper thermochemical conversion process for oil palm fibre biomass and the set-up of related equipment require the determination of kinetic parameters (activation energy, pre-exponential factor, and reaction order) of the pyrolysis process and detailed understanding of the pyrolysis mechanism. Furthermore, future association with industries and government on the utilization of the oil palm mesocarp fibre waste biomass would contribute for income generation amongst local farmers and minimizing the problem of waste disposal after the harvesting season. The characterization of physical and chemical properties can add up to the current knowledge on the biochar produced from oil palm mesocarp fibre. It also adds novelty to this study due to limited studies reported regarding the utilization of oil palm mesocarp fibre waste biomass for production of biochar to remove dyes.

REFERENCES

Abdullah, H., Mediaswanti, K. A. & Wu, H. 2010. Biochar as a fuel: 2. Significant differences in fuel quality and ash properties of biochars from various biomass components of Mallee trees. *Energy & Fuels,* 24**,** 1972-1979.

Abnisa, F., Arami-Niya, A., Daud, W. W. & Sahu, J. 2013. Characterization of bio-oil and bio-char from pyrolysis of palm oil wastes. *BioEnergy Research,* 6**,** 830-840.

Abnisa, F., Daud, W. M. A. W., Husin, W. N. W. & Sahu, J. N. 2011. Utilization possibilities of palm shell as a source of biomass energy in Malaysia by producing bio-oil in pyrolysis process. *Biomass and Bioenergy,* 35**,** 1863-1872.

Ahmad, A., Loh, M. & Aziz, J. 2007. Preparation and characterization of activated carbon from oil palm wood and its evaluation on methylene blue adsorption. *Dyes and Pigments,* 75**,** 263-272.

Alam, M. Z., Muyibi, S. A., Mansor, M. F. & Wahid, R. 2007. Activated carbons derived from oil palm empty-fruit bunches: Application to environmental problems. *Journal of Environmental Sciences,* 19**,** 103-108.

Babu, B. R., Parande, A., Raghu, S. & Kumar, T. P. 2007. Cotton textile processing: waste generation and effluent treatment. *Journal of cotton science*.

Bajpai, P. 2016. Structure of Lignocellulosic Biomass. *Pretreatment of Lignocellulosic Biomass for Biofuel Production.* Springer.

Banerjee, S., Chattopadhyaya, M. C., Srivastava, V. & Sharma, Y. C. 2014. Adsorption studies of methylene blue onto activated saw dust: kinetics, equilibrium, and thermodynamic studies. *Environmental Progress & Sustainable Energy,* 33**,** 790-799.

Beis, S., Onay, Ö. & Koçkar, Ö. 2002. Fixed-bed pyrolysis of safflower seed: influence of pyrolysis parameters on product yields and compositions. *Renewable Energy,* 26**,** 21-32.

Bhatia, L., Johri, S. & Ahmad, R. 2012. An economic and ecological perspective of ethanol production from renewable agro waste: a review. *Amb Express,* 2**,** 65.

Bhatnagar, A. & Jain, A. 2005. A comparative adsorption study with different industrial wastes as adsorbents for the removal of cationic dyes from water. *Journal of Colloid and Interface Science,* 281**,** 49-55.

Brebu, M. & Vasile, C. 2010. Thermal degradation of lignin—a review. *Cellulose Chemistry & Technology,* 44**,** 353.

Bridgwater, A., Meier, D. & Radlein, D. 1999. An overview of fast pyrolysis of biomass. *Organic geochemistry,* 30**,** 1479-1493.

Bridgwater, A. V. & Grassi, G. 2012. *Biomass pyrolysis liquids upgrading and utilization*, Springer Science & Business Media.

Brown, D. & Laboureur, P. 1983a. The aerobic biodegradability of primary aromatic amines. *Chemosphere,* 12**,** 405-414.

Brown, D. & Laboureur, P. 1983b. The degradation of dyestuffs: part I primary biodegradation under anaerobic conditions. *Chemosphere,* 12**,** 397-404.

Bryers, R. W. 1996. Fireside slagging, fouling, and high-temperature corrosion of heat-transfer surface due to impurities in steam-raising fuels. *Progress in energy and combustion science,* 22**,** 29-120.

Chen, W.-H. & Lin, B.-J. 2016. Characteristics of products from the pyrolysis of oil palm fiber and its pellets in nitrogen and carbon dioxide atmospheres. *Energy,* 94**,** 569-578.

Christie, R. M. 2007. *Environmental aspects of textile dyeing*, Elsevier.

Collard, F.-X. & Blin, J. 2014. A review on pyrolysis of biomass constituents: Mechanisms and composition of the products obtained from the conversion of cellulose, hemicelluloses and lignin. *Renewable and Sustainable Energy Reviews,* 38**,** 594-608.

Corbman, B. P. 1983. *Textiles. Fiber to fabric*.

Delee, W., O'neill, C., Hawkes, F. R. & Pinheiro, H. M. 1998. Anaerobic treatment of textile effluents: a review. *Journal of Chemical Technology & Biotechnology: International Research in Process, Environmental AND Clean Technology,* 73**,** 323-335.

Demirbas, A. 2004a. Combustion characteristics of different biomass fuels. *Progress in energy and combustion science,* 30**,** 219-230.

Demirbas, A. 2004b. Effects of temperature and particle size on bio-char yield from pyrolysis of agricultural residues. *Journal of analytical and applied pyrolysis,* 72**,** 243-248.

Demirbas, A. 2005. Potential applications of renewable energy sources, biomass combustion problems in boiler power systems and combustion related environmental issues. *Progress in energy and combustion science,* 31**,** 171-192.

Demirbas, A. 2006. Effect of temperature on pyrolysis products from four nut shells. *Journal of analytical and applied pyrolysis,* 76**,** 285-289.

Demirbas, A. 2011. Competitive liquid biofuels from biomass. *Applied Energy,* 88**,** 17-28.

Demirbaş, A. 2000. Mechanisms of liquefaction and pyrolysis reactions of biomass. *Energy conversion and management,* 41**,** 633-646.

Demirbaş, A. 2001. Biomass resource facilities and biomass conversion processing for fuels and chemicals. *Energy conversion and Management,* 42**,** 1357-1378.

Demirbas, A. & ARIN, G. 2002. An overview of biomass pyrolysis. *Energy sources,* 24**,** 471-482.

Dorez, G., Ferry, L., Sonnier, R., Taguet, A. & Lopez-cuesta, J.-M. 2014. Effect of cellulose, hemicellulose and lignin contents on pyrolysis and combustion of natural fibers. *Journal of Analytical and Applied Pyrolysis,* 107**,** 323-331.

Elnour, A. Y., Alghyamah, A. A., Shaikh, H. M., Poulose, A. M., Al-zahrani, S. M., Anis, A. & Al-wabel, M. I. 2019. Effect of Pyrolysis Temperature on Biochar Microstructural Evolution, Physicochemical Characteristics, and Its Influence on Biochar/Polypropylene Composites. *Applied Sciences*, 9**,** 1149.

Ertaş, M. & Alma, M. H. 2010. Pyrolysis of laurel (Laurus nobilis L.) extraction residues in a fixed-bed reactor: Characterization of bio-oil and bio-char. *Journal of Analytical and Applied Pyrolysis,* 88**,** 22-29.

Fan, S., Tang, J., Wang, Y., LI, H., Zhang, H., Tang, J., Wang, Z. & LI, X. 2016. Biochar prepared from co-pyrolysis of municipal sewage sludge and tea waste for the adsorption of methylene blue from aqueous solutions: kinetics, isotherm, thermodynamic and mechanism. *Journal of Molecular Liquids,* 220**,** 432-441.

Fan, S., Wang, Y., Wang, Z., Tang, J., Tang, J. & Li, X. 2017. Removal of methylene blue from aqueous solution by sewage sludge-derived biochar: adsorption kinetics, equilibrium, thermodynamics and mechanism. *Journal of environmental chemical engineering,* 5**,** 601-611.

Fu, L., Mccallum, S. A., Miao, J., Hart, C., Tudryn, G. J., Zhang, F. & Linhardt, R. J. 2015. Rapid and accurate determination of the lignin content of lignocellulosic biomass by solid-state NMR. *Fuel,* 141**,** 39-45.

Geng, A. 2014. Upgrading of oil palm biomass to value-added products. *Biomass and Bioenergy.* Springer.

Ghosh, D. & Bhattacharyya, K. G. 2002. Adsorption of methylene blue on kaolinite. *Applied clay science,* 20**,** 295-300.

González, J. F., González-garcía, C. M., Ramiro, A., Gañán, J., Ayuso, A. & Turegano, J. 2006. Use of energy crops for domestic heating with a mural boiler. *Fuel Processing Technology,* 87**,** 717-726.

Güllü, D. & Demirbaş, A. 2001. Biomass to methanol via pyrolysis process. *Energy Conversion and Management,* 42**,** 1349-1356.

Guo, J. & Lua, A. 2000. Kinetic study on pyrolysis of extracted oil palm fiber. Isothermal and non-isothermal conditions. *Journal of Thermal Analysis and Calorimetry,* 59**,** 763-774.

Guo, M., Song, W. & Buhain, J. 2015. Bioenergy and biofuels: history, status, and perspective. *Renewable and Sustainable Energy Reviews,* 42**,** 712-725.

Gupta, V. 2009. Application of low-cost adsorbents for dye removal–a review. *Journal of environmental management,* 90**,** 2313-2342.

Gupta, V., Carrott, P., Ribeiro Carrott, M. & Suhas 2009. Low-cost adsorbents: growing approach to wastewater treatment—a review. *Critical Reviews in Environmental Science and Technology,* 39**,** 783-842.

Hameed, B. & Ahmad, A. 2009. Batch adsorption of methylene blue from aqueous solution by garlic peel, an agricultural waste biomass. *Journal of hazardous materials,* 164**,** 870-875.

Hameed, B., Mahmoud, D. & Ahmad, A. 2008a. Sorption equilibrium and kinetics of basic dye from aqueous solution using banana stalk waste. *Journal of Hazardous Materials,* 158**,** 499-506.

Hameed, B., Mahmoud, D. & Ahmad, A. 2008b. Sorption of basic dye from aqueous solution by pomelo (Citrus grandis) peel in a batch system. *Colloids and Surfaces A: Physicochemical and Engineering Aspects,* 316**,** 78-84.

Heo, H. S., Park, H. J., Yim, J.-H., Sohn, J. M., Park, J., Kim, S.-S., Ryu, C., Jeon, J.-K. & Park, Y.-K. 2010. Influence of operation variables on fast pyrolysis of Miscanthus sinensis var. purpurascens. *Bioresource technology,* 101**,** 3672-3677.

Ho, Y.-S. 2006. Review of second-order models for adsorption systems. *Journal of hazardous materials,* 136**,** 681-689.

Hossain, M. A., Ganesan, P., Jewaratnam, J. & Chinna, K. 2017a. Optimization of process parameters for microwave pyrolysis of oil palm fiber (OPF) for hydrogen and biochar production. *Energy Conversion and Management,* 133**,** 349-362.

Hossain, M. A., Ganesan, P. B., Sandaran, S. C., Rozali, S. B. & Krishnasamy, S. 2017b. Catalytic microwave pyrolysis of oil palm fiber (OPF) for the biochar production. *Environmental Science and Pollution Research,* 24**,** 26521-26533.

Hunger, K. 2007. *Industrial dyes: chemistry, properties, applications*, John Wiley & Sons.

Ibrahim, N., Kamarudin, S. K. & Minggu, L. J. 2014. Biofuel from biomass via photo-electrochemical reactions: An overview. *Journal of Power Sources,* 259**,** 33-42.

Ioannidou, O. & Zabaniotou, A. 2007. Agricultural residues as precursors for activated carbon production—a review. *Renewable and Sustainable Energy Reviews,* 11**,** 1966-2005.

Isikgor, F. & Becer, C. R. Lignocellulosic Biomass: a sustainable platform for production of bio-based chemicals and polymers. Polym Chem 2015; 6: 4497-559.

Isikgor, F. H. & Becer, C. R. 2015. Lignocellulosic biomass: a sustainable platform for the production of bio-based chemicals and polymers. *Polymer Chemistry,* 6**,** 4497-4559.

Islam, M. R., Parveen, M. & Haniu, H. 2010. Properties of sugarcane waste-derived bio-oils obtained by fixed-bed fire-tube heating pyrolysis. *Bioresource Technology,* 101**,** 4162-4168.

Karaosmanoğlu, F., Tetik, E. & Göllü, E. 1999. Biofuel production using slow pyrolysis of the straw and stalk of the rapeseed plant. *Fuel processing technology,* 59**,** 1-12.

Kelly-yong, T. L., Lee, K. T., Mohamed, A. R. & Bhatia, S. 2007. Potential of hydrogen from oil palm biomass as a source of renewable energy worldwide. *Energy Policy,* 35**,** 5692-5701.

Khawam, A. 2007. *Application of solid-state kinetics to desolvation reactions.* The University of Iowa.

Khor, K., Lim, K. & Zainal, Z. 2009. Characterization of bio-oil: a by-product from slow pyrolysis of oil palm empty fruit bunches. *American Journal of Applied Sciences,* 6**,** 1647-1652.

Kim, K. H., Kim, J.-Y., Cho, T.-S. & Choi, J. W. 2012. Influence of pyrolysis temperature on physicochemical properties of biochar obtained from the fast pyrolysis of pitch pine (Pinus rigida). *Bioresource technology,* 118**,** 158-162.

Komnitsas, K. A. & Zaharaki, D. 2016. Morphology of modified biochar and its potential for phenol removal from aqueous solutions. *Frontiers in Environmental Science,* 4**,** 26.

Kumar, P. S., Ramalingam, S. & Sathishkumar, K. 2011. Removal of methylene blue dye from aqueous solution by activated carbon prepared from cashew nut shell as a new low-cost adsorbent. *Korean Journal of Chemical Engineering,* 28**,** 149-155.

Kwapinski, W., Byrne, C. M., Kryachko, E., Wolfram, P., Adley, C., Leahy, J. J., Novotny, E. H. & Hayes, M. H. 2010. Biochar from biomass and waste. *Waste and Biomass Valorization,* 1**,** 177-189.

Lam, M. K. & Lee, K. T. 2011. Renewable and sustainable bioenergies production from palm oil mill effluent (POME): win–win strategies toward better environmental protection. *Biotechnology Advances,* 29**,** 124-141.

Lapuerta, M., Hernández, J. J. & Rodríguez, J. 2007. Comparison between the kinetics of devolatilisation of forestry and agricultural wastes from the middle-south regions of Spain. *Biomass and Bioenergy,* 31**,** 13-19.

Li, J., Dai, J., Liu, G., Zhang, H., Gao, Z., Fu, J., He, Y. & Huang, Y. 2016. Biochar from microwave pyrolysis of biomass: A review. *Biomass and Bioenergy,* 94**,** 228-244.

Liu, P., Liu, W.-J., Jiang, H., Chen, J.-J., Li, W.-W. & Yu, H.-Q. 2012. Modification of bio-char derived from fast pyrolysis of biomass and its application in removal of tetracycline from aqueous solution. *Bioresource technology,* 121**,** 235-240.

Liu, W.-J., Zeng, F.-X., Jiang, H. & Zhang, X.-S. 2011. Preparation of high adsorption capacity bio-chars from waste biomass. *Bioresource technology,* 102**,** 8247-8252.

Liu, Z. & Han, G. 2015. Production of solid fuel biochar from waste biomass by low temperature pyrolysis. *Fuel,* 158**,** 159-165.

Lua, A. C., Yang, T. & Guo, J. 2004. Effects of pyrolysis conditions on the properties of activated carbons prepared from pistachio-nut shells. *Journal of analytical and applied pyrolysis,* 72**,** 279-287.

Mahamad, M. N., Zaini, M. A. A. & Zakaria, Z. A. 2015. Preparation and characterization of activated carbon from pineapple waste biomass for dye removal. *International Biodeterioration & Biodegradation,* 102**,** 274-280.

Maschio, G., Koufopanos, C. & Lucchesi, A. 1992. Pyrolysis, a promising route for biomass utilization. *Bioresource technology,* 42**,** 219-231.

Mohammed, M., Salmiaton, A., Azlina, W. W., Amran, M. M., Fakhru'l-razi, A. & Taufiq-yap, Y. 2011. Hydrogen rich gas from oil palm biomass as a potential source of renewable energy in Malaysia. *Renewable and Sustainable Energy Reviews,* 15**,** 1258-1270.

Nethaji, S. & Sivasamy, A. 2011. Adsorptive removal of an acid dye by lignocellulosic waste biomass activated carbon: equilibrium and kinetic studies. *Chemosphere,* 82**,** 1367-1372.

Nguyen, B. T., Lehmann, J., Hockaday, W. C., Joseph, S. & Masiello, C. A. 2010. Temperature sensitivity of black carbon decomposition and oxidation. *Environmental science & technology,* 44**,** 3324-3331.

Oladoja, N., Aboluwoye, C., Oladimeji, Y., Ashogbon, A. & Otemuyiwa, I. 2008. Studies on castor seed shell as a sorbent in basic dye contaminated wastewater remediation. *Desalination,* 227**,** 190-203.

Onay, O. 2007. Influence of pyrolysis temperature and heating rate on the production of bio-oil and char from safflower seed by pyrolysis, using a well-swept fixed-bed reactor. *Fuel Processing Technology,* 88**,** 523-531.

Onay, Ö., Beis, S. & Koçkar, Ö. M. 2001. Fast pyrolysis of rape seed in a well-swept fixed-bed reactor. *Journal of analytical and applied pyrolysis,* 58**,** 995-1007.

Onay, O. & Koçkar, O. M. 2004. Fixed-bed pyrolysis of rapeseed (Brassica napus L.). *Biomass and Bioenergy,* 26**,** 289-299.

Ong, S.-T., ha, S.-T., Keng, P.-S., Lee, C.-k. & Hung, Y.-T. 2012. Removal of dyes from wastewaters by low-cost adsorbents. *Handbook of environment and waste management: Air and water pollution control.* World Scientific.

Özçimen, D. & Ersoy-meriçboyu, A. 2010. Characterization of biochar and bio-oil samples obtained from carbonization of various biomass materials. *Renewable Energy,* 35**,** 1319-1324.

Padhi, B. 2012. Pollution due to synthetic dyes toxicity & carcinogenicity studies and remediation. *International Journal of Environmental Sciences,* 3**,** 940.

Pagga, U. & Brown, D. 1986. The degradation of dyestuffs: Part II Behaviour of dyestuffs in aerobic biodegradation tests. *Chemosphere,* 15**,** 479-491.

Parikh, J., Channiwala, S. & Ghosal, G. 2005. A correlation for calculating HHV from proximate analysis of solid fuels. *Fuel,* 84**,** 487-494.

Payne, K. B. & Abdel-fattah, T. M. 2004. Adsorption of divalent lead ions by zeolites and activated carbon: effects of pH, temperature, and ionic strength. *Journal of Environmental Science and Health, Part A,* 39**,** 2275-2291.

Prahas, D., Kartika, Y., Indraswati, N. & Ismadji, S. 2008. The use of activated carbon prepared from jackfruit (Artocarpus heterophyllus) peel waste for methylene blue removal. *Journal of Environmental Protection Science,* 2**,** 1-10.

Rai, H. S., Bhattacharyya, M. S., Singh, J., Bansal, T., Vats, P. & Banerjee, U. 2005. Removal of dyes from the effluent of textile and dyestuff manufacturing industry: a review of emerging techniques with reference to biological treatment. *Critical reviews in environmental science and technology,* 35**,** 219-238.

Rezaiyan, J. & Cheremisinoff, N. P. 2005. *Gasification technologies: a primer for engineers and scientists*, CRC press.

Robinson, T., Mcmullan, G., Marchant, R. & Nigam, P. 2001. Remediation of dyes in textile effluent: a critical review on current treatment technologies with a proposed alternative. *Bioresource technology,* 77**,** 247-255.

Sadaka, S. & Boateng, A. A. 2009. *Pyrolysis and bio-oil,* [Cooperative Extension Service], University of Arkansas, US Department of Agriculture and county governments cooperating.

Saidu, M., Salim, M. R. & Yuzir, M. A. M. 2011. Cultivation of oyster mushroom (Pleurotus spp.) on palm oil mesocarp fibre. *African Journal of Biotechnology,* 10**,** 15973-15976.

Salema, A. A. & Ani, F. N. 2010. Microwave Pyrolysis of Oil Palm Fibres. *Jurnal Mekanikal,* 30**,** 77-86.

Salema, A. A. & Ani, F. N. 2012. Pyrolysis of oil palm empty fruit bunch biomass pellets using multimode microwave irradiation. *Bioresource Technology,* 125**,** 102-107.

Salman, J. & Hameed, B. 2010. Effect of preparation conditions of oil palm fronds activated carbon on adsorption of bentazon from aqueous solutions. *Journal of hazardous materials,* 175**,** 133-137.

Shafie, S., Mahlia, T., Masjuki, H. & Ahmad-yazid, A. 2012. A review on electricity generation based on biomass residue in Malaysia. *Renewable and Sustainable Energy Reviews,* 16**,** 5879-5889.

Shariff, A., Aziz, M., Syairah, N. & Abdullah, N. 2014. Slow Pyrolysis of Oil Palm Empty Fruit Bunches for Biochar Production and Characterisation. *Journal of Physical Science,* 25.

Shuit, S. H., Tan, K. T., Lee, K. T. & Kamaruddin, A. 2009. Oil palm biomass as a sustainable energy source: A Malaysian case study. *Energy,* 34**,** 1225-1235.

Sing, K. S. 1991. Characterization Of Porous Solids: An Introductory Survey. *Studies in Surface Science and Catalysis.* Elsevier.

Skoulou, V. & Zabaniotou, A. 2007. Investigation of agricultural and animal wastes in Greece and their allocation to potential application for energy production. *Renewable and sustainable energy reviews,* 11**,** 1698-1719.

Slopiecka, K., Bartocci, P. & Fantozzi, F. 2012. Thermogravimetric analysis and kinetic study of poplar wood pyrolysis. *Applied Energy,* 97**,** 491-497.

Sohi, S., Krull, E., Lopez-capel, E. & Bol, R. 2010. A review of biochar and its use and function in soil. *Advances in agronomy,* 105**,** 47-82.

Srivastava, V. C., Swamy, M. M., Mall, I. D., Prasad, B. & Mishra, I. M. 2006. Adsorptive removal of phenol by bagasse fly ash and activated carbon: equilibrium, kinetics and thermodynamics. *Colloids and surfaces a: physicochemical and engineering aspects,* 272**,** 89-104.

Stolz, A. 2001. Basic and applied aspects in the microbial degradation of azo dyes. *Applied microbiology and biotechnology,* 56**,** 69-80.

Sukiran, M. A., Chin, C. M. & Bakar, N. K. 2009. Bio-oils from pyrolysis of oil palm empty fruit bunches. *American Journal of Applied Sciences,* 6**,** 869-875.

Sulaiman, F., Abdullah, N., Gerhauser, H. & Shariff, A. 2011. An outlook of Malaysian energy, oil palm industry and its utilization of wastes as useful resources. *Biomass and bioenergy,* 35**,** 3775-3786.

Sumathi, S., Chai, S. & Mohamed, A. 2008. Utilization of oil palm as a source of renewable energy in Malaysia. *Renewable and Sustainable Energy Reviews,* 12**,** 2404-2421.

Sun, L., Chen, D., Wan, S. & Yu, Z. 2015. Performance, kinetics, and equilibrium of methylene blue adsorption on biochar derived from eucalyptus saw dust modified with citric, tartaric, and acetic acids. *Bioresource technology,* 198**,** 300-308.

Sun, L., Wan, S. & Luo, W. 2013. Biochars prepared from anaerobic digestion residue, palm bark, and eucalyptus for adsorption of cationic methylene blue dye: characterization, equilibrium, and kinetic studies. *Bioresource Technology,* 140**,** 406-413.

Sun, Z., Jin, B., Zhang, M., Liu, R. & Zhang, Y. 2008. Experimental studies on cotton stalk combustion in a fluidized bed. *Energy,* 33**,** 1224-1232.

Sung, C. T. B. 2016. Availability, use, and removal of oil palm biomass in Indonesia.

Tan, I., Hameed, B. & Ahmad, A. 2007. Equilibrium and kinetic studies on basic dye adsorption by oil palm fibre activated carbon. *Chemical Engineering Journal,* 127**,** 111-119.

Tillman, D. A. 2000. Biomass cofiring: the technology, the experience, the combustion consequences. *Biomass and bioenergy,* 19**,** 365-384.

Tripathi, M., Sahu, J. & Ganesan, P. 2016. Effect of process parameters on production of biochar from biomass waste through pyrolysis: A review. *Renewable and Sustainable Energy Reviews,* 55**,** 467-481.

Vamvuka, D. & Zografos, D. 2004. Predicting the behaviour of ash from agricultural wastes during combustion. *Fuel,* 83**,** 2051-2057.

Vyazovkin, S. & Wight, C. A. 1999. Model-free and model-fitting approaches to kinetic analysis of isothermal and nonisothermal data. *Thermochimica acta,* 340**,** 53-68.

Wan Asma, I., Mahanim, S., Zulkafli, H., Othman, S. & Mori, Y. Malaysian oil palm biomass. Regional workshop on UNEP/DTIE/IETC in collaboration with GEC, 2010.

Wang, S., Zhu, Z., Coomes, A., Haghseresht, F. & Lu, G. 2005. The physical and surface chemical characteristics of activated carbons and the adsorption of methylene blue from wastewater. *Journal of colloid and interface science,* 284**,** 440-446.

Wang, Y.-J., Sun, R.-J., Xiao, A.-Y., Wang, S.-Q. & Zhou, D.-M. 2010. Phosphate affects the adsorption of tetracycline on two soils with different characteristics. *Geoderma,* 156**,** 237-242.

Werther, J., Saenger, M., Hartge, E.-U., Ogada, T. & Siagi, Z. 2000. Combustion of agricultural residues. *Progress in energy and combustion science,* 26**,** 1-27.

Wu, T. Y., Mohammad, A. W., Jahim, J. M. & Anuar, N. 2009a. A holistic approach to managing palm oil mill effluent (POME): Biotechnological advances in the sustainable reuse of POME. *Biotechnology Advances,* 27**,** 40-52.

Wu, Y., Wu, S., Li, Y. & Gao, J. 2009b. Physico-chemical characteristics and mineral transformation behavior of ashes from crop straw. *Energy & Fuels,* 23**,** 5144-5150.

Yamada, H., Tanaka, R., Sulaiman, O., Hashim, R., Hamid, Z., Yahya, M., KosugI, A., Arai, T., Murata, Y. & Nirasawa, S. 2010. Old oil palm trunk: a promising source of sugars for bioethanol production. *Biomass and Bioenergy,* 34**,** 1608-1613.

Yao, Y., Gao, B., Inyang, M., Zimmerman, A. R., Cao, X., Pullammanappallil, P. & Yang, L. 2011. Biochar derived from anaerobically digested sugar beet tailings: Characterization and Phosphate Removal Potential. *Bioresource technology,* 102**,** 6273-6278.

Yazdani, M., Bahrami, H. & Arami, M. 2014. Preparation and characterization of chitosan/feldspar biohybrid as an adsorbent: optimization of adsorption process via response surface modeling. *The Scientific World Journal,* 2014.

Zahari, M. W., Hassan, O. A., Wong, H. & Liang, J. 2003. Utilization of oil palm frond-based diets for beef and dairy production in Malaysia. *Asian Australasian Journal Of Animal Sciences,* 16**,** 625-634.

Zaini, M. A. A., Okayama, R. & Machida, M. 2009. Adsorption of aqueous metal ions on cattle-manure-compost based activated carbons. *Journal of hazardous materials,* 170**,** 1119-1124.

Zaini, M. A. A., Zakaria, M., Setapar, S. M.-. & Che-Yunus, M. 2013. Sludge-adsorbents from palm oil mill effluent for methylene blue removal. *Journal of Environmental Chemical Engineering,* 1**,** 1091-1098.

Zeng, F., Liu, W., Jiang, H., Yu, Zeng, R. J. & Guo, Q. 2011. Separation of phthalate esters from bio-oil derived from rice husk by a basification–acidification process and column chromatography. *Bioresource technology,* 102**,** 1982-1987.

Zevenhoven-onderwater, M., Backman, R., Skrifvars, B.-J. & Hupa, M. 2001. The ash chemistry in fluidised bed gasification of biomass fuels. Part I: predicting the chemistry of melting ashes and ash–bed material interaction. *Fuel,* 80**,** 1489-1502.

Zhang, L., Xu, C. C. & Champagne, P. 2010. Overview of recent advances in thermo-chemical conversion of biomass. *Energy Conversion and Management,* 51**,** 969-982.

Zhang, X., Tu, M. & Paice, M. G. 2011. Routes to potential bioproducts from lignocellulosic biomass lignin and hemicelluloses. *BioEnergy Research,* 4**,** 246-257.

Zhong, C. & Wei, X. 2004. A comparative experimental study on the liquefaction of wood. *Energy,* 29**,** 1731-1741.