

UNIVERSITI PUTRA MALAYSIA

PRODUCTION AND CHARACTERIZATION OF BIOCHAR DERIVED FROM OIL PALM WASTES, AND OPTIMIZATION FOR ZINC ADSORPTION

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By

SEYED ALI ZAMANI

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy

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In dedication to:

My parents, my wife, and my children that dedicated their life to my progression.



Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfillment of the requirement for the degree of Doctor of Philosophy

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Today, using low cost materials such as agricultural wastes as an adsorbent for heavy metals removal has gained attention in water and waste water treatment. This research aims to produce biochar (a porous material with high carbon content and low density) from three different types of oil palm wastes via pyrolysis process in a lab scale fixed bed reactor. The raw feed stocks for the pyrolysis experiment include oil palm frond (OPF), oil palm empty fruit bunches (OPEFB), and oil palm Mesocarp fiber (OPMF). The synthesized biochars were then characterized for their physiochemical properties using CHNS elemental analysis, proximate analysis, scanning electron microscopy (SEM), BET surface area, and Fourier transform infrared spectroscopy (FTIR).

The adsorption capacity of produced biochars for removing zinc from aqueous solution was investigated by performing batch adsorption experiments. The result of batch adsorption experiments showed that oil palm empty fruit bunches biochar (OPEFBB) had the best efficiency for zinc removal and therefore was chosen for further optimization study.

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The estimation and modeling capacities of two statistical tools; response surface methodology (RSM) and artificial neural networks (ANNs) in determining and optimizing the effect of pyrolysis conditions on percentage of yield and adsorption capacity of OPEFBB toward zinc removal were evaluated. The effect of three independent variables namely: highest treatment temperature (HTT), heating rate (HR) and residence time (RT) on OPEFBB percentage of yield and adsorption capacity were determined. A central composite design was utilized to determine the

effect of these factors as well as the interaction of them on responses. Based on central composite design, two second order regression models were developed for OPEFBB adsorption capacity and percentage of yield. The optimum actual values for percentage of yield and adsorption capacity were 25.49% and 15.18mg/g, respectively, under the predicted conditions of 615°C for HTT, 8°C/min for HR, and 128 minute for RT. The input and output of the RSM design was used in artificial neural networks for training purpose. The incremental back propagation algorithm demonstrated the best results and which has been used as learning algorithm for ANN in combination with Genetic Algorithm in the optimization. The estimated production conditions to reach the optimum actual values of yield at 25.38% and adsorption capacity of 15.29mg/g were HTT of 625°C, HR of 9° C/min and RT of 130 min.

In both RSM and ANN methods, percentage of yield and adsorption capacity of OPEFBB were mostly influenced by the highest treatment temperature (HTT) followed by heating rate (HR) and residence time (RT). The performance of RSM and ANNs were compared in terms of root mean square error (RMSE), coefficient of determination (R²), and absolute average deviation (AAD). The results demonstrated that both models fitted the experimental data well; however the predicted values confirmed that ANN outperformed RSM due to superiority of ANN model in capturing non linear behavior and better estimating capability rather than RSM.

The batch adsorption experiments for removal of zinc by optimum product were carried out by determining the impact of solution pH, biochar dosage and heavy metal concentration on the adsorption process. The results suggest that solution pH is one of the most important factors influencing the adsorption capacity. At low pHs, the removal of zinc ions was low due to high concentration of protons in sorption media and competition of protons with zinc ions for binding sites. By increasing pH, the removal of zinc showed an upward trend and reached the maximum value at pH6. After that by rising pH, precipitation and hydroxyl formation occurred which masked the true adsorption. Biochar dosage and heavy metal concentration also influenced the removal of zinc and the optimum values were found to be 10 g/l and 80 mg/l respectively.

Four adsorption isotherms namely: Langmuir, Freundlich, Dubinin–Radushkevich, and Temkin were applied for modeling the adsorption equilibrium data. Among them Langmuir isotherm could describe the adsorption data better by coefficient of determination of 0.9988 and the maximum adsorption capacity was at 19.27 mg/g. From Dubinin equation, ion exchange mechanism was found to be predominant mechanism in the adsorption of zinc by OPEFBB.

Abstrak tesis yang dibentangkan kepada senat Universiti Putra Malaysia untuk memenuhi keperluan untuk ijazah Doktor Falsafah

PENGELURAN DAN PENCIRIAN BIOCHAR DIPEROLEHI DARIPADA SISA KELAPA SAWIT, DAN OPTIMISASI UNTUK PENJERAPAN ZINC

Oleh

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Pengerusi:Profesor Robiah Bt. Yunus, PhDFakulti:Kejuruteraan

Hari ini, penggunaan bahan-bahan kos rendah seperti sisa pertanian sebagai bahan penjerap untuk mengambil logam berat daripada larutan akueus telah mendapat perhatian untuk rawatan air dan sisa air. Kajian ini bertujuan untuk menghasilkan biochar (bahan berliang yang tinggi kandungan karbon dan berketumpatan rendah) daripada tiga jenis bahan buangan kelapa sawit yang berlainan melalui proses pirolisis dalam reaktor lapisan tetap skala makmal. Stok bahan-bahan mentah untuk eksperimen pirolisis adalah termasuk pelepah kelapa sawit (OPF), tandan buah kosong kelapa sawit (OPEFB), dan serat mesocarp kelapa sawit (OPMF). Biochar yang telah disintesis kemudian dicirikan kepada sifat-sifat fisiokimianya menggunakan analisis unsure CHNS, analisis proksimat, mikroskop imbasan elektron (SEM), luas permukaan (BET) dan spektroskopi inframerah transformasi fourier (FTIR). Kapasiti penjerapan biochars yang dihasilkan bagi mengeluarkan zink dari larutan akueus telah disiasat dengan melakukan eksperimen penjerapan batch. Keputusan eksperimen penjerapan batch menunjukkan yang tandan buah kosong kelapa sawit biochar (OPEFBB) mempunyai kecekapan yang terbaik untuk penyingkiran zink dan oleh itu telah dipilih untuk kajian pengoptimuman seterusnya.

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Anggaran dan kapasiti permodelan dua alat statistik; kaedah permukaan respon (RSM) dan rangkaian neural tiruan (ANN) dalam menentukan dan mengoptimumkan kesan keadaan pirolisis kepada peratusan penghasilan dan kapasiti penjerapan OPEFBB terhadap penyingkiran zink telah dinilai. Kesan tiga pembolehubah bebas iaitu: suhu rawatan paling tinggi (htt), kadar pemanasan (HR) dan masa tinggal (RT) terhadap peratusan penghasilan OPEFBB dan kapasiti penjerapan telah ditentukan. Reka bentuk komposit pusat telah digunakan untuk menentukan kesan faktor-faktor ini serta interaksi mereka pada respon. Berdasarkan reka bentuk komposit pusat, dua model regresi peringkat kedua telah dicipta untuk kapasiti penjerapan OPEFBB dan

peratusan penghasilan. Nilai optimum untuk peratusan penghasilan dan kapasiti penjerapan adalah masing-masing 25.49% dan 15.18 mg/g di bawah kondisi ramalan 615°C untuk htt, 8°C/min untuk HR, dan 128 minit untuk RT. Input dan output reka bentuk RSM telah digunakan didalam rangkaian neural buatan sebagai latihan. Tambahan algoritma perambatan balik menunjukkan hasil yang terbaik dan digunakan sebagai algoritma pembelajaran untuk kombinasi ANN dan algoritma genetik untuk pengoptimuman. Kondisi yang dianggarkan untuk mencecah nilai optimum untuk peratusan penghasilan 25.38 dan 15.29 untuk kapasiti penjerapan adalah pada htt 625°C, HR 9°C / min dan RT 130 min.

Dalam kedua-dua kaedah RSM dan ANN, peratusan penghasilan dan kapasiti penjerapan OPEFBB kebanyakannya dipengaruhi oleh suhu rawatan paling tinggi diikuti dengan kadar pemanasan dan masa tinggal. Prestasi RSM dan ANN dibandingkan dari segi punca min ralat kuasa dua (RMSE), pekali penentuan (R2), dan sisihan purata mutlak (AAD). Keputusan menggambarkan bahawa kedua-dua model sesuai dengan data uji kaji, namun nilai-nilai yang diramalkan mengesahkan keupayaan ANN mengatasi RSM kerana keunggulan model ANN dalam menangkap tingkah laku bukan linear dan boleh menganalisis dan menganggar kuasa lebih baik daripada RSM.

Eksperimen penjerapan batch untuk penyingkiran zink dengan produk optimum telah dijalankan dengan menentukan kesan larutan pH, dos biochar dan kepekatan logam berat terhadap proses penjerapan. Keputusan menunjukkan bahawa larutan pH adalah salah satu faktor yang paling penting yang mempengaruhi keupayaan penjerapan. Pada pH rendah, penyingkiran ion zink adalah rendah kerana kepekatan proton yang tinggi dalam media penyerapan dan pelengkapan proton dengan ion zink berlaku untuk laman mengikat. Dengan meningkatkan pH, penyingkiran zink menunjukkan trend menaik dan mencapai nilai maksimum pada pH6 dan selepas itu dengan kenaikan pH, pemendakan dan pembentukan hidroksil berlaku yang menunjukkan penjerapan yang sebenar. Dos biochar dan kepekatan logam berat juga mempengaruhi penyingkiran zink dan nilai optimum didapati masing-masing 10 g / L dan 80 mg / L. Empat isoterma penjerapan iaitu: Langmuir, Freundlich, Dubinin-Radushkevich dan Temkin digunakan untuk model data keseimbangan penjerapan. Antaranya Langmuir isoterma boleh menggambarkan data penjerapan yang lebih baik dengan pekali penentuan 0.9988 dan kapasiti penjerapan maksimum didapati pada 19,27 mg / g. Daripada persamaan Dubinin, mekanisme pertukaran ion didapati sebagai mekanisme utama dalam penjerapan zink oleh OPEFBB.

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This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as partial fulfillment of the requirements for the degree of Doctor of Philosophy. The members of the Supervisory Committee were as follows:

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- The research conducted and the writing of this thesis was under our supervision;
- Supervision responsibilities as stated in the Universiti Putra Malaysia (Graduate Studies) Rules 2003 (Revision 2012-2013) are adhered to.

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LIST OF ABBREVIATIONS

AAD	Absolute average deviation
AAS	Atomic adsorption spectrometer
AI	Artificial intelligence
ANN	Artificial neural network
ANNs	Artificial neural networks
ANOVA	Analysis of variance
ASTM	American society for testing and materials
BBP	Batch backpropagation
BC	Biochar
BET	Brunauer-Emmett-Teller
ВЈН	Barett-Joyner-Halenda
CCC	Circumscribed center composite
CCD	Central composite design
CCF	Face centered composite
CCI	Inscribed central composite
CV	Coefficient of variation
DIN	German institute for standardization
DOE	Design of experiment
D-R	Dubinin-Radushkevich
FC	Fixed carbon
FTIR	Fourier transform infrared
GA	Genetic algorithms
НМ	Heavy metal
HR	Heating rate
НТС	Hydrothermal carbonization
HTT	Highest treatment temperature
HW	hard wood
IBP	Incremental backpropagation
IR	Infrared
ISO	International organization for standardization

	IUPAC	International union of pure and applied chemistry
	LM	Light microscopy
	MAE	Mean absolute error
	MSE	Mean square error
	NNs	Neural networks
	OPEFB	Oil palm empty fruit bunches
	OPEFBB	Oil palm empty fruit bunches biochar
	OPF	Oil palm frond
	OPFB	Oil palm frond biochar
	OPMF	Oil palm mesocarp fiber
	OPMFB	Oil palm mesocarp fiber biochar
	РНЕ	Phenanthrene
	PID	Proportional-integral-derivative
	PRESS	predicted residuals sum of squares
	PSO	Particle swarm optimization
	Q	Adsorption capacity
	QP	Quick propagation
	R ²	Coefficient of determination
	RIO	Rotation inherit optimization
	R _L	Equilibrium parameter
	RMSE	Root mean square error
	RSM	Response surface methodology
	RT	Residence time
	SD	Standard deviation
	SEM	Scanning electron microscopy
	SG	Switch grass
	SW	Soft wood
	TEM	Transmission electron microscopy
	VLSI	Very large scale integration
	VM	Volatile matter
	Y	Yield
	Zn	Zinc

CHAPTER 1

INTRODUCTION

1.1 Background and problem statement

Biochar is a solid residue which is obtained from thermochemical conversion of biomass substrates in an oxygen limited environment. It has attracted considerable attention due to its capability to be used as soil amendment in large scale for improvement of soil fertility, nutrient retention, crop production, increasing carbon storage and decreasing Green House Gas emissions (Brown et al. 2009; Lehmann 2007; Sohi et al. 2009).

Biochar can be obtained from different thermochemical processes such as pyrolysis, gasification, hydrothermal carbonization (HTC), and flash pyrolysis under various conditions. The production parameters as well as the nature of the parent material highly affect the structure and the physiochemical properties of the produced biochar (Lehmann and Joseph 2009; Manya 2012).

Biochar has a porous structure with extensive surface area and relatively high degree of carbon content in its matrix. These properties of biochar along with relatively low cost production, suggesting that biochar can act as a surface sorbent for removing hazardous contaminant from aquatic environment. Therefore, using biochar is a new alternative in controlling contaminants in environment in addition to traditional materials such as activated carbon and zeolite.

Malaysia is the major oil palm producer in the world which it contributes to production of 50% of word oil palm production (Foo and Hameed 2009). The large amount of waste produced from palm oil mill industries is a problem in Malaysia as palm biomasses contribute to vast amount of biomass production in Malaysia. An approach to overcome this problem could be the utilization of these wastes as the feedstock to produce value added products such as biochar with relatively high fixed carbon content and low ash content.

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Significant amount of work has been reported on biochar production from plant wastes and agricultural byproducts for the organic pollutants sorption purpose, which reflects the importance of reusing wastes for controlling pollution in environment (Nguyen et al. 2007; Deng et al. 2013; Shi et al. 2014; Tsai and Chen 2013; Wang et al. 2010; Cheng et al. 2013; Chen and Chen 2009; Yu et al. 2010, etc.) but, only a small number of articles are available on heavy metal adsorption by biochar and underlying mechanisms associated with it. Biochars from broiler litter (Uchimiya et

al. 2010), dairy manure (Cao et al. 2009), wood/bark (Mohan et al. 2007), biochar from rice husk and pinewood hydrothermal liquefaction (Liu and Zhang. 2009), biochar prepared from pyrolysis of manure (Koldynska et al. 2012), switch grass-derived biochar (Kumar et al. 2011) have been shown to adsorb heavy metals in significant amounts (such as Cd, Pb, As and Cu, Ni, U (VI)). However, there are very few works on adsorption capacity of palm wastes- derived biochars in adsorbing different heavy metals.

Among different types of heavy metals, zinc (Zn) is one of the most broadly used metals in industries and one of the most potential source of pollution (Han et al. 2013). Zn contamination in natural water is a worldwide problem, which has been reported in many countries. The provision of Zinc in free drinking water has been always a challenge for scientists since the environmentally admissible levels and concentration limit based on health criteria in water, especially in drinking water, decreases continuously.

Various methods for removal of heavy metals from water and waste water have been developed. Traditional methods such as oxidation/precipitation, coagulation, adsorption, ion exchange, and membrane technologies were reported to be effective in decreasing heavy metal concentration in aquatic environment (Akbal and comic 2011; Malamis et al. 2011; Boudrahem et al. 2011). High cost of operation of these technologies along with their disposal problems leads to extensive researches on possibility of using waste biomaterials and developing alternative low cost technologies for treatment of water and waste water from heavy metal contaminants (Sud et al. 2008). Biochars have been shown to be potential candidates in the area of removal of toxic metals due to their low cost.

Several influential factors have been addressed on the adsorption mechanism of Zn(II) which can be classified in two groups of sorbent characteristics and adsorption process conditions. Among adsorption conditions, solution pH, adsorbate and adsorbent dosage are important parameters which should be considered. Therefore the study on removal mechanism of the treatment processes under pH changes, variance in bio-sorbent dosage and Zn concentration, gives essential information on the process design in large scale treatment systems.

Production of efficient sorbent for waste water and water treatment has been always a concern. Among the sorbent characteristics, surface area, surface functionalities and acceptable level of yield are important in adsorption process design. These characteristics of biochar are controlled by its production conditions and primary feed stock properties. In assessing the effect of production conditions, employing an adequate experimental design is another key point. Response surface methodology (RSM) is a helpful tool in studying the effect of factors and their interactions on specific response to optimize the response of interest. Artificial intelligence and specifically artificial neural network which is simulated from biological neural system with strong capability of learning and prediction, has also demonstrated to be a powerful method for modeling complex problems. Utilizing these two powerful techniques in optimizing production parameters will lead to production of effective bio-sorbent.

1.2 Objectives

The objectives of this research are as follow:

- 1- To produce and characterize cost effective, environmental friendly biochars from selected wastes of oil palm industry namely Oil Palm Mesocarp Fiber (OPMF),Oil Palm Empty Fruit Bunches (OPEFB), and Oil Palm Frond (OPF)
- 2- To model and optimize the process using RSM and ANN for predicting the percentage of yield and heavy metal adsorption capacity of selected pyrolysis product
- 3- To investigate the adsorption capability of produced biochars as heavy metal adsorbent for Zinc

Finding cost effective, environmental friendly bio-sorbent from the wastes of oil palm industry to solve the contamination of zinc in polluted water and waste water would be important for sustainable development.

1.3 Scope of the study

The scope of this research is to produce biochars from different oil palm wastes, to characterize them and to determine their application for heavy metal adsorption, to select the best adsorbent among them and optimization of it, to characterize the optimized biochar, and to investigate the best adsorption conditions.

The first step was preparing the raw materials from three different types of oil palm wastes namely: OPEFB, OPMF, and OPF and subsequently characterizing the physical and chemical properties of the wastes.

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The second step was producing biochars from these palm wastes and evaluating the physiochemical properties of the obtained biochars by different methods and techniques, which includes elemental analysis, proximate analysis, determining the surface morphology, surface area, and surface functional groups using CHNS elemental analyzer, Proximate analysis method, Scanning Electron Microscopy (SEM), N₂ adsorption and applying Brunauer-Emmett-Teller (BET) model, Fourier transform infrared (FTIR), respectively.

In the third step, adsorption capacity of produced biochars for zinc removal was evaluated by performing the batch adsorption experiments. The best adsorbent was selected among the three potential adsorbents and was employed for the subsequent optimization process.

In the optimization step, the best conditions for producing the highest heavy metal adsorbent biochar with optimum percentage of yield were explored. Several experiments at different stages (production and adsorption stages) have been performed to produce the optimum production conditions according to Response surface methodology Central Composite Design (CCD).

Response surface methodology and being more specific, Central Composite Design (CCD) has been used to find the response surface area and also to find optimum conditions for producing a biochar based on the optimum percentage of yield and adsorption capacity for removing targeted heavy metal.

The Artificial Neural Networks (ANNs) has also been used to model and optimize the conditions for producing biochar in terms of percentage of yield and adsorption capacity. The results obtained using the optimum conditions proposed by ANN were compared to the results of RSM and then the best method and conditions were selected. The products obtained using these conditions were characterized as well.

In the last step, the effect of pH on heavy metal precipitation was investigated to analyze its effect on the adsorption. The effects of other experimental conditions such as biochar dosage and heavy metal concentration on the adsorption process were also investigated. To compare and evaluate produced biochars' adsorption capacities, the Langmuir, Freundlich, Dubinin-Radushkevich (D-R), Temkin adsorption isotherms were employed to correlate the sorption data.

Based on the above explanations, product of low cost, environmental friendly biosorbents namely biochar, from oil palm industry has been considered. The synthesized biochar is expected to act efficiently in removal of zinc from aqueous solution as the pyrolysis parameters will be optimized for this purposes. (Chen et al, 2011; Han et al, 2013; Kolodynska et al, 2012).

1.4 Organization of the thesis

This thesis consists of five chapters. The introduction in Chapter 1 begins with the background and the significance of the study and ends with the objectives and scopes of the research work. Extensive review of related literature and analytical research in producing biochars, characterization of biochars and removal of heavy metal by low

cost adsorbents, optimization theory, response surface methodology and artificial intelligence and other analytical methods along with their application in current research work are presented in chapter2. Chapter 3 discusses the general materials and methods used in the study, which begins with the production of biochar from the biomass by focusing on the highest treatment temperature, Heating rate, and Residence time in order to obtain a high performance biochar in terms of heavy metal adsorption beside the characterization methods that have been investigated.

Additionally, it covers the statistical analysis and artificial neural network modeling for optimization of biochar production conditions to reach the optimum percentage of yield and adsorption capacity using Response Surface Methodology Central Composite Design (CCD) and artificial neural networks. Chapter 4 is devoted to analyzing the results, evaluation and interpretation of them and comparison of the achieved results with expected ones utilizing various techniques, discussing the characteristics of produced biochars and adsorption of heavy metal. The final chapter is a conclusion that is the declaration of achievement of objectives and ideas for direction of future work that needs to be done.

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