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

SEYED ALI ZAMANI

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

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

June 2015

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

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

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Chairman : Professor Robiah Bt. Yunus, PhD
Faculty : Engineering

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.

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 (R^2), 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

SEYED ALI ZAMANI

Jun 2015

Pengerusi : Profesor Robiah Bt. Yunus, PhD
Fakulti : 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.

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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I wish to express my sincere gratitude and appreciation to my supervisor Professor Robiah bt. Yunus, my co-supervisors, and also to numerous individuals who have contributed towards the completion of this thesis.

I certify that a Thesis Examination Committee has met on 30 June 2015 to conduct the final examination of Seyed Ali Zamani on his thesis entitled "Production and Characterization of Biochar Derived from Oil Palm Wastes, and Optimization for Zinc Adsorption" in accordance with the Universities and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The Committee recommends that the student be awarded the Doctor of Philosophy.

Members of the Thesis Examination Committee were as follows:

Salmiaton binti Ali, PhD
Associate Professor
Faculty of Engineering
Universiti Putra Malaysia
(Chairman)

Suraya binti Abdul Rashid, PhD
Associate Professor
Faculty of Engineering
Universiti Putra Malaysia
(Internal Examiner)

Azni bin Hj Idris, PhD
Professor
Faculty of Engineering
Universiti Putra Malaysia
(Internal Examiner)

Xiao Dong Chen, PhD
Professor
Monash University
Australia
(External Examiner)

ZULKARNAIN ZAINAL, PhD
Professor and Deputy Dean
School of Graduate Studies
Universiti Putra Malaysia

Date: 12 August 2015

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:

Robiah Bt. Yunus,PhD
Professor
Faculty of Engineering
Universiti Putra Malaysia
(Chairman)

SamsuriAbd. Wahid, PhD
Senior Lecturer
Faculty of Agriculture
Universiti Putra Malaysia
(Member)

Mohamad Amran b. MohdSalleh, PhD
Associate Professor
Faculty of Engineering
Universiti Putra Malaysia
(Member)

____
ROBIAH BINTI YUNUS, PhD
Professor and Dean
School of Graduate Studies
Universiti Putra Malaysia

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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
BJH	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
HM	Heavy metal
HR	Heating rate
HTC	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
PHE	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.

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.

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), N_2 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.

REFERENCES

Abnisa, F., Arami-Niya, A., Daud, W. M. a. W., & Sahu, J. N. (2013). Characterization of Bio-oil and Bio-char from Pyrolysis of Palm Oil Wastes. *BioEnergy Research*, *6*(2), 830–840.

Aghav, R. M., Kumar, S., & Mukherjee, S. N. (2011). Artificial neural network modeling in competitive adsorption of phenol and resorcinol from water environment using some carbonaceous adsorbents. *Journal of hazardous materials*, *188*(1-3), 67–77.

Ahmad, a a, & Hameed, B. H. (2010). Effect of preparation conditions of activated carbon from bamboo waste for real textile wastewater. *Journal of hazardous materials*, *173*(1-3), 487–93.

Akbal, F., & Camcı, S. (2011). Copper, chromium and nickel removal from metal plating wastewater by electrocoagulation. *Desalination*, *269*(1-3), 214–222.

Alslaibi, T. M., Abustan, I., Ahmad, M. A., & Foul, A. A. (2013). Application of response surface methodology (RSM) for optimization of Cu 2+ , Cd 2+ , Ni 2+ , Pb 2+ , Fe 2+ , and Zn 2+ removal from aqueous solution using microwaved olive stone activated carbon. *Journal of Chemical Technology & Biotechnology*, *88*(12), 2141–2151.

Altun, T., & Pehlivan, E. (2012). Removal of Cr(VI) from aqueous solutions by modified walnut shells. *Food Chemistry*, *132*(2), 693–700.

Angin, D. (2014). Production and characterization of activated carbon from sour cherry stones by zinc chloride. *Fuel*, *115*, 804–811.

Angın, D. (2013). Effect of pyrolysis temperature and heating rate on biochar obtained from pyrolysis of safflower seed press cake. *Bioresource technology*, *128*, 593–7.

Antal, M. J. (2003). The Art , Science , and Technology of Charcoal Production †, 1619–1640.

Antal, M. J., Mochidzuki, K., & Paredes, L. S. (2003). Flash Carbonization of Biomass, 3690–3699.

Arami-Niya, A., Wan Daud, W. M. A., S. Mjalli, F., Abnisa, F., & Shafeeyan, M. S. (2012). Production of microporous palm shell based activated carbon for methane adsorption: Modeling and optimization using response surface methodology. *Chemical Engineering Research and Design*, *90*(6), 776–784.

Argun, M. E., & Dursun, S. (2008). A new approach to modification of natural adsorbent for heavy metal adsorption. *Bioresource technology*, *99*(7), 2516–27.

Arief, V. O., Trilestari, K., Sunarso, J., Indraswati, N., & Ismadji, S. (2008). Recent Progress on Biosorption of Heavy Metals from Liquids Using Low Cost Biosorbents: Characterization, Biosorption Parameters and Mechanism Studies. *CLEAN - Soil, Air, Water*, *36*(12), 937–962.

ASTM D1102,1984, “ Standard Test Method s for Ash in Wood ”, ASTM Iternational, West Conshohoken, PA, reapproved (2013)

ASTM D1762-84, 2007, “ Standard Test Methods for Chemical Analysis of Wood Char coal” ASTM International, West Conshohoken, PA, 2007

ASTM D4442, 1992, “Standard Test Methods for Direct Moisture Content Measurement of Wood and Wood-Base Materials” ASTM International, West Conshohocken, PA, 2003

ASTM E872, 1982, “ Standard Test Methods for volatile matter in the analysis of the particulate wood fuels ” ASTM International, West Conshohocken, PA, reapproved (2013)

Auta, M., & Hameed, B. H. (2011). Optimized waste tea activated carbon for adsorption of Methylene Blue and Acid Blue 29 dyes using response surface methodology. *Chemical Engineering Journal*, *175*, 233–243.

Azargohar, R., Nanda, S., Kozinski, J. a., Dalai, A. K., & Sutarto, R. (2014). Effects of temperature on the physicochemical characteristics of fast pyrolysis bio-chars derived from Canadian waste biomass. *Fuel*, *125*, 90–100.

Babel, S., & Kurniawan, T. A. (2003). Low-cost adsorbents for heavy metals uptake from contaminated water: a review. *Journal of hazardous materials*, *97*(1-3), 219–43. Retrieved from http://www.ncbi.nlm.nih.gov/pubmed/12573840

Babu, B. V. (2008). Biomass pyrolysis : a state-of- the-art review, *031*, 393–414.

Bahng, M.-K., Mukarakate, C., Robichaud, D. J., & Nimlos, M. R. (2009). Current technologies for analysis of biomass thermochemical processing: a review. *Analytica chimica acta*, *651*(2), 117–38.

Bajpai, S., Gupta, S. K., Dey, A., Jha, M. K., Bajpai, V., Joshi, S., & Gupta, A. (2012). Application of Central Composite Design approach for removal of chromium (VI) from aqueous solution using weakly anionic resin: modeling, optimization, and study of interactive variables. *Journal of hazardous materials*, *227-228*, 436–44.

Balat, M., Balat, M., Kırtay, E., & Balat, H. (2009). Main routes for the thermo-conversion of biomass into fuels and chemicals. Part 1: Pyrolysis systems. *Energy Conversion and Management*, *50*(12), 3147–3157.

Balci, B., Keskinkan, O., & Avci, M. (2011). Use of BDST and an ANN model for prediction of dye adsorption efficiency of Eucalyptus camaldulensis barks in fixed-bed system. *Expert Systems with Applications*, *38*(1), 949–956.

Barrett, E. P., Joyner, L. G., & Halenda, P. P. (1951). The determination of pore volume and area distributions in porous substances. I. Computations from nitrogen isotherms. *Journal of the American Chemical society*, *73*(1), 373–380.

Basri, M., Rahman, R. N. Z. R. A., Ebrahimpour, A., Salleh, A. B., Gunawan, E. R., & Rahman, M. B. A. (2007). Comparison of estimation capabilities of response surface methodology (RSM) with artificial neural network (ANN) in lipase-catalyzed synthesis of palm-based wax ester. *BMC biotechnology*, *7*, 53.

Bayat, B. (2002a). Comparative study of adsorption properties of Turkish fly ashes I . The case of nickel (II), copper (II) and zinc (II), *95*, 251–273.

Bayat, B. (2002b). Comparative study of adsorption properties of Turkish fly ashes. II. The case of chromium (VI) and cadmium (II). *Journal of hazardous materials*, *95*(3), 275–90. Retrieved from http://www.ncbi.nlm.nih.gov/pubmed/12423942

Beesley, L., Moreno-Jiménez, E., Gomez-Eyles, J. L., Harris, E., Robinson, B., & Sizmur, T. (2011). A review of biochars' potential role in the remediation, revegetation and restoration of contaminated soils. *Environmental pollution (Barking, Essex : 1987)*, *159*(12), 3269–82.

Bhatnagar, A., & Sillanpää, M. (2010). Utilization of agro-industrial and municipal waste materials as potential adsorbents for water treatment—A review. *Chemical Engineering Journal*, *157*(2-3), 277–296.

Bhattacharya, a. K., Mandal, S. N., & Das, S. K. (2006). Adsorption of Zn(II) from aqueous solution by using different adsorbents. *Chemical Engineering Journal*, *123*(1-2), 43–51.

Bhatti, M. S., Reddy, A. S., Kalia, R. K., & Thukral, A. K. (2011). Modeling and optimization of voltage and treatment time for electrocoagulation removal of hexavalent chromium. *Desalination*, *269*(1-3), 157–162.

Bingöl, D., Hercan, M., Elevli, S., & Kiliç, E. (2012). Comparison of the results of response surface methodology and artificial neural network for the biosorption of lead using black cumin. *Bioresource technology*, *112*, 111–5.

Boparai, H. K., Joseph, M., & O'Carroll, D. M. (2011). Kinetics and thermodynamics of cadmium ion removal by adsorption onto nano zerovalent iron particles. *Journal of hazardous materials*, *186*(1), 458–65.

Boudrahem, F., & Soualah, A. (2011). Pb (II) and Cd (II) Removal from Aqueous Solutions Using Activated Carbon Developed from Coffee Residue Activated with Phosphoric Acid and Zinc Chloride, (Ii), 1946–1955.

Box, G. E. P., & Wilson, K. B. (1951). On the experimental attainment of optimum conditions. *Journal of the Royal Statistical Society. Series B (Methodological)*, *13*(1), 1–45.

Brewer, C. E., Schmidt-rohr, K., Satrio, J. a, & Brown, R. C. (2009). Characterization of Biochar from Fast Pyrolysis and Gasification Systems. *Environmental Progress*, *28*(3), 386–396.

Brewer, C. E., Unger, R., Schmidt-rohr, K., & Brown, R. C. (2011). Criteria to Select Biochars for Field Studies based on Biochar Chemical Properties, 312–323.

Brodowski, S., Amelung, W., Haumaier, L., Abetz, C., & Zech, W. (2005). Morphological and chemical properties of black carbon in physical soil fractions as revealed by scanning electron microscopy and energy-dispersive X-ray spectroscopy. *Geoderma*, *128*(1-2), 116–129.

Brown, R. a., Kercher, A. K., Nguyen, T. H., Nagle, D. C., & Ball, W. P. (2006). Production and characterization of synthetic wood chars for use as surrogates for natural sorbents. *Organic Geochemistry*, *37*(3), 321–333.

Brown, R. C., Amonette, J. E., & National, N. (2009). Review of the pyrolysis platform for coproducing bio-oil and biochar †, 547–562.

Brunauer, S., Emmett, P. H., & Teller, E. (1938). Adsorption of gases in multimolecular layers. *Journal of the American Chemical Society*, *60*(2), 309–319.

Bulut, E., Özacar, M., & Şengil, İ. A. (2008). Adsorption of malachite green onto bentonite: Equilibrium and kinetic studies and process design. *Microporous and Mesoporous Materials*, *115*(3), 234–246.

Cantrell, K. B., Hunt, P. G., Uchimiya, M., Novak, J. M., & Ro, K. S. (2012). Impact of pyrolysis temperature and manure source on physicochemical characteristics of biochar. *Bioresource technology*, *107*, 419–28.

Cao, Xinde, Ma, L., Gao, B., & Harris, W. (2009). Dairy-manure derived biochar effectively sorbs lead and atrazine. *Environmental science & technology*, *43*(9), 3285–91. Retrieved from http://www.ncbi.nlm.nih.gov/pubmed/19534148

Cao, Xuefei, Zhong, L., Peng, X., Sun, S., Li, S., Liu, S., & Sun, R. (2014). Comparative study of the pyrolysis of lignocellulose and its major components: characterization and overall distribution of their biochars and volatiles. *Bioresource technology*, *155*, 21–7.

Carrier, M., Loppinet-Serani, A., Denux, D., Lasnier, J.-M., Ham-Pichavant, F., Cansell, F., & Aymonier, C. (2011). Thermogravimetric analysis as a new method to determine the lignocellulosic composition of biomass. *Biomass and Bioenergy*, *35*(1), 298–307.

Cavas, L., Karabay, Z., Alyuruk, H., Doğan, H., & Demir, G. K. (2011). Thomas and artificial neural network models for the fixed-bed adsorption of methylene blue by a beach waste Posidonia oceanica (L.) dead leaves. *Chemical Engineering Journal*, *171*(2), 557–562.

Cetin, E., Moghtaderi, B., Gupta, R., & Wall, T. . (2004). Influence of pyrolysis conditions on the structure and gasification reactivity of biomass chars. *Fuel*, *83*(16), 2139–2150.

Chen, B., & Chen, Z. (2009). Sorption of naphthalene and 1-naphthol by biochars of orange peels with different pyrolytic temperatures. *Chemosphere*, *76*(1), 127–33.

Chen, T., Zhang, Y., Wang, H., Lu, W., Zhou, Z., Zhang, Y., & Ren, L. (2014). Influence of pyrolysis temperature on characteristics and heavy metal adsorptive performance of biochar derived from municipal sewage sludge. *Bioresource technology*, *164*, 47–54.

Chen, X., Chen, G., Chen, L., Chen, Y., Lehmann, J., McBride, M. B., & Hay, A. G. (2011). Adsorption of copper and zinc by biochars produced from pyrolysis of hardwood and corn straw in aqueous solution. *Bioresource technology*, *102*(19), 8877–84.

Chen, Y.-H., & Li, F.-A. (2010). Kinetic study on removal of copper(II) using goethite and hematite nano-photocatalysts. *Journal of colloid and interface science*, *347*(2), 277–81.

Cheng, G., Sun, L., Jiao, L., Peng, L.-X., Lei, Z.-H., Wang, Y.-X., & Lin, J. (2013). Adsorption of methylene blue by residue biochar from copyrolysis of dewatered sewage sludge and pine sawdust. *Desalination and Water Treatment*, *51*(37-39), 7081–7087.

Chowdhury, Z. Z., Zain, S. M., Khan, R. A., Arami-Niya, A., & Khalid, K. (2012). Process variables optimization for preparation and characterization of novel adsorbent from lignocellulosic waste. *BioResources*, *7*(3), 3732–3754.

Chun, Y., Sheng, G., Chiou, C. T., & Xing, B. (2004). Compositions and sorptive properties of crop residue-derived chars. *Environmental science & technology*, *38*(17), 4649–55. Retrieved from http://www.ncbi.nlm.nih.gov/pubmed/15461175

Crombie, K., Mašek, O., Sohi, S. P., Brownsort, P., & Cross, A. (2013). The effect of pyrolysis conditions on biochar stability as determined by three methods. *GCB Bioenergy*, *5*(2), 122–131.

Cséfalvay, E., Pauer, V., & Mizsey, P. (2009). Recovery of copper from process waters by nanofiltration and reverse osmosis. *Desalination*, *240*(1-3), 132–142.

Cummer, K. R., & Brown, R. C. (2002). Ancillary equipment for biomass gasiÿcation, *23*, 113–128.

Dabrowski, a. (2001). Adsorption--from theory to practice. *Advances in colloid and interface science*, *93*(1-3), 135–224. Retrieved from http://www.ncbi.nlm.nih.gov/pubmed/23550655

Dave, P. N., & Chopda, L. V. (2014). Application of Iron Oxide Nanomaterials for the Removal of Heavy Metals. *Journal of Nanotechnology*, *2014*, 1–14.

Definition, P., & Guidelines, S. (2012). Standardized Product Definition and Product Testing Guidelines for Biochar That Is Used in Soil, (January 2011), 1–47.

Demirbas, A. (2003). Relationships between lignin contents and fixed carbon contents of biomass samples, *44*, 1481–1486.

Demirbas, A. (2004). Effects of temperature and particle size on bio-char yield from pyrolysis of agricultural residues. *Journal of Analytical and Applied Pyrolysis*, *72*(2), 243–248.

Demirbas, A. (2008). Heavy metal adsorption onto agro-based waste materials : A review, *157*, 220–229.

Deng, G., Wang, X., Shi, X., & Hong, Q. (2013). Adsorption characteristics of phenol in aqueous solution by Pinus massoniana biochar. *Applied Mechanics and Materials*.

Dos Santos, A. B., Cervantes, F. J., & van Lier, J. B. (2007). Review paper on current technologies for decolourisation of textile wastewaters: perspectives for anaerobic biotechnology. *Bioresource technology*, *98*(12), 2369–85.

Dubinin, M. M. (1960). The potential theory of adsorption of gases and vapors for adsorbents with energetically nonuniform surfaces. *Chemical Reviews*, *60*(2), 235–241.

Dubinin, M. M. (1975). Progress in surface and membrane science. *Academic Press, New York*.

Fagundes-Klen, M. R., Veit, M. T., Silva, E. A. Da, Bergamasco, R., Martins, T. D., & Canevesi, R. L. S. (2011). Modelagem do efeito do pH na biossorção de metais pela alga marinha Sargassum filipendula. *Acta Scientiarum. Technology*, *33*(4), 439–446.

Foo, K Y, & Hameed, B. H. (2010). Insights into the modeling of adsorption isotherm systems, *156*, 2–10.

Foo, K.Y., & Hameed, B. H. (2009). Utilization of biodiesel waste as a renewable resource for activated carbon: Application to environmental problems. *Renewable and Sustainable Energy Reviews*, *13*(9), 2495–2504.

Freundlich, H. M. F. (1906). Over the adsorption in solution. *J. Phys. Chem*, *57*(385471), 1100–1107.

Fu, F., & Wang, Q. (2011). Removal of heavy metal ions from wastewaters: a review. *Journal of environmental management*, *92*(3), 407–18.

Gani, A., & Naruse, I. (2007). Effect of cellulose and lignin content on pyrolysis and combustion characteristics for several types of biomass. *Renewable Energy*, *32*(4), 649–661.

Gerente, C., Lee, V. K. C., Cloirec, P. Le, & McKay, G. (2007). Application of Chitosan for the Removal of Metals From Wastewaters by Adsorption—Mechanisms and Models Review. *Critical Reviews in Environmental Science and Technology*, *37*(1), 41–127.

Ghaffari, a, Abdollahi, H., Khoshayand, M. R., Bozchalooi, I. S., Dadgar, a, & Rafiee-Tehrani, M. (2006). Performance comparison of neural network training algorithms in modeling of bimodal drug delivery. *International journal of pharmaceutics*, *327*(1-2), 126–38.

Ghaffari Moghaddam, M., Bin H. Ahmad, F., Basri, M., & Basyaruddin Abdul Rahman, M. (2010). Artificial neural network modeling studies to predict the yield of enzymatic synthesis of betulinic acid ester. *Electronic Journal of Biotechnology*, *13*(3), 1–12.

Ghosh, A., Sinha, K., & Saha, P. Das. (2013). Central composite design optimization and artificial neural network modeling of copper removal by chemically modified orange peel. *Desalination and Water Treatment*, *51*(40-42), 7791–7799.

Giudicianni, P., Cardone, G., & Ragucci, R. (2013). Cellulose, hemicellulose and lignin slow steam pyrolysis: Thermal decomposition of biomass components mixtures. *Journal of Analytical and Applied Pyrolysis*, *100*, 213–222.

Gomez-Serrano, V., Pastor-Villegas, J., Perez-Florindo, A., Duran-Valle, C., & Valenzuela-Calahorro, C. (1996). FT-IR study of rockrose and of char and activated carbon. *Journal of analytical and applied pyrolysis*, *36*(1), 71–80.

Gorgievski, M., Božić, D., Stanković, V., Štrbac, N., & Šerbula, S. (2013). Kinetics, equilibrium and mechanism of Cu2+, Ni2+ and Zn2+ ions biosorption using wheat straw. *Ecological Engineering*, *58*, 113–122.

Gouamid, M., Ouahrani, M. R., & Bensaci, M. B. (2013). Adsorption Equilibrium, Kinetics and Thermodynamics of Methylene Blue from Aqueous Solutions using Date Palm Leaves. *Energy Procedia*, *36*, 898–907.

Goyal, M., & Bansal, R. (2005). *Activated Carbon Adsorption*. CRC Press.

Gregg, S. J., & Sing, K. S. W. (1983). Adsorption, Surface Area, and Porosity.

Güçlü, D., & Dursun, S. (2010). Artificial neural network modelling of a large-scale wastewater treatment plant operation. *Bioprocess and biosystems engineering*, *33*(9), 1051–8.

Guo, J., & Chong Lua, A. (1998). Characterization of chars pyrolyzed from oil palm stones for the preparation of activated carbons. *Journal of Analytical and Applied Pyrolysis*, *46*(2), 113–125. Retrieved from http://linkinghub.elsevier.com/retrieve/pii/S0165237098000746

Gupta, V. K., Carrott, P. J. M., & Ribeiro Carrott, M. M. L. (2009). Low-Cost Adsorbents: Growing Approach to Wastewater Treatment—a Review. *Critical Reviews in Environmental Science and Technology*, *39*(10), 783–842.

Haas, T. J., Nimlos, M. R., & Donohoe, B. S. (2009). Real-Time and Post-reaction Microscopic Structural Analysis of Biomass Undergoing Pyrolysis. *Energy & Fuels*, *23*(7), 3810–3817. Retrieved from http://pubs.acs.org/doi/abs/10.1021/ef900201b

Hafizi, a., Ahmadpour, a., Koolivand-Salooki, M., Heravi, M. M., & Bamoharram, F. F. (2013). Comparison of RSM and ANN for the investigation of linear alkylbenzene synthesis over H14[NaP5W30O110]/SiO2 catalyst. *Journal of Industrial and Engineering Chemistry*, *19*(6), 1981–1989.

Han, Y., Boateng, A. a, Qi, P. X., Lima, I. M., & Chang, J. (2013). Heavy metal and phenol adsorptive properties of biochars from pyrolyzed switchgrass and woody biomass in correlation with surface properties. *Journal of environmental management*, *118*, 196–204.

Haykin, S. S. (2009). *Neural networks and learning machines* (Vol. 3). Pearson Education Upper Saddle River.

Hernández-fernández, F. J., Ríos, A. P. D. L., Ginestá, A., Lozano, L. J., Moreno, J. I., Godínez, C., … Cartagena, E.-. (2010). Use of ionic liquids as green solvents for extraction of Zn 2 + , Cd 2 + , Fe 3 + and Cu 2 + from aqueous solutions, *21*, 631–636.

Ho, Y. S., Porter, J. F., & Mckay, G. (2002). DIVALENT METAL IONS ONTO PEAT : COPPER , NICKEL AND LEAD SINGLE COMPONENT SYSTEMS, 1–33.

Hoshmand, R. (2006). *Design of Experiments for Agriculture and the Natural Sciences Second Edition*. CRC Press.

Hua, M., Zhang, S., Pan, B., Zhang, W., Lv, L., & Zhang, Q. (2012). Heavy metal removal from water/wastewater by nanosized metal oxides: a review. *Journal of hazardous materials*, *211-212*, 317–31.

Huang, J.-H., Zeng, G.-M., Zhou, C.-F., Li, X., Shi, L.-J., & He, S.-B. (2010). Adsorption of surfactant micelles and Cd2+/Zn2+ in micellar-enhanced ultrafiltration. *Journal of hazardous materials*, *183*(1-3), 287–93.

Hubbe, M. A., Hasan, S. H., & Ducoste, J. J. (2011). Cellulosic substrates for removal of pollutants from aqueous systems: A review. 1. Metals. *BioResources*, *6*(2), 2161–2287.

Huber, G. W., Iborra, S., & Corma, A. (2006). Synthesis of Transportation Fuels from Biomass : Chemistry , Catalysts , and Engineering, *2*, 4044–4098.

Imamoglu, M., & Tekir, O. (2008). Removal of copper (II) and lead (II) ions from aqueous solutions by adsorption on activated carbon from a new precursor hazelnut husks. *Desalination*, *228*(1-3), 108–113.

Inyang, M., Gao, B., Yao, Y., Xue, Y., Zimmerman, A. R., Pullammanappallil, P., & Cao, X. (2012). Removal of heavy metals from aqueous solution by biochars derived from anaerobically digested biomass. *Bioresource technology*, *110*, 50–6.

Inyang, M., Gao, B., Zimmerman, A., Zhang, M., & Chen, H. (2014). Synthesis, characterization, and dye sorption ability of carbon nanotube–biochar nanocomposites. *Chemical Engineering Journal*, *236*, 39–46.

Jimenez-Cordero, D., Heras, F., Alonso-Morales, N., Gilarranz, M. a., & Rodriguez, J. J. (2013). Porous structure and morphology of granular chars from flash and conventional pyrolysis of grape seeds. *Biomass and Bioenergy*, *54*, 123–132.

Kardam, A., Raj, K. R., Arora, J. K., & Srivastava, S. (2012). Artificial Neural Network Modeling for Biosorption of Pb (II) Ions on Nanocellulose Fibers. *Bionanoscience*, *2*(3), 153–160.

Khajeh, M., & Barkhordar, A. (2013). Modelling of solid-phase tea waste extraction for the removal of manganese from food samples by using artificial neural network approach. *Food chemistry*, *141*(2), 712–7.

Khajeh, M., Moghaddam, M. G., & Shakeri, M. (2012). Application of artificial neural network in predicting the extraction yield of essential oils of Diplotaenia cachrydifolia by supercritical fluid extraction. *The Journal of Supercritical Fluids*, *69*(June 2010), 91–96.

Khan, M. a, Bushra, R., Ahmad, A., Nabi, S. a, Khan, D. a, & Akhtar, A. (2014). Ion exchangers as adsorbents for removing metals from aquatic media. *Archives of environmental contamination and toxicology*, *66*(2), 259–69.

Khuri, A. I., & Mukhopadhyay, S. (2010). Response surface methodology. *Wiley Interdisciplinary Reviews: Computational Statistics*, *2*(2), 128–149.

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*, 158–62.

Kim, W.-K., Shim, T., Kim, Y.-S., Hyun, S., Ryu, C., Park, Y.-K., & Jung, J. (2013). Characterization of cadmium removal from aqueous solution by biochar produced from a giant Miscanthus at different pyrolytic temperatures. *Bioresource technology*, *138*, 266–70.

Kołodyńska, D., Wnętrzak, R., Leahy, J. J., Hayes, M. H. B., Kwapiński, W., & Hubicki, Z. (2012). Kinetic and adsorptive characterization of biochar in metal ions removal. *Chemical Engineering Journal*, *197*, 295–305.

Kong, H., He, J., Gao, Y., Wu, H., & Zhu, X. (2011). Cosorption of phenanthrene and mercury(II) from aqueous solution by soybean stalk-based biochar. *Journal of agricultural and food chemistry*, *59*(22), 12116–23.

Kuhlbusch, T. A. J. (1995). Method for determining black carbon in residues of vegetation fires. *Environmental science & technology*, *29*(10), 2695–2702.

Kumar, M. P. S., & Phanikumar, B. R. (2013). Response surface modelling of Cr6+ adsorption from aqueous solution by neem bark powder: Box-Behnken experimental approach. *Environmental science and pollution research international*, *20*(3), 1327–43.

Kumar, S., Loganathan, V. a, Gupta, R. B., & Barnett, M. O. (2011). An Assessment of U(VI) removal from groundwater using biochar produced from hydrothermal carbonization. *Journal of environmental management*, *92*(10), 2504–12.

Kumar, Y. P., King, P., & Prasad, V. S. R. K. (2006). Zinc biosorption on Tectona grandis L.f. leaves biomass: Equilibrium and kinetic studies. *Chemical Engineering Journal*, *124*(1-3), 63–70.

Kwapinski, W., Byrne, C. M. P., Kryachko, E., Wolfram, P., Adley, C., Leahy, J. J., … Hayes, M. H. B. (2010). Biochar from Biomass and Waste. *Waste and Biomass Valorization*, *1*(2), 177–189.

Kyzas, G., & Kostoglou, M. (2014). Green Adsorbents for Wastewaters: A Critical Review. *Materials*, *7*(1), 333–364.

Langmuir, I. (1918). The adsorption of gases on plane surfaces of glass, mica and platinum. *Journal of the American Chemical society*, *40*(9), 1361–1403.

Lazić, Ž. R. (2004). *Design and Analysis of Experiments: Section 2.3*. Wiley Online Library.

Lee, Y., Park, J., Ryu, C., Gang, K. S., Yang, W., Park, Y.-K., … Hyun, S. (2013). Comparison of biochar properties from biomass residues produced by slow pyrolysis at 500°C. *Bioresource technology*, *148*, 196–201.

Lehmann, J. (2007a). A handful of carbon. *Nature*, *447*(7141), 143–144.

Lehmann, J. (2007b). Bio-energy in the black. *Frontiers in Ecology and the Environment*, *5*(7), 381–387.

Lehmann, J., & Joseph, S. (2009). *Biochar for environmental management: science and technology*. Earthscan.

Lesmana, S. O., Febriana, N., Soetaredjo, F. E., Sunarso, J., & Ismadji, S. (2009). Studies on potential applications of biomass for the separation of heavy metals from water and wastewater. *Biochemical Engineering Journal*, *44*(1), 19–41.

Li, C., Xie, F., Ma, Y., Cai, T., Li, H., Huang, Z., & Yuan, G. (2010). Multiple heavy metals extraction and recovery from hazardous electroplating sludge waste via ultrasonically enhanced two-stage acid leaching. *Journal of hazardous materials*, *178*(1-3), 823–33.

Li, S., Xu, S., Liu, S., Yang, C., & Lu, Q. (2004). Fast pyrolysis of biomass in free-fall reactor for hydrogen-rich gas. *Fuel Processing Technology*, *85*(8-10), 1201–1211.

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*(17), 8247–52.

Liu, Z., & Zhang, F.-S. (2009). Removal of lead from water using biochars prepared from hydrothermal liquefaction of biomass. *Journal of hazardous materials*, *167*(1-3), 933–9.

Lua, A. C., & Guo, J. (1998). Preparation and characterization of chars from oil palm waste. *Carbon*, *36*(11), 1663–1670.

Lua, A. C., & Yang, T. (2004). Effects of vacuum pyrolysis conditions on the characteristics of activated carbons derived from pistachio-nut shells. *Journal of colloid and interface science*, *276*(2), 364–72.

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*(2), 279–287.

Mahvi, a. H. (2009). Application of agricultural fibers in pollution removal from aqueous solution. *International Journal of Environmental Science & Technology*, *5*(2), 275–285.

Malamis, S, & Katsou, E. (2013). A review on zinc and nickel adsorption on natural and modified zeolite, bentonite and vermiculite: examination of process parameters, kinetics and isotherms. *Journal of hazardous materials*, *252-253*, 428–61.

Malamis, Simos, Katsou, E., & Haralambous, K. J. (2010). Study of Ni(II), Cu(II), Pb(II), and Zn(II) Removal Using Sludge and Minerals Followed by MF/UF. *Water, Air, & Soil Pollution*, *218*(1-4), 81–92.

Malghani, S., Gleixner, G., & Trumbore, S. E. (2013). Chars produced by slow pyrolysis and hydrothermal carbonization vary in carbon sequestration potential and greenhouse gases emissions. *Soil Biology and Biochemistry*, *62*, 137–146.

Manyà, J. J. (2012). Pyrolysis for biochar purposes: a review to establish current knowledge gaps and research needs. *Environmental science & technology*, *46*(15), 7939–54.

Mayer, Z. A., Eltom, Y., Stennett, D., Schr, E., & Apfelbacher, A. (2014). Characterization of Engineered Biochar for Soil Management, *33*(2).

McKendry, P. (2002). Energy Production from Biomass (part 1): Overview of Biomass. *Bioresource Technology*, *83*(1), 37–46.

Mehrotra, S., Prakash, O., Mishra, B. N., & Dwevedi, B. (2008). Efficiency of neural networks for prediction of in vitro culture conditions and inoculum properties for optimum productivity. *Plant Cell, Tissue and Organ Culture*, *95*(1), 29–35.

Meng, J., Wang, L., Liu, X., Wu, J., Brookes, P. C., & Xu, J. (2013). Physicochemical properties of biochar produced from aerobically composted swine manure and its potential use as an environmental amendment. *Bioresource technology*, *142*, 641–6.

Meyer, S., Glaser, B., & Quicker, P. (2011). Technical, economical, and climate-related aspects of biochar production technologies: a literature review. *Environmental science & technology*, *45*(22), 9473–83.

Moghaddam, M. G. (2011). Comparison of Response Surface Methodology and Artificial Neural Network in Predicting the Microwave-Assisted Extraction Procedure to Determine Zinc in Fish Muscles. *Food and Nutrition Sciences*, *02*(08), 803–808.

Mohan, D., Kumar, H., Sarswat, A., Alexandre-Franco, M., & Pittman, C. U. (2014). Cadmium and lead remediation using magnetic oak wood and oak bark fast pyrolysis bio-chars. *Chemical Engineering Journal*, *236*, 513–528.

Mohan, D., Pittman, C. U., Bricka, M., Smith, F., Yancey, B., Mohammad, J., … Gong, H. (2007). Sorption of arsenic, cadmium, and lead by chars produced from fast pyrolysis of wood and bark during bio-oil production. *Journal of colloid and interface science*, *310*(1), 57–73.

Montgomery, D. C. (2008). *Design and analysis of experiments*. John Wiley & Sons.

Mukherjee, a., Zimmerman, a. R., & Harris, W. (2011). Surface chemistry variations among a series of laboratory-produced biochars. *Geoderma*, *163*(3-4), 247–255.

Mukome, F. N. D., Zhang, X., Silva, L. C. R., Six, J., & Parikh, S. J. (2013). Use of chemical and physical characteristics to investigate trends in biochar feedstocks. *Journal of agricultural and food chemistry*, *61*(9), 2196–204.

Myers, R. H., Montgomery, D. C., & Anderson-Cook, C. M. (2009). *Response surface methodology: process and product optimization using designed experiments* (Vol. 705). John Wiley & Sons.

Nagajyoti, P. C., Lee, K. D., & Sreekanth, T. V. M. (2010). Heavy metals, occurrence and toxicity for plants: a review. *Environmental Chemistry Letters*, *8*(3), 199–216.

Nam, S., & Namkoong, W. (2012). Irradiation effect on leaching behavior and form of heavy metals in fly ash of municipal solid waste incinerator. *Journal of hazardous materials*, *199-200*, 440–7.

Nazghelichi, T., Aghbashlo, M., & Kianmehr, M. H. (2011). Optimization of an artificial neural network topology using coupled response surface methodology and genetic algorithm for fluidized bed drying. *Computers and Electronics in Agriculture*, *75*(1), 84–91.

Ncibi, M. C. (2008). Applicability of some statistical tools to predict optimum adsorption isotherm after linear and non-linear regression analysis. *Journal of hazardous materials*, *153*(1-2), 207–12.

Nelofer, R., Ramanan, R. N., Rahman, R. N. Z. R. A., Basri, M., & Ariff, A. B. (2012). Comparison of the estimation capabilities of response surface methodology and artificial neural network for the optimization of recombinant lipase production by E. coli BL21. *Journal of industrial microbiology & biotechnology*, *39*(2), 243–54.

Nguyen, C., & Do, D. . (2001). The Dubinin–Radushkevich equation and the underlying microscopic adsorption description. *Carbon*, *39*(9), 1327–1336.

Nguyen, T. H., Cho, H.-H., Poster, D. L., & Ball, W. P. (2007). Evidence for a pore-filling mechanism in the adsorption of aromatic hydrocarbons to a natural wood char. *Environmental science & technology*, *41*(4), 1212–7. Retrieved from http://www.ncbi.nlm.nih.gov/pubmed/17593721

Novak, J. M., Cantrell, K. B., & Watts, D. W. (2012). Compositional and Thermal Evaluation of Lignocellulosic and Poultry Litter Chars via High and Low Temperature Pyrolysis. *BioEnergy Research*, *6*(1), 114–130.

Ofomaja, A. E. (2010). Equilibrium studies of copper ion adsorption onto palm kernel fibre. *Journal of environmental management*, *91*(7), 1491–9.

Oguz, E., & Ersoy, M. (2010). Removal of Cu2+ from aqueous solution by adsorption in a fixed bed column and Neural Network Modelling. *Chemical Engineering Journal*, *164*(1), 56–62.

Ozçimen, D., & Ersoy-Meriçboyu, A. (2009). Removal of copper from aqueous solutions by adsorption onto chestnut shell and grapeseed activated carbons. *Journal of hazardous materials*, *168*(2-3), 1118–25.

Özçimen, D., & Ersoy-Meriçboyu, A. (2010). Characterization of biochar and bio-oil samples obtained from carbonization of various biomass materials. *Renewable Energy*, *35*(6), 1319–1324.

Panwar, N. L., Kothari, R., & Tyagi, V. V. (2012). Thermo chemical conversion of biomass – Eco friendly energy routes. *Renewable and Sustainable Energy Reviews*, *16*(4), 1801–1816.

Pasangulapati, V., Ramachandriya, K. D., Kumar, A., Wilkins, M. R., Jones, C. L., & Huhnke, R. L. (2012). Effects of cellulose, hemicellulose and lignin on thermochemical conversion characteristics of the selected biomass. *Bioresource technology*, *114*, 663–9.

Pastor-Villegas, J., Meneses Rodríguez, J. M., Pastor-Valle, J. F., & García García, M. (2007). Changes in commercial wood charcoals by thermal treatments. *Journal of Analytical and Applied Pyrolysis*, *80*(2), 507–514.

Pellera, F.-M., Giannis, A., Kalderis, D., Anastasiadou, K., Stegmann, R., Wang, J.-Y., & Gidarakos, E. (2012). Adsorption of Cu(II) ions from aqueous solutions on biochars prepared from agricultural by-products. *Journal of environmental management*, *96*(1), 35–42.

Pilkington, J. L., Preston, C., & Gomes, R. L. (2014). Comparison of response surface methodology (RSM) and artificial neural networks (ANN) towards efficient extraction of artemisinin from Artemisia annua. *Industrial Crops and Products*, *58*, 15–24.

Ranjan, D., Mishra, D., & Hasan, S. H. (2011). Bioadsorption of Arsenic : An Artificial Neural Networks and Response Surface Methodological Approach, 9852–9863.

Rao, M. M., Rao, G. P. C., Seshaiah, K., Choudary, N. V, & Wang, M. C. (2008). Activated carbon from Ceiba pentandra hulls, an agricultural waste, as an adsorbent in the removal of lead and zinc from aqueous solutions. *Waste management (New York, N.Y.)*, *28*(5), 849–58.

Rawat, A. P., Giri, K., & Rai, J. P. N. (2014). Biosorption kinetics of heavy metals by leaf biomass of Jatropha curcas in single and multi-metal system. *Environmental monitoring and assessment*, *186*(3), 1679–87.

Reddad, Z., Gerente, C., Andres, Y., & Le Cloirec, P. (2002). Adsorption of several metal ions onto a low-cost biosorbent: kinetic and equilibrium studies. *Environmental science & technology*, *36*(9), 2067–73. Retrieved from http://www.ncbi.nlm.nih.gov/pubmed/12026994

Reddy, T. A. (2011). Applied Data Analysis and Modeling for Energy Engineers and Scientists.

Regmi, P., Garcia Moscoso, J. L., Kumar, S., Cao, X., Mao, J., & Schafran, G. (2012). Removal of copper and cadmium from aqueous solution using switchgrass biochar produced via hydrothermal carbonization process. *Journal of environmental management*, *109*, 61–9.

Rio, S., Faur-Brasquet, C., Le Coq, L., Courcoux, P., & Le Cloirec, P. (2005). Experimental design methodology for the preparation of carbonaceous sorbents from sewage sludge by chemical activation--application to air and water treatments. *Chemosphere*, *58*(4), 423–37.

Ronsse, F., van Hecke, S., Dickinson, D., & Prins, W. (2013). Production and characterization of slow pyrolysis biochar: influence of feedstock type and pyrolysis conditions. *GCB Bioenergy*, *5*(2), 104–115.

RUSTOM, I., L ÓPEZ- LEIVA, M. H., & Nair, B. M. (1991). Optimization of extraction of peanut proteins with water by response surface methodology. *Journal of Food Science*, *56*(6), 1660–1663.

Rutherford, D. W., Wershaw, R. L., Rostad, C. E., & Kelly, C. N. (2012). Effect of formation conditions on biochars: Compositional and structural properties of cellulose, lignin, and pine biochars. *Biomass and Bioenergy*, *46*, 693–701.

Saha, D., Bhowal, A., & Datta, S. (2010). Artificial neural network modeling of fixed bed biosorption using radial basis approach. *Heat and mass transfer*, *46*(4), 431–436.

Salman, J. M., & Hameed, B. H. (2010). Effect of preparation conditions of oil palm fronds activated carbon on adsorption of bentazon from aqueous solutions. *Journal of hazardous materials*, *175*(1-3), 133–7.

Samsuri, a. W., Sadegh-Zadeh, F., & Seh-Bardan, B. J. (2013). Characterization of biochars produced from oil palm and rice husks and their adsorption capacities for heavy metals. *International Journal of Environmental Science and Technology*, *11*(4), 967–976.

Samsuri, A. W., Sadegh-Zadeh, F., & Seh-Bardan, B. J. (2013). Adsorption of As(III) and As(V) by Fe coated biochars and biochars produced from empty fruit bunch and rice husk. *Journal of Environmental Chemical Engineering*, *1*(4), 981–988.

Schwarzenbach, R. P., Escher, B. I., Fenner, K., Hofstetter, T. B., Johnson, C. A., von Gunten, U., & Wehrli, B. (2006). The challenge of micropollutants in aquatic systems. *Science (New York, N.Y.)*, *313*(5790), 1072–7.

Seolatto, A. A., Martins, T. D., Bergamasco, R., Tavares, C. R. G., Cossich, E. S., & da Silva, E. A. (2014). Biosorption study of Ni2+ and Cr3+ by Sargassum filipendula: kinetics and equilibrium. *Brazilian Journal of Chemical Engineering*, *31*(1), 211–227.

Shanmugaprakash, M., & Sivakumar, V. (2013). Development of experimental design approach and ANN-based models for determination of Cr(VI) ions uptake rate from aqueous solution onto the solid biodiesel waste residue. *Bioresource technology*, *148*, 550–9.

Shi, L., Zhang, G., Wei, D., Yan, T., Xue, X., Shi, S., & Wei, Q. (2014). Preparation and utilization of anaerobic granular sludge-based biochar for the adsorption of methylene blue from aqueous solutions. *Journal of Molecular Liquids*.

Sohi, S., Lopez-capel, E., Krull, E., & Bol, R. (2009). Biochar , climate change and soil : A review to guide future research, (February).

Song, W., & Guo, M. (2012). Quality variations of poultry litter biochar generated at different pyrolysis temperatures. *Journal of Analytical and Applied Pyrolysis*, *94*, 138–145.

Sud, D., Mahajan, G., & Kaur, M. P. (2008). Agricultural waste material as potential adsorbent for sequestering heavy metal ions from aqueous solutions - a review. *Bioresource technology*, *99*(14), 6017–27.

Sun, H., Hockaday, W. C., Masiello, C. a., & Zygourakis, K. (2012). Multiple Controls on the Chemical and Physical Structure of Biochars. *Industrial & Engineering Chemistry Research*, *51*(9), 3587–3597.

Sun, Y., Gao, B., Yao, Y., Fang, J., Zhang, M., Zhou, Y., … Yang, L. (2014). Effects of feedstock type, production method, and pyrolysis temperature on biochar and hydrochar properties. *Chemical Engineering Journal*, *240*, 574–578.

Tang, J., Xu, G., Xiao, J., & Spinosa, L. (2011). Review on biosorption of heavy metals by activated sludge, (51038003), 4550–4553.

Temkin, M. I., & Pyzhev, V. (1940). Kinetics of ammonia synthesis on promoted iron catalysts. *Acta physiochim. URSS*, *12*(3), 217–222.

Thommes, M. (2010). Physical Adsorption Characterization of Nanoporous Materials. *Chemie Ingenieur Technik*, *82*(7), 1059–1073.

Tong, X., Li, J., Yuan, J., & Xu, R. (2011). Adsorption of Cu(II) by biochars generated from three crop straws. *Chemical Engineering Journal*, *172*(2-3), 828–834.

Tovar-Gómez, R., Moreno-Virgen, M. R., Dena-Aguilar, J. a., Hernández-Montoya, V., Bonilla-Petriciolet, a., & Montes-Morán, M. a. (2013). Modeling of fixed-bed adsorption of fluoride on bone char using a hybrid neural network approach. *Chemical Engineering Journal*, *228*, 1098–1109.

Tsai, W.-T., & Chen, H.-R. (2013). Adsorption kinetics of herbicide paraquat in aqueous solution onto a low-cost adsorbent, swine-manure-derived biochar. *International Journal of Environmental Science and Technology*, *10*(6), 1349–1356.

Tsai, Wen-Tien, Liu, S.-C., Chen, H.-R., Chang, Y.-M., & Tsai, Y.-L. (2012). Textural and chemical properties of swine-manure-derived biochar pertinent to its potential use as a soil amendment. *Chemosphere*, *89*(2), 198–203.

Turan, N. G., Mesci, B., & Ozgonenel, O. (2011). Artificial neural network (ANN) approach for modeling Zn(II) adsorption from leachate using a new biosorbent. *Chemical Engineering Journal*, *173*(1), 98–105.

Uchimiya, M., Lima, I. M., Thomas Klasson, K., Chang, S., Wartelle, L. H., & Rodgers, J. E. (2010). Immobilization of heavy metal ions (CuII, CdII, NiII, and PbII) by broiler litter-derived biochars in water and soil. *Journal of agricultural and food chemistry*, *58*(9), 5538–44.

Uchimiya, M., Wartelle, L. H., Klasson, K. T., Fortier, C. a, & Lima, I. M. (2011). Influence of pyrolysis temperature on biochar property and function as a heavy metal sorbent in soil. *Journal of agricultural and food chemistry*, *59*(6), 2501–10.

Union, I., Pure, O. F., & Chemistry, A. (1985). INTERNATIONAL UNION OF PURE COMMISSION ON COLLOID AND SURFACE CHEMISTRY INCLUDING CATALYSIS * REPORTING PHYSISORPTION DATA FOR GAS / SOLID SYSTEMS with Special Reference to the Determination of Surface Area and Porosity, *57*(4), 603–619.

Uras, Ü., Carrier, M., Hardie, A. G., & Knoetze, J. H. (2012). Physico-chemical characterization of biochars from vacuum pyrolysis of South African agricultural wastes for application as soil amendments. *Journal of Analytical and Applied Pyrolysis*, *98*, 207–213.

Vining, G. G. (2008). Adapting Response Surface Methodology for Computer and Simulation Experiments. In *The Grammar of Technology Development* (pp. 127–134). Springer.

Wang, H., Lin, K., Hou, Z., Richardson, B., & Gan, J. (2010). Sorption of the herbicide terbuthylazine in two New Zealand forest soils amended with biosolids and biochars. *Journal of Soils and Sediments*, *10*(2), 283–289.

Wang, L. (2013). Removal of Disperse Red dye by bamboo-based activated carbon: optimisation, kinetics and equilibrium. *Environmental science and pollution research international*, *20*(7), 4635–46.

Wang, Y., Hu, Y., Zhao, X., Wang, S., & Xing, G. (2013). Comparisons of Biochar Properties from Wood Material and Crop Residues at Di ff erent Temperatures and Residence Times.

Weber, T. W., & Chakravorti, R. K. (1974). Pore and solid diffusion models for fixed- bed adsorbers. *AIChE Journal*, *20*(2), 228–238.

White, J. E., Catallo, W. J., & Legendre, B. L. (2011). Biomass pyrolysis kinetics: A comparative critical review with relevant agricultural residue case studies. *Journal of Analytical and Applied Pyrolysis*, *91*(1), 1–33.

Wiedner, K., Naisse, C., Rumpel, C., Pozzi, A., Wieczorek, P., & Glaser, B. (2013). Chemical modification of biomass residues during hydrothermal carbonization – What makes the difference, temperature or feedstock? *Organic Geochemistry*, *54*, 91–100.

Witek-Krowiak, A., Chojnacka, K., Podstawczyk, D., Dawiec, A., & Pokomeda, K. (2014). Application of response surface methodology and artificial neural network methods in modelling and optimization of biosorption process. *Bioresource technology*, *160*, 150–60.

Wu, W., Yang, M., Feng, Q., Mcgrouther, K., Wang, H., Lu, H., & Chen, Y. (2012). Chemical characterization of rice straw-derived biochar for soil amendment. *Biomass and Bioenergy*, *47*, 268–276.

Wu, Y., Zhou, J., Wen, Y., Jiang, L., & Wu, Y. (2012). Biosorption of heavy metal ions (Cu(2+), Mn (2+), Zn (2+), and Fe (3+)) from aqueous solutions using activated sludge: comparison of aerobic activated sludge with anaerobic activated sludge. *Applied biochemistry and biotechnology*, *168*(8), 2079–93.

Xin, S., Yang, H., Chen, Y., Wang, X., & Chen, H. (2013). Assessment of pyrolysis polygeneration of biomass based on major components: Product characterization and elucidation of degradation pathways. *Fuel*, *113*, 266–273.

Xu, X., Cao, X., & Zhao, L. (2013). Comparison of rice husk- and dairy manure-derived biochars for simultaneously removing heavy metals from aqueous solutions: role of mineral components in biochars. *Chemosphere*, *92*(8), 955–61.

Xu, X., Cao, X., Zhao, L., Wang, H., Yu, H., & Gao, B. (2013). Removal of Cu, Zn, and Cd from aqueous solutions by the dairy manure-derived biochar. *Environmental science and pollution research international*, *20*(1), 358–68.

Yang, H., Yan, R., Chen, H., Lee, D. H., & Liang, D. T. (2006). Mechanism of Palm Oil Waste Pyrolysis in a Packed Bed, *44*(11), 1321–1328.

Yang, H., Yan, R., Chen, H., Lee, D. H., & Zheng, C. (2007). Characteristics of hemicellulose, cellulose and lignin pyrolysis. *Fuel*, *86*(12-13), 1781–1788.

Yang, H., Yan, R., Chin, T., Liang, D. T., Chen, H., & Zheng, C. (2004). Thermogravimetric Analysis - Fourier Transform Infrared Analysis of Palm Oil Waste Pyrolysis, *11*(December 1996), 1814–1821.

Yao, Y., Gao, B., Chen, J., Zhang, M., Inyang, M., Li, Y., … Yang, L. (2013). Engineered carbon (biochar) prepared by direct pyrolysis of Mg-accumulated tomato tissues: characterization and phosphate removal potential. *Bioresource technology*, *138*, 8–13.

Yetilmezsoy, K., & Demirel, S. (2008). Artificial neural network (ANN) approach for modeling of Pb(II) adsorption from aqueous solution by Antep pistachio (Pistacia Vera L.) shells. *Journal of hazardous materials*, *153*(3), 1288–300.

Yu, X., Pan, L., Ying, G., & Kookana, R. S. (2010). Enhanced and irreversible sorption of pesticide pyrimethanil by soil amended with biochars. *Journal of Environmental Sciences*, *22*(4), 615–620.

Zamboulis, D., Peleka, E. N., Lazaridis, N. K., & Matis, K. a. (2011). Metal ion separation and recovery from environmental sources using various flotation and sorption techniques. *Journal of Chemical Technology & Biotechnology*, *86*(3), 335–344.

Zhang, G., Zhang, Q., Sun, K., Liu, X., Zheng, W., & Zhao, Y. (2011). Sorption of simazine to corn straw biochars prepared at different pyrolytic temperatures. *Environmental pollution (Barking, Essex : 1987)*, *159*(10), 2594–601.

Zhang, L., Xu, C. (Charles), & Champagne, P. (2010). Overview of recent advances in thermo-chemical conversion of biomass. *Energy Conversion and Management*, *51*(5), 969–982.

Zhang, W., Mao, S., Chen, H., Huang, L., & Qiu, R. (2013). Pb(II) and Cr(VI) sorption by biochars pyrolyzed from the municipal wastewater sludge under different heating conditions. *Bioresource technology*, *147*, 545–52.

Zhao, X., Ouyang, W., Hao, F., Lin, C., Wang, F., Han, S., & Geng, X. (2013). Bioresource Technology Properties comparison of biochars from corn straw with different pretreatment and sorption behaviour of atrazine. *Bioresource Technology*, *147*, 338–344.

Zhou, Y.-F., & Haynes, R. J. (2010). Sorption of Heavy Metals by Inorganic and Organic Components of Solid Wastes: Significance to Use of Wastes as Low-Cost Adsorbents and Immobilizing Agents. *Critical Reviews in Environmental Science and Technology*, *40*(11), 909–977.