ADSORPTION STUDIES OF HEAVY METALS ON ACTIVATED CARBON PREPARED FROM AGRICULTURAL WASTE

MUHAMAD FAIZAL BIN PAKIR MOHAMED LATIFF

UNIVERSITI SAINS MALAYSIA

2018

ADSORPTION STUDIES OF HEAVY METALS ON ACTIVATED CARBON PREPARED FROM AGRICULTURAL WASTE

by

MUHAMAD FAIZAL BIN PAKIR MOHAMED LATIFF

Thesis submitted in fulfilment of the
requirements for the degree of
Doctor of Philosophy

March 2018

ACKNOWLEDGEMENTS

In the name of Allah, The Most Beneficent and The Most Merciful. All praises to Allah the Almighty for giving me the strengths, guidance, and patience in completing this thesis. First and foremost, I would like to express my deepest gratitude to my family for their endless love and support for me to pursue my PhD degree. My deepest appreciation goes to Professor Dr Ismail Abustan and Associate Professor Dr Mohd Azmier Ahmad for serving as successful supervisors of this research project and for providing me with the insights and guidance to recognise my mistake. Their valuable suggestion and encouragement enable me to handle this project with confidence. Furthermore, I would like to thank both of them for landing me adequate freedom and flexibility while working on this project. Their understanding, comprehensive experience, and personal guidance have provided an excellent basis for the present thesis.

I would like to express my thanks to Mr Zaini and Mr Syamsul for their technical guidance and support towards my experimental work in the laboratories at School of Civil Engineering and School of Chemical Engineering. Besides, special acknowledgement goes to all PhD students; for sharing their knowledge, professional advice and guidelines throughout the whole project. Useful discussions and suggestions from them are deeply appreciated. Last but not least, I would like to express the deepest appreciation to those who have directly and indirectly contributed to the accomplishment and outcome of this project. Thank you so much.

Muhamad Faizal Pakir Mohamed Latiff
March 2018

TABLE OF CONTENTS

CHAPTER THREE: MATERIALS AND METHODS

CHAPTER FOUR: RESULTS AND DISCUSSION

Appendix C: Plots of Separation Factor Versus Adsorbate Initial Concentration

LIST OF TABLES

LIST OF FIGURES

LIST OF SYMBOLS

B	Constant for Temkin isotherm	mg/g h
C_e	Concentration of adsorbate at equilibrium	mg/L
C_t	Concentration of adsorbate at time, t	mg/L
C_o	Initial/inlet adsorbate concentration	mg/L
K_F	Adsorption or distribution coefficient for Freundlich isotherm	mg/g $(L/mg)^{1/n}$
K_L	Rate of adsorption for Langmuir isotherm	L/mg
k_1	Adsorption rate constant for pseudo-first-order	1/h
k_2	Adsorption rate constant for pseudo-second-order	g/mg h
N	Total number of experiments required/data point	-
n	Constant for Freundlich isotherm	-
Q_o	Adsorption capacity for Langmuir isotherm	mg/g
q_e	Amount of adsorbate adsorbed per unit mass of adsorbent at equilibrium	mg/g
q_t	Amount of adsorbate adsorbed per unit mass of adsorbent at time, t	mg/g
q_t, cal	Calculated adsorption uptake at time, t	mg/g
q_t, exp	Experimental adsorption uptake at time, t	mg/g
R	Universal gas constant	8.314 J/mol K
R_L	Separation factor	-
R^2	Correlation coefficient	-
S_{BET}	BET surface area	m^2/g
V_{meso}	Mesopore volume	cm^3/g
V_T	Total pore volume	cm^3/g

w_c	Dry weight of prepared activated carbon	g
w_o	Dry weight of precursor	g
w_{KOH}	Dry weight of potassium hydroxide	g

LIST OF ABBREVIATIONS

AC	Activated carbon
ANOVA	Analysis of variance
CC	Corncob
CCAC	Corncob Activated Carbon
BET	Brunauer-Emmett-Teller
CCD	Central composite design
EA	Elemental analysis
GAC	Granular activated carbon
IR	Impregnation ratio
IUPAC	International Union of Pure and Applied Chemistry
PAC	Powder activated carbon
RSC	Rubber seed coat
RSCAC	Rubber seed coat activated carbon
RSM	Response surface methodology
SEM	Scanning electron microscopy
2FI	Two-factor interaction

KAJIAN PENJERAPAN LOGAM BERAT OLEH KARBON TERAKTIF DISEDIAKAN DARIPADA SISA PERTANIAN

ABSTRAK

Karbon teraktif (KT) komersial yang didapati sekarang masih dianggap mahal disebabkan oleh penggunaan bahan mentah yang tidak boleh diperbaharui seperti arang batu bitumen. Oleh itu, penyelidikan ini menyiasat potensi penggunaan sisa pertanian seperti kelongsong biji getah (KBG) dan tongkol jagung (TJ) yang terdapat di Malaysia sebagai pelopor untuk penyediaan karbon teraktif dimana ianya boleh diguna bagi menyingkirkan dua jenis logam berat iaitu Cu (II) dan Zn (II) daripada larutan akuas. Pengaktifan fiziko-kimia yang merangkumi penjerapan isi dengan kalium hidroksida (KOH) diikuti oleh gasifikasi karbon dioksida (CO_2) telah digunakan untuk penghasilan karbon teraktif. Keputusan rekabentuk eksperimen mendedahkan bahawa suhu pengaktifan karbon dioksida, masa pengaktifan CO_2 dan nisbah jerap isi (NJI) adalah faktor-faktor penting yang mempengaruhi hasil karbon teraktif dan prestasi penjerapan untuk logam Cu (II) dan Zn (II). Keadaan optima yang diperolehi untuk menyediakan KBGKT-CU adalah pada suhu 793 °C, tempoh pengaktifan 1 jam dan NJI 2.46. Bagi KBGKT-ZN, kondisi optima penyediaan adalah pada suhu 797 °C, tempoh pengaktifan 1 jam dan NJI 2.61. Bagi TJKT-CU, kondisi optima penyediaan adalah pada suhu 762 °C, tempoh pengaktifan 2.7 jam dan NJI 3.25. Untuk TJKT-ZN, kondisi optima penyediaan adalah pada suhu 768 °C, tempoh pengaktifan 3 jam dan NJI 3.5. Semua karbon teraktif yang telah terhasil luas permukaan (>500 m^2/g) yang tinggi dan isipadu liang (>0.41 m^3/g). KBGKT dan TJKT masing-masing menunjukkan jenis struktur liang yang homogen dan heterogen.

Kesan-kesan kepekatan awal bahan jerap (10-100 mg/L), masa sentuh, suhu larutan (30-60 °C), pH larutan (2-6), garis sesuhu dan kinetik dan bagi sistem-sistem penjerapan tersebut dinilai melalui kajian penjerapan kelompok. Penjerapan logam Cu (II) dan Zn (II) meningkat dengan peningkatan kepekatan awal dan masa sentuh. Penjerapan logam Cu (II) dan Zn (II) pada kesemua KT adalah terbaik dipadankan oleh model garis sesuhu Freundlich. Penjerapan logam Cu (II) dan Zn (II) bagi semua karbon teraktif dipadankan dengan baik oleh model Freundlich dan model kinetik pseudo tertib kedua. Kajian lapisan tetap menunjukkan bahawa tempoh kelesuan untuk Zn (II) adalah lebih besar daripada Cu (II) dan peningkatan dalam ketinggian lapisan menghasilkan tempoh keletihan yang lebih tinggi.

ADSORPTION STUDIES OF HEAVY METALS ON ACTIVATED CARBON PREPARED FROM AGRICULTURAL WASTE

ABSTRACT

Commercially available activated carbon (AC) is still considered expensive due to the use of non-renewable and relatively expensive starting material such as bituminous coal. Therefore, this study investigates the potential use of agricultural waste such as rubber seed coat (RSC) and corncob (CC) that available in Malaysia, as the precursor for the preparation of AC which can be applied for the removal of two types of heavy metal, which are Cu (II) and Zn (II) from aqueous solution. Physiochemical activation consisting of potassium hydroxide (KOH) impregnation plus carbon dioxide (CO_2) gasification was used to prepare the ACs. The optimum preparation conditions of RSCAC-CU were found at activation temperature of 793 °C, activation time of 1h and KOH impregnation ratio (IR) of 2.46. As for RSCAC-ZN, the optimum preparation conditions were at activation temperature of 797 °C, activation time of 1h and IR of 2.61. Meanwhile, the optimum preparation conditions of CCAC-CU were found at activation temperature of 762 °C, activation time of 2.7h and IR of 3.25. For CCAC-ZN, the optimum preparation conditions were at activation temperature of 768 °C, activation time of 3h and IR of 3.5. All the activated carbons prepared were high BET surface area (>500 m^2/g) and pore volume (>0.41 m^3/g). RSCAC and CCAC demonstrated homogeneous and heterogeneous type pore structures, respectively. The effects of adsorbate initial concentration (10-100 mg/L), contact time, solution temperature (30-60 °C), solution pH (2-6), isotherms and kinetics of the adsorption systems were evaluated through batch adsorption test. The

Cu (II) and Zn (II) adsorption uptakes increased with increasing initial concentration and optimum contact time. Adsorptions of Cu (II) and Zn (II) on all ACs were best fitted by the Freundlich isotherm model. Adsorption kinetics of Cu (II) and Zn (II) followed pseudo-second-order on all the ACs. Fixed bed study showed that the exhaustion period for Zn (II) was greater than Cu (II) and the increase in bed heights resulted in higher exhaustion period.

CHAPTER ONE

INTRODUCTION

1.1 Research Overview

This chapter covers the scenario on heavy metal water pollution in Malaysia. The needs to find a more effective way to solve the problem by applying adsorption process using activated carbons produced from agricultural waste are provided. The problem statement, objectives and the organisation of the thesis are highlighted.

1.2 Industrial Wastewater Pollution

Water is the most precious resources for living things on the earth. Human started their civilisation besides the rivers because of the water source. The revolution towards industrially based economy has changed the lifestyle of human. A variety of toxic and harmful matters that brings severe impacts to human as well as flora and fauna is discharged by industrial activities (Charles et al., 2016). The industry of textile mill products, mining, tanneries, petrochemical, electroplating and electronics projects. electroplating and metal finishing contributes to effluent containing heavy metals such as plumbum, copper, zinc and chromium pollutants (Lee et al., 2016). These metals cause significant pollution load of water resources and increase the severe consequences for the environment. In addition heavy metals are not decay into nonhazardous harmless final component but continuously build up in living organisms, causing a lot of various ailments diseases and syndromes to human (Vareda et al., 2016).

1.3 Use of Activated Carbons for Heavy Metal Removal

Several methods are used for the removal and retrieval of heavy metals from wastewaters such as precipitation, ion exchange, electrolysis, coagulation, solvent extraction, filtration and membrane technology (Qi et al., 2016). Most of the methods applied are reported to be complicated for low heavy metal concentration of wastewater (Jian et al., 2015). Activated carbon adsorption is a considerable way to remove heavy metal from the aqueous state.

Emphasis on the adsorbent with low-cost precursors particularly from agrowastes for the heavy metals removal attracted more attention (Yahya et al., 2015). These biomaterials signify a fascinating and attractive alternative as adsorbents due to their high surface area and low-cost (Khanday et al., 2016). Furthermore, agrowastes are plentiful, renewable, and biodegradable resources that have the capability to adsorb heavy metals from wastewater (Gokce and Aktas, 2014). Certain agrowastes such as fern (Rosales et al., 2015), sawdust (Kazemi et al., 2016), rice bran (Zafar et al., 2015), wheat straw (Kaya et al., 2014), corncobs (Jiang et al., 2016) have been used for the removal of heavy metals from aqueous solution.

1.4 Problem Statement

Due to the high usage of water by the industry such as metal finishing, electronics, tanneries, electroplating, petrochemical and textile mill, heavy metals contamination has become one of the largest problems which demand a smart solution. Activated carbon adsorption has been established to be advanced contrasted to other methods in the concept of its ease of design, simple operation, and high efficiency. Thus, to overcome the problem, producing activated carbon with high adsorption performance from an alternative material that readily available is a need.