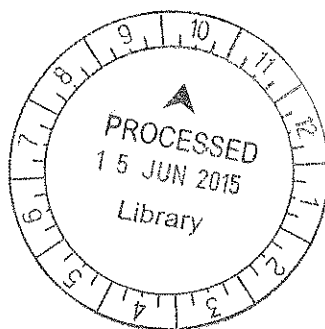


THE REMOVAL OF CHROMIUM(VI) BY A NOVEL HEAT-TREATED
BIOCARBON

JENNY CHAU HUI FOONG

DISSERTATION SUBMITTED IN PARTIAL FULFILMENT OF THE
REQUIREMENTS FOR THE DEGREE OF
BACHELOR OF BIOTECHNOLOGY (HONOURS)



TP
248
2
JEN
2015

FACULTY OF SCIENCE, TECHNOLOGY,
ENGINEERING AND MATHEMATICS
INTI INTERNATIONAL UNIVERSITY
PUTRA NILAI, MALAYSIA

2015

NON-PLAGIARISM DECLARATION

By this letter I declare that I have written this dissertation completely by myself, and that I have used no other sources or resources than the ones mentioned.

I have indicated all quotes and citations that were literally taken from publications, or that were in close accordance with the meaning of those publications, as such. All sources and other resources used are stated in the references.

Moreover I have not handed in a dissertation similar in contents elsewhere.

In case of proof that the dissertation has not been constructed in accordance with this declaration, the Faculty of Science, Technology, Engineering and Mathematics has the right to consider the research dissertation as a deliberate act that has been aimed at making correct judgment of the candidate's expertise, insights and skills impossible.

I acknowledge that the assessor of this item may, for the purpose of assessing this item,

- reproduce this assessment item and provide a copy to another member of the University; and/or,
- communicate a copy of this assessment item to a plagiarism checking service (which may then retain a copy of the assessment item on its database for the purpose of future plagiarism checking).

In case of plagiarism the examiner has the right to fail me and take action as prescribed by the rules regarding Academic Misconduct practiced by INTI International University.

JENNY CHAU HUI FOONG

Name

I11007501

I.D.Number

CHAU

Signature

7 May 2015

Date

ACKNOWLEDGEMENT

First, I would like to appreciate my supervisor, Associate Professor Dr. Palsan Sannasi bin Abdullah for guiding me in carrying out this research and dissertation writing with patience. Besides, I would like to thank my colleagues who help me in carrying out the experiment. Last but not least, I would like to thank my parents for their financial and moral supports.

ABSTRACT

The capability of a novel heat-treated biocarbon had been investigated. Study for the effects of contact time, biocarbon dosage, pH and concentration on the removal of Cr(VI) by biocarbon were conducted under room temperature ($25^{\circ}\text{C} \pm 2^{\circ}\text{C}$) with volume of 25 mL Cr(VI) solution and agitation speed of 250 rpm. Standard curve of 1,5-diphenylcarbazide assay was prepared for the determination of residual concentration of Cr(VI). Equation of $y = 0.6695x$ was generated from the standard curve. All the experiments were repeated for three times in order to get an average value. The results obtained were analyzed by using SPSS (One Way ANOVA, Fisher's LSD Post Hoc Tests and Duncan's Test). Graphs of % removal and uptake of Cr(VI) against the effects (contact time, biocarbon dosage, pH and concentration) were prepared. Value of pH_{pzc} was determined in order to understand the effect of pH on the biosorption of Cr(VI) and the value was 6.55. Adsorption isotherms (Langmuir and Freundlich) were used to investigate the biosorption behavior of the biocarbon. The equilibrium data was fitted with Freundlich isotherm (R^2 of 0.9963).

Keywords: biocarbon; biosorption; Cr(VI); pH_{pzc} ; adsorption isotherms

TABLE OF CONTENT

	PAGE
DECLARATION	ii
ACKNOWLEDGEMENT	iii
ABSTRACT	iv
TABLE OF CONTENT	v-vi
LIST OF TABLES	vii
LIST OF FIGURES	viii-ix
LIST OF ABBREVIATIONS	x-xi
CHAPTER	
1. INTRODUCTION	1
1.1 Overview	1
1.2 Study objectives	4
2. LITERATURE REVIEW	5
2.1 Heavy metal chromium(VI)	5
2.2 Conventional methods used to remove chromium(VI)	5
2.3 Biosorption	6
2.3.1 Biocarbon	6
2.4 Advantages of using biosorbent	7
2.4.1 Efficient	7
2.4.2 Cost-effective	7
2.4.3 Capability for recovery and regeneration	7
2.4.4 No generation of sludge	8
2.4.5 Wide range of target pollutants	8
3. MATERIALS AND METHODS	9
3.1 Heat-treated biocarbon	9
3.2 Preparation of chromium(VI) solution	9
3.3 Preparation of other chemical solutions	9
3.4 Standard curve of chromium(VI)	9
3.5 Determination of residual concentration of chromium(VI)	11
3.6 Determination of chromium(VI) removal	11
3.7 Experimental designs	12
3.7.1 Effect of contact time	12
3.7.2 Effect of biocarbon dosage	13
3.7.3 Effect of pH	13
3.7.3.1 Point zero charge	14

3.7.4	Effect of concentration	14
3.8	Adsorption isotherms	15
4.	RESULTS AND DISCUSSION	17
4.1	Standard curve of chromium(VI)	17
4.2	Effect of contact time	17
4.3	Effect of biocarbon dosage	19
4.4	Effect of pH	21
4.4.1	Point zero charge	23
4.5	Effect of concentration	24
4.6	Adsorption isotherms	26
5.	CONCLUSION AND RECOMMENDATIONS	31
5.1	Conclusion	31
5.2	Recommendations	31
	REFERENCES	33
	APPENDICES	39

LIST OF TABLES

Table		Page
1.1	Type of metals and some of their health effects on human	2
1.2	Comparisons between different aspects of biosorption and conventional method	3
3.1	Required volumes and components for the preparation of standard curve	10
3.2	Different types of isotherms (linear form)	16
4.1	Linear regression data for Langmuir and Freundlich isotherms	27

LIST OF FIGURES

Figure		Page
4.1	Standard curve [Conditions: concentration of Cr(VI): 0.20 mg/L, 0.40 mg/L, 0.60 mg/L, 0.80 mg/L, and 1.0 mg/L; pH: 2; room temperature: $25^{\circ}\text{C} \pm 2^{\circ}\text{C}$]	17
4.2	Mean % removal of Cr(VI) against contact time (hour). Readings are mean \pm standard error of mean ($n = 3$). [Conditions: agitation speed: 250 rpm; biocarbon dose: 0.125 g; contact time: 1 hour, 2 hours, 3 hours, 4 hours and 5 hours; pH: 2; room temperature: $25^{\circ}\text{C} \pm 2^{\circ}\text{C}$; volume of Cr(VI) solution: 25 mL; particle size: $\leq 150\ \mu\text{m}$; initial concentration of Cr(VI): 103.44 mg/L]	18
4.3	Mean Cr(VI) uptake, q_e (mg/g) against contact time (hour). Readings are mean \pm standard error of mean ($n = 3$). [Conditions: agitation speed: 250 rpm; biocarbon dose: 0.125 g; contact time: 1 hour, 2 hours, 3 hours, 4 hours and 5 hours; pH: 2; room temperature: $25^{\circ}\text{C} \pm 2^{\circ}\text{C}$; volume of Cr(VI) solution: 25 mL; particle size: $\leq 150\ \mu\text{m}$; initial concentration of Cr(VI): 103.44 mg/L]	19
4.4	Mean % removal of Cr(VI) against amount of biocarbon (g). Readings are mean \pm standard error of mean ($n = 3$). [Conditions: agitation speed: 250 rpm; biocarbon dose: 0.125 g, 0.25 g and 0.5 g; contact time: 4 hours; pH: 2; room temperature: $25^{\circ}\text{C} \pm 2^{\circ}\text{C}$; volume of Cr(VI) solution: 25 mL; particle size: $\leq 150\ \mu\text{m}$; initial concentration of Cr(VI): 97.83 mg/L]	20
4.5	Mean Cr(VI) uptake, q_e (mg/g) against amount of biocarbon (g). Readings are mean \pm standard error of mean ($n = 3$). [Conditions: agitation speed: 250 rpm; biocarbon dose: 0.125 g, 0.25 g and 0.5 g; contact time: 4 hours; pH: 2; room temperature: $25^{\circ}\text{C} \pm 2^{\circ}\text{C}$; volume of Cr(VI) solution: 25 mL; particle size: $\leq 150\ \mu\text{m}$; initial concentration of Cr(VI): 97.83 mg/L]	20
4.6	Mean % removal of Cr(VI) against pH. Readings are mean \pm standard error of mean ($n = 3$). [Conditions: agitation speed: 250 rpm; biocarbon dose: 0.125 g; pH: 2, 4, 6 and 8; contact time: 4 hours; room temperature: $25^{\circ}\text{C} \pm 2^{\circ}\text{C}$; volume of Cr(VI) solution: 25 mL; particle size: $\leq 150\ \mu\text{m}$; initial concentration of Cr(VI): 103.44 mg/L]	22
4.7	Mean Cr(VI) uptake, q_e (mg/g) against pH. Readings are mean \pm standard error of mean ($n = 3$). [Conditions: agitation speed: 250 rpm; biocarbon dose: 0.125 g; pH: 2, 4, 6 and 8; contact time: 4 hours; room temperature: $25^{\circ}\text{C} \pm 2^{\circ}\text{C}$; volume of Cr(VI) solution: 25 mL; particle size: $\leq 150\ \mu\text{m}$; initial concentration of Cr(VI): 103.44 mg/L]	22

4.8	pH _i -pH _f against pH _i . [Conditions: agitation speed: 150 rpm; biocarbon dose: 0.1 g; pH: 1, 2, 3, 4, 5, 6, 7, 8, 9 and 10; contact time: 24 hours; room temperature: 25°C ± 2°C; volume of NaCl solution: 50 mL; particle size: ≤150 µm]	24
4.9	Mean % removal of Cr(VI) against initial concentration of Cr(VI). Readings are mean ± standard error of mean (n = 3). [Conditions: agitation speed: 250 rpm; concentration of Cr(VI): 10 mg/L, 20 mg/L, 40 mg/L, 60 mg/L, 80 mg/L and 100 mg/L; biocarbon dose: 0.125 g; pH: 2; contact time: 3 hours; room temperature: 25°C ± 2°C; volume of Cr(VI) solution: 25 mL; particle size: ≤150 µm]	25
4.10	Mean Cr(VI) uptake, q _e (mg/g) against initial concentration of Cr(VI). Readings are mean ± standard error of mean (n = 3). [Conditions: agitation speed: 250 rpm; concentration of Cr(VI): 10 mg/L, 20 mg/L, 40 mg/L, 60 mg/L, 80 mg/L and 100 mg/L; biocarbon dose: 0.125 g; pH: 2; contact time: 3 hours; room temperature: 25°C ± 2°C; volume of Cr(VI) solution: 25 mL; particle size: ≤150 µm]	26
4.11	Langmuir-type 1 isotherm (linear form) for removal of Cr(VI) by heat-treated biocarbon [Conditions: agitation speed: 250 rpm; biocarbon dose: 0.125 g; pH: 2; contact time: 3 hours; room temperature: 25°C ± 2°C; volume of Cr(VI) solution: 25 mL; particle size: ≤150 µm]	28
4.12	Langmuir-type 2 isotherm (linear form) for removal of Cr(VI) by heat-treated biocarbon [Conditions: agitation speed: 250 rpm; biocarbon dose: 0.125 g; pH: 2; contact time: 3 hours; room temperature: 25°C ± 2°C; volume of Cr(VI) solution: 25 mL; particle size: ≤150 µm]	28
4.13	Langmuir-type 3 isotherm (linear form) for removal of Cr(VI) by heat-treated biocarbon [Conditions: agitation speed: 250 rpm; biocarbon dose: 0.125 g; pH: 2; contact time: 3 hours; room temperature: 25°C ± 2°C; volume of Cr(VI) solution: 25 mL; particle size: ≤150 µm]	29
4.14	Langmuir-type 4 isotherm (linear form) for removal of Cr(VI) by heat-treated biocarbon [Conditions: agitation speed: 250 rpm; biocarbon dose: 0.125 g; pH: 2; contact time: 3 hours; room temperature: 25°C ± 2°C; volume of Cr(VI) solution: 25 mL; particle size: ≤150 µm]	29
4.15	Freundlich isotherm (linear form) for removal of Cr(VI) by heat-treated biocarbon [Conditions: agitation speed: 250 rpm; biocarbon dose: 0.125 g; pH: 2; contact time: 3 hours; room temperature: 25°C ± 2°C; volume of Cr(VI) solution: 25 mL; particle size: ≤150 µm]	30

LIST OF ABBREVIATIONS

Cr(VI)	Hexavalent chromium
Chromium(VI)	Hexavalent chromium
g/cm ³	Gram per cubic centimetre
pH _{pzc}	Point zero charge
mg/L	Milligram per litre
cm	Centimetre
m	Metre
μm	Micrometre
w/v	Weight per volume
%	Percentage
HCl	Hydrochloric acid
M	Molarity
NaCl	Sodium chloride
NaOH	Sodium hydroxide
H ₂ SO ₄	Sulphuric acid
mL	Millilitre
nm	Nanometre
mm	Millimetre
mg/g	Milligram per gram
g	Gram
L	Litre
°C	Degree Celsius
SPSS	Statistical product and service solutions
ANOVA	Analysis of variance
LSD	Least significant difference
rpm	Revolutions per minute
H ⁺	Hydrogen ion
OH ⁻	Hydroxide ion
pH _i	Initial pH

pHr
FTIR
vs.

Final pH
Fourier transform infrared spectroscopy
Versus

CHAPTER 1

INTRODUCTION

1.1 OVERVIEW

Heavy metal refers to the term, which describes any metal groups or metalloids with density of more than $4 \pm 1 \text{ g/cm}^3$ (Mohammed, Kapri, & Goel, 2011). Heavy metal is non-biodegradable and tends to be accumulated in body of animal after each consumption. High concentration of heavy metal is toxic to all life forms.

Examples of heavy metal are chromium, cadmium, copper and lead. (Singh, Gautam, Mishra, & Gupta, 2011). Sources of heavy metal are leakage of petrol, effluent from industry such as electroplating. High concentration of heavy metal in the human body causes a lots of bad health effects. Some of the examples of metal and their effects on human health are listed in Table 1.1.

Water quality index and heavy metal evaluation index are being used to detect and evaluate the source and level of water pollution. This is to determine the safety of drinking water for human being (Prasanna, Praveena, Chidambaram, Nagarajan, & Elayaraja, 2012). There are two main approaches in treating waste of heavy metal, which are conventional approach and biological approach.

Examples of conventional approach are ion-exchange resins and chemical precipitation (Sannasi, 2013). Living and non-living sources such as the bacteria and rice husk are being used in biological approach. Conventional approach brings some shortcomings (Table 1.2). Hence, biological approach is being used instead of conventional approach in treating the waste of heavy metal (Ahalya, Kanamadi, & Ramachandra, 2005).

Table 1.1 Types of metal and some of their health effects on human.

Type of metal	Health effects on human
Arsenic	-Hypertension -Damage of hepatic -Impacts on cardiovascular system
Cadmium	-Fragility of bone -Lung cancer
Lead	-Affect erythropoiesis -Anemia -Affect reproductive system in male

Source: Adapted from Lee et al., 2003; Wu et al., 2001; Tandon, Chatterjee, Bhargava, Shukla, & Bihari, 2001.

Table 1.2 Comparisons between different aspects of biosorption and conventional method.

Biosorption	Aspect	Conventional method
<ul style="list-style-type: none"> -Microorganisms -Animal's waste -Plant's product 	Example(s)	<ul style="list-style-type: none"> -Chemical precipitation -Coagulation and flocculation -Ion exchange resins
<ul style="list-style-type: none"> -Wide range of target pollutants -Eco-friendly towards the environments -Low cost -Can be reused -No generation of sludge -Effective 	Advantage(s)	<ul style="list-style-type: none"> -Simple procedure -Effective -Can be reuse (example: resins in ion exchange)
<ul style="list-style-type: none"> -Removal of one metal ion may be affected by presence of another type of metal ion -Sensitive to operating condition (example: pH) -Lack of specificity in binding of metal 	Disadvantage(s)	<ul style="list-style-type: none"> -High cost -Incomplete removal of metal -Generation of sludge -Not efficient at low metal concentration -Target on specific type of metal -Not effective for multi-metal

Source: Adapted from Sannasi, 2013; Vinodhini & Das, 2009; Ghosh et al., 2014; Gupta & Mote, 2014; Makeswari & Santhi, 2012; Oliveira, Palmieri, & Garcia, 2011; Rao & Prabhakar, 2011; Doble & Kumar, 2005

1.2 STUDY OBJECTIVES

The present study aims in investigating different effects towards the removal of Chromium(VI) by a novel heat-treated biocarbon:

- i. To determine the effect of contact time, biocarbon dosage, pH and concentration towards the removal of Cr(VI).
- ii. To determine the pH_{pzc} value of the heat-treated biocarbon.
- iii. To investigate the Cr(VI) removal characteristic by the heat-treated biocarbon using Langmuir and Freundlich isotherms.