

**CARBON FROM AGRICULTURAL WASTE AS  
AN ADSORBENT IN THE REMOVAL OF  
CHROMIUM AND NICKEL IONS FROM  
AQUEOUS SOLUTION**

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**UNIVERSITI MALAYSIA PERLIS  
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by

**NOR HARLINA BINTI HAJI HASSAN**

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in fulfillment of the requirements for the degree of  
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## **DEDICATION**

This work is dedicated to my husband, Bazli Azmi for his full support and to my childrens Muhammad Irfan, Muhammad Nabil, Nurul Irdina, Nurul Nabihah and Nurul Hasanah for appreciating and understanding Ummi.

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## TABLE OF CONTENTS

	Page
<b>DEDICATION</b>	ii
<b>ACKNOWLEDGEMENTS</b>	iii
<b>TABLE OF CONTENTS</b>	v
<b>LIST OF TABLES</b>	x
<b>LIST OF FIGURES</b>	xii
<b>LIST OF APPENDICES</b>	xv
<b>NOMENCLATURE</b>	xvi
<b>LIST OF ABBREVIATION</b>	xvii
<b>ABSTRAK</b>	xix
<b>ABSTRACT</b>	xxi
 <b>CHAPTER ONE: INTRODUCTION</b>	
1.1 Agricultural waste	1
1.2 Sugarcane bagasse	2
1.3 Rice straw	3
1.4 Wastewater treatment	4
1.5 Problem statement	5
1.6 Research Objectives	6
1.7 Research Scope	6

## CHAPTER TWO: LITERATURE REVIEW

2.1	Treatment of Industrial Wastewater containing heavy metals	7
2.2	Heavy metals	11
2.2.1	Nickel	11
2.2.2	Chromium	12
2.3	Adsorption	12
2.3.1	Types of adsorption	13
2.3.2	Factors which affect adsorption	14
2.4	Activated Carbon	
2.4.1	Preparation of activated carbon	18
2.4.2	Pyrolysis	18
2.4.3	Activation	19
2.5	Removal of metal ions from aqueous solution by agricultural waste adsorbent	20
2.5.1	Preparation of adsorbent from agricultural waste	21
2.6	Review study characterization of raw materials and prepared adsorbents	23
2.7	Adsorption equilibrium	28
2.8	Adsorption capacity	28
2.9	Adsorption isotherms	29
2.9.1	Langmuir Isotherm	30
2.9.2	Freundlich isotherm	32
2.10	Adsorption kinetic	33
2.10.1	Order of reaction	34
2.10.2	Intra-particle diffusion model	35

## CHAPTER THREE: METHODOLOGY

3.1	Raw materials	37
3.2	Solutions preparation	37
3.2.1	Stock solution of metal ions	38
3.2.2	Atomic Absorption Spectrometry (AAS)	38
3.3	Production of adsorbent	40
3.4	Characterization of adsorbents	42
3.4.1	Yield	42
3.4.2	Density	42
3.4.3	pH	43
3.4.4	Total Ash Content	43
3.4.5	Moisture content	44
3.4.6	Surface area	44
3.4.7	Functional Groups	45
3.4.8	Surface morphology	47
3.5	Adsorption study	46
3.6	Batch Adsorption experiment	46
3.6.1	Adsorption isotherm and kinetic study	47
3.7	Batch adsorption studies at various conditions	48
3.7.1	Effect of pH	48
3.7.2	Effect of contact time	48
3.7.3	Effect of adsorbent doses	49
3.7.4	Effect of particle sizes of adsorbents	49



3.7.5	Effect of initial metal concentration	49
3.7.6	Effect of temperature	50

## CHAPTER 4: RESULTS AND DISCUSSION

4.1	Characterization of adsorbents	51
4.1.1	Yield of adsorbents	51
4.1.2	Physical and chemical properties of adsorbents	52
4.1.3	Functional Groups	58
4.1.3(a)	Functional groups of sugarcane bagasse and pyrolyzed sugarcane bagasse	58
4.1.3(b)	Functional groups of rice straw and pyrolyzed rice straw	62
4.1.4	Surface Morphology changes and elemental composition	66
4.1.5	Relationship between pyrolysis temperature and removal efficiency of adsorbent	71
4.1.6	Selection of adsorbents for Adsorption study	72
4.2	Equilibrium studies of nickel and chromium adsorption onto RSC and SBC at various conditions	74
4.2.1	Effect of pH	74
4.2.2	Effect of contact time	78
4.2.3	Effect of adsorbent dose	80
4.2.4	Effect of particle size	82
4.2.5	Effect of initial concentration and temperature	84
4.3	Adsorption isotherms	89
4.3.1	Langmuir adsorption models	89
4.3.2	Freundlich adsorption models	94

4.4	Adsorption kinetics	95
4.4.1	Pseudo-first-order and pseudo-second-order kinetic models	99
4.4.2	Intra-particle diffusion studies	104
<b>CHAPTER FIVE: CONCLUSION AND RECOMMENDATIONS</b>		104
5.1	Conclusion	107
5.2	Recommendations	110
<b>REFERENCES</b>		111

## LIST OF TABLES

Table 1.1	The proximate and ultimate analyses of sugarcane bagasse (unit: wt. %)	3
Table 1.2	The proximate and ultimate analyses of rice straw (unit: wt. %)	4
Table 2.1	Maximum effluent discharge standards of heavy metals in surface water and their toxication (Kurniawan <i>et al.</i> , 2006)	7
Table 2.2	Parameter limits of effluent of standards A and B	9
Table 2.3	Summary of the treatability of physico-chemical treatments for inorganic effluent (Kurniawan <i>et al.</i> , 2006)	10
Table 2.4	Pore diameter	15
Table 2.5	Summary of modified agricultural waste as adsorbents for the removal of heavy metal ions from aqueous solution	23
Table 2.6	Summary of Physical modification of agricultural waste	25
Table 2.7	Summary of Chemical modification of agricultural waste	27
Table 2.8	The value of separation factor $R_L$	32
Table 3.1	Maximum absorbance wavelength of heavy metals	39
Table 3.2	Working conditions of Atomic Absorption Spectrometer AAnalyser 700	39
Table 4.1	Micropore volume, total pore volume and pore size of RSC and SBC as a function of carbonization temperature	57
Table 4.2	Interpretation results of FTIR spectra of raw sugarcane bagasse	60
Table 4.3	Surface functional groups of SB, SBC and CAC	61
Table 4.4	Interpretation results of FTIR spectra of raw rice straw	63
Table 4.5	Surface functional groups of RS and RSC	65
Table 4.6	Elements and chemical composition of adsorbents using EDX	71

Table 4.7	Physical and chemical properties of the selected adsorbents (Carbonization temperature: 700 °C)	73
Table 4.8	The effect of initial metal ions concentration and temperature on the equilibrium adsorption capacity of RSC and SBC	88
Table 4.9	Langmuir parameters of adsorption isotherms for (a) nickel and (b) chromium adsorption on SBC and RSC at different temperatures	93
Table 4.10	Freundlich parameters of adsorption isotherms for (a) nickel and (b) chromium adsorption on SBC and RSC at different temperatures	98
Table 4.11	Pseudo first-order kinetics results of removal of (a) nickel and (b) chromium onto RSC and SBC	101
Table 4.12	Pseudo second-order kinetics results of onto RSC and SBC	103
Table 4.13	Intra-particle diffusion rates (k) and relative particle film thickness (I) values for the plots of $q_t$ versus $t^{1/2}$	106

## LIST OF FIGURES

Figure 2.1	Schematic representation of porosity in activated carbons	16
Figure 3.1	Calibration curve for Nickel(II)	39
Figure 3.2	Calibration curve for Chromium(VI)	40
Figure 3.3	Flow diagram of pyrolysis process	41
Figure 4.1	Effect of temperature on % yield	52
Figure 4.2	Effect of temperature on apparent density	53
Figure 4.3	Surface area of carbon at different pyrolysis temperatures	55
Figure 4.4	The apparent of SBC and RSC produced at different pyrolysis Temperature of 300 – 700 °C	55
Figure 4.5	FT-IR spectra of raw sugarcane bagasse	59
Figure 4.6	The Overlay FT-IR spectra of raw sugarcane bagasse (SB), sugarcane bagasse carbon (SBC 300 - 700) at different pyrolysis temperatures of 300 - 700 °C and commercial activated carbon (CAC)	61
Figure 4.7	FT-IR spectra of rice straw	63
Figure 4.8	The Overlay FT-IR spectra of raw rice straw (RS), rice straw carbon (RSC 300 - 700) at different pyrolysis temperatures of 300 - 700 °C	65
Figure 4.9	Scanning electron micrograph of sugarcane bagasse carbon produced at different pyrolysis temperature	67
Figure 4.10	Scanning electron micrograph of rice straw carbon produced at different pyrolysis temperature	69
Figure 4.11	Effect of pyrolysis temperature on removal efficiency of Ni(II) and Cr(VI) on RSC and SBC	73
Figure 4.12	Effect of pH on the adsorption of Cr(VI) by RSC and SBC	76
Figure 4.13	Effect of pH on the adsorption of Ni(II) by RSC and SBC	77

Figure 4.14	Precipitation curve for Cr(VI) and Ni(II)	77
Figure 4.15	Effect of contact time on the removal of chromium	78
Figure 4.16	Effect of contact time on the removal of nickel	79
Figure 4.17	Effect of adsorbent dose of RSC and SBC on chromium adsorption	81
Figure 4.18	Effect of adsorbent dose of RSC and SBC on nickel adsorption	81
Figure 4.19	Effect of particle size of RSC and SBC on chromium adsorption	83
Figure 4.20	Effect of particle size of RSC and SBC on nickel adsorption	83
Figure 4.21	Effect of initial concentration and temperature on the removal of nickel onto SBC	86
Figure 4.22	Effect of initial concentration and temperature on the removal of nickel onto RSC	86
Figure 4.23	Effect of initial concentration and temperature on the removal of chromium onto SBC	87
Figure 4.24	Effect of initial concentration and temperature on the removal of chromium onto RSC	87
Figure 4.25a	Langmuir isotherms at different temperatures of nickel removal on SBC	91
Figure 4.25b	Langmuir isotherms at different temperatures of nickel removal on RSC	92
Figure 4.26a	Langmuir isotherms at different temperatures of chromium removal on SBC	92
Figure 4.26B	Langmuir isotherms at different temperatures of chromium removal on RSC	93
Figure 4.27a	Freundlich isotherms at different temperatures of nickel removal on SBC	96
Figure 4.27b	Freundlich isotherms at different temperatures of nickel removal on RSC	96

Figure 4.28a	Freundlich isotherms at different temperatures of chromium removal on SBC	97
Figure 4.28b	Freundlich isotherms at different temperatures of chromium removal on RSC	97
Figure 4.29a	Pseudo-first-order kinetic plots for the removal of nickel by RSC and SBC	100
Figure 4.29b	Pseudo-first-order kinetic plots for the removal of chromium by RSC and SBC	101
Figure 4.30a	Pseudo-second-order kinetic plots for the removal of nickel by RSC and SBC	102
Figure 4.30b	Pseudo-second-order kinetic plots for the removal of chromium by RSC and SBC	102
Figure 4.31a	Plots of intra-particle diffusion model for adsorption of nickel on RSC and SBC at 25 °C	105
Figure 4.31b	Plots of intra-particle diffusion model for adsorption of chromium on RSC and SBC at 25 °C	106

## LIST OF APPENDICES

<b>Appendix A:</b> Perkin-Elmer Atomic Absorption Spectrometer model AAnalyser 700	122
<b>Appendix B:</b> Surface area and porosity analyzer model Micromeritics Tristar 3000	123
<b>Appendix C:</b> Perkin-Elmer-RX 1 FT-IR System	124
<b>Appendix D:</b> SEM model JEOL JSM-6460 LA	125

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## NOMENCLATURE

Symbol	Description	Unit
$C_e$	The concentration at equilibrium in solution	mg/L
$C_i$	The initial concentration in the solution	mg/L
$C_t$	The concentration at time, t in solution	mg/L
$I$	The constant of intraparticle diffusion	mg/g
$K_a$	Langmuir constant	L/mg
$K_f$	Freundlich constant	L/g
$k_1$	The rate constant of pseudo-first order adsorption	L/min
$k_2$	The rate constant of pseudo-second order adsorption	g/mg min
$k_{id}$	The initial rate intraparticle diffusion	g/mg min <sup>1/2</sup>
$M$	The mass of adsorbent	g
$n$	Dimensionless empirical constant	-
$q_e$	The concentration of solute adsorbed on the solid at equilibrium	mg/g
$q_i$	The initial concentration of solute adsorbed on the solid	mg/g
$q_m$	Maximum adsorption capacity	mg/g
$q_t$	The concentration of solute adsorbed on the solid at time, t (Adsorption capacity at time, t)	mg/g
$R$	The removal efficiency	%
$R_L$	Dimensionless constant separation factor	-
$T$	Time	min
$V$	Volume of the solution	L

## LIST OF ABBREVIATION

Aluminium oxide	$\text{Al}_2\text{O}_3$
Ammonium persulphate	$\text{NH}_4\text{S}_2\text{O}_8$
American Society for Testing and Materials Standard	ASTM
Atomic Absorption spectrometry	AAS
Brunauer-Emmet-Teller	BET
Biochemical Oxygen Demand	BOD
Chemical oxygen Demand	COD
Energy Dispersive X-ray	EDX
Environmental Protection Agency	EPA
Fourier Transform Infrared	FT-IR
Granular activated carbon	GAC
Hydrochloric acid	HCl
International Union of Pure and Applied Chemistry	IUPAC
Nickel(II) sulphate-6-hydrate	$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$
Phosphoric acid	$\text{H}_3\text{PO}_4$
Phosphoric pentoxide	$\text{P}_2\text{O}_5$
Potassium dichromate	$\text{K}_2\text{Cr}_2\text{O}_7$
Potassium hydroxide	KOH
Potassium oxide	$\text{K}_2\text{O}$
Powder activated carbon	PAC
Rice straw	RS
Rice straw carbon	RSC

Scanning Electron Microscopy	SEM
Silicon dioxide	SiO <sub>2</sub>
Sugarcane bagasse	SB
Sugarcane bagasse carbon	SBC
Sodium hydroxide	NaOH
Sulfuric acid	H <sub>2</sub> SO <sub>4</sub>
Zinc chloride	ZnCl <sub>2</sub>

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## **Karbon daripada sisa pertanian sebagai penjerap dalam penyingkiran ion-ion kromium dan nikel dari larutan akueus**

### **ABSTRAK**

Objektif kajian ini adalah untuk menghasilkan karbon daripada hampas tebu dan jerami padi melalui teknik pirolisis sebagai penjerap kepada nikel(II) dan kromium(VI) dan untuk menentukan keadaan optima bagi hubungan dengan masa sentuhan, pH larutan, dos penjerap, saiz zarah penjerap, kepekatan awal larutan dan suhu. Juga penjerapan garis sesuhu dan kelakuan kinetik penjerapan bagi penyingkiran nikel(II) dan kromium(VI) oleh setiap penjerap akan ditentukan.

Hampas tebu dan jerami padi adalah sisa pertanian tempatan yang murah dan mudah didapati. Bahan-bahan mentah tersebut telah dipirolisis pada julat suhu 300 – 700°C selama 30 minit dengan kadar pembakaran purata 30 °C/minit.

Penjerap-penjerap itu telah dikaji ciri-ciri seperti hasilan, ketumpatan, pH, kandungan abu, kadungan lembapan, keluasan permukaan dan keliangan dengan menggunakan Penganalisa keluasan permukaan dan keliangan BET, gugusan permukaan dengan menggunakan Pengubah Fourier inframerah, morfologi permukaan dengan menggunakan Elektron mikroskop imbasan dan elemen serta komposisi kimianya dengan menggunakan Serakan tenaga sinar-X.

Penjerapan didapati telah dipengaruhi oleh suhu pirolisis dan luas permukaan. Penjerap-penjerap yang dihasilkan pada suhu 700 °C telah dipilih untuk kajian penjerapan ini kerana ia menghasilkan peratus penyingkiran yang tertinggi. Keupayaan penyingkiran maksimum Ni(II) ke atas RSC dan SBC adalah masing-masing 85.65% dan 21.79%, dan Cr(VI) ke atas RSC dan SBC pula adalah masing-masing 61.81% dan 76.10%

Operasi parameter-parameter termasuk masa sentuhan (15 – 210 minit), pH larutan (1.0 – 10.0), suhu (25, 30, 45 and 55 °C), saiz partikel (1.18 mm, 600 µm, 300 µm and 150 µm), dos penjerap (0.04, 0.10, 0.20, 0.40, 0.6 and 1.0 g) dan kepekatan awal larutan (10, 25, 50, 75 and 100 mg/L). Eksperimen-eksperimen telah dijalankan secara berkelompok. Masa sentuhan, banyaknya penjerap, suhu, saiz partikel dan kepekatan awal larutan ion logam berat telah memberi kesan kepada muatan penjerapan, namun begitu yang paling penting keputusannya bergantung kepada pH larutan.

Data telah dianalisis dengan menggunakan persamaan Langmuir dan Freundlich. Kebolegunaan penjerapan telah ditunjukkan dengan model garis sesuhu Langmuir and Freundlich. Ia menunjukkan bahawa model garis sesuhu Langmuir padan data dengan baik bagi nikel(II) and chromium(VI). Nilai koefisien pembetulan  $R^2$  yang tinggi dan factor pemisah tak berdimensi,  $R_L$  yang didapati menunjukkan bahawa penjerapan kedua-dua penjerap adalah baik. Model kinetik pseudo tertib pertama, pseudo tertib kedua dan model resapan intrazarah telah digunakan dengan menganalisis data eksperimen kinetik. Ia

menunjukkan kedua-dua penjerap mematuhi kinetik pseudo tertib kedua dengan baik. Kebolehan kedua-dua penjerap menjerap nikel(II) and kromium(VI) juga telah dibandingkan. Ia menunjukkan bahawa muatan penjerapan karbon jerami padi lebih baik bagi penjerapan nikel(II) kerana kehadiran gugusan oksigen permukaan, caj permukaan, tinggi kandungan silica dan sifat-sifat nikel sendiri. Sebaliknya karbon hampas tebu mempunyai muatan penjerapan yang tinggi terhadap kromium(VI) kerana mempunyai keluasan permukaan yang tinggi, caj permukaan dan sifat-sifat kromium itu sendiri.

## ***Carbon from agricultural waste as an adsorbent in the removal of chromium and nickel ions from aqueous solution***

### ***ABSTRACT***

*The objectives of this study were to produce carbon from sugarcane bagasse and rice straw by pyrolysis technique as an adsorbent for heavy metal removal and to determine the optimum condition with respect to contact time, pH of solution, adsorbent doses, particle sizes of adsorbent, initial metal concentration and temperature. Also adsorption isotherm and adsorption kinetic behavior of nickel(II) and chromium(VI) removal by each adsorbent will be determined.*

*Sugarcane bagasse and rice straw are inexpensive and locally available agricultural waste. The raw materials were pyrolyzed at different temperatures ranging from 300 – 700 °C for 30 minutes with the average heating rate of 30 °C/minute.*

*The adsorbents were characterized for the yield, density, pH, ash content, moisture content, surface area and porosity by using BET surface area and porosity analyzer, functional groups by using Fourier Transform Infrared, surface morphology by using Scanning Electron Microscope and element and chemical composition by using Energy Dispersive X-ray.*

*Adsorptions were found to be effected by pyrolyzing temperature and surface area. The adsorbents that produced at 700 °C have been chosen for this adsorption study because it produced the highest percentage of removal. The maximum removal efficiency of Ni(II) on RSC and SBC as 85.65% and 21.79 %, respectively and Cr(VI) on RSC and SBC as 61.81 % and 76.10 %, respectively.*

*The operation parameters included contact time (15 – 210 minutes), pH of solution (1.0 – 10.0), temperature (25, 30, 45 and 55 °C), particle sizes of adsorbents (1.18 mm, 600 µm, 300 µm and 150 µm), adsorbents doses (0.04, 0.10, 0.20, 0.40, 0.6 and 1.0 g) and initial concentrations of adsorbates (10, 25, 50, 75 and 100 mg/L). The experimental tests were conducted in batch process. The contact time, amount of adsorbent, temperature, particle size of adsorbent and initial concentration of the metal ions solutions affect the adsorption efficiency but most importantly depended on the pH of solution.*

*The experimental isotherms data were analyzed by using Langmuir and Freundlich equation. The applicability of adsorption was described by using the Freundlich and Langmuir adsorption isotherm. It was found that Langmuir isotherm model fit well the data for nickel(II) and chromium(VI). The measured high linearity of correlation coefficient,  $R^2$  and the values dimensionless separation factor,  $R_L$  indicated a favorable adsorption of both Ni(II) and Cr(VI) onto RSC and SBC, respectively. While, the adsorption kinetics, pseudo-first order model, pseudo second order model and intra-*

particle diffusion model were analyzed on the experimental kinetics data. It was found that the pseudo second order kinetic model described the adsorption kinetic of both adsorbent well. The performance of both adsorbent in the removal of nickel(II) and chromium(VI) were also compared. It was found that the adsorption capacity of rice straw carbon on nickel(II) was high may be due to the present of surface oxygen groups, surface charge, high silica content and the properties of nickel. While, the adsorption capacity of sugarcane bagasse carbon on chromium(VI) was high was caused by the high surface area of the adsorbent, surface charge and the properties of chromium..

## CHAPTER ONE

### INTRODUCTION

#### 1.1 Agricultural waste

Principal sources of agricultural waste are mainly farming activities or agro-industry, such as crops harvesting, abattoirs and tanneries. Waste includes organic sludge effluents, used pesticides and fertilizers, chemical containers and crop residues. Waste is often defined as something unwanted and has no economic value. However, increasingly waste generation may provide a source with certain economic values for another usage. Whereas new products can be generated from various kinds of crop residues with appropriate technology, for examples generation of energy from palm oil waste, production of compost or fertilizer from rice hull and converting rice husk to carbon and etc. Furthermore, waste if not handled properly will effect to human health and the environment (IMPAK, 2006).

Agricultural waste which is available and inexpensive in some places may be a better option for adsorbent production. A few adsorbents that stand out for high adsorption capacities are agricultural waste such as coconut shell and coirpith. These adsorbents are efficient and can be effectively used for inorganic effluent treatment containing metal ions (Babel and Kurniawan, 2004). Recently, various low cost adsorbents derived from agricultural waste, industrial by-products or natural materials, had been investigated intensively for heavy metal removal from contaminated wastewater (Kurniawan *et al.*, 2006).