

ACID IMPREGNATED HONEYDEW RIND ACTIVATED CARBON FOR
CHROMIUM AND ZINC REMOVAL

ZALILAH MURNI MAT ALI @ YUNUS

A thesis submitted in
fulfillment of the requirement for the award of the degree of
Doctor of Philosophy in Science

Faculty of Applied Sciences and Technology
Universiti Tun Hussein Onn Malaysia

AUGUST 2017

DEDICATION

Dedicated to my late grandparents who taught me the need of education in life. Also to my family, siblings and all beautiful souls who have kept my spirit boosted and who have not turned their backs every single day in this journey; rain and shine. To my husband and my dear kids Azraei, Khairie and Yasmin; thank you for the smiles and laughter.

May Allah s.w.t. shower countless blessings upon us hereafter.

ACKNOWLEDGEMENTS

The most sincere gratitude goes to my main supervisor, Assoc. Prof. Dr Norzila bt Othman who has opened a door for me to pursue PhD in this interesting topic of research. Her remarkable expertise, professionalism and outstanding support are the most important elements in the successful of the thesis. A huge sincere appreciation also deserves to my co-supervisors; Assoc. Prof. Dr. Rafidah bt Hamdan and Dr. Nurun Najwa Ruslan who have been understanding and helpful. Their personal guidance and contributions are highly recognized. Thanks to all colleagues who have inspired me with precious motivations and beautiful words throughout this journey.

I would like to thank all staff of Faculty Civil and Environmental Engineering, for the approval to conduct the research in their lab and for the research facilities. Many thank also goes to all dedicated technical staff of Material Lab and Polymer Ceramic Lab (Faculty of Mechanical Engineering) Chemistry Lab and Food Microbiology Lab (Faculty of Applied Sciences and Technology, FAST) and Microelectronics and Nanotechnology-Shamsudin Research Centre (MiNT-SRC) and staff of Malaysia Agricultural Development and Research Institute (MARDI) for their assistance in the sample analysis work. My appreciation also goes to Centre of Graduate School (CGS) and Postgraduate Committee of FAST for their assistance in academic activity. My special thank to all research group members of Micropollutant Research Centre, UTHM (MPRC) for sharing their passion, motivation and friendship.

Financial support from Ministry of Higher Education (MOHE) under Skim Latihan Akademik IPTA (SLAI) and Fundamental Research Grant Scheme No 1230, are gratefully acknowledged.

ABSTRACT

Heavy metal contamination in aqueous media and industrial discharges are among the significant environmental problems, which have to be encountered due to the toxic nature and the accumulation of these metal ions in the food chains. This study has upcycled an agricultural waste namely honeydew rind (HDR) as a precursor in activated carbon (AC) adsorbent preparation using chemical activation process for Cr(III) and Zn(II) removal from synthetic wastewater. Prior to the AC production, physicochemical characteristics of the HDR were analyzed by means of XRF, FESEM, TGA and FTIR. Optimization of sulfuric acid (H_2SO_4) and phosphoric acid (H_3PO_4) of 10%–30% v/v impregnation agent generated honeydew rind impregnated activated carbon (ACS) and honeydew rind impregnated activated carbon (ACP). Optimization of carbonization temperature involved temperature of 430°C–490°C for H_2SO_4 and 450°C–510°C for H_3PO_4 . Batch experiment study was conducted at constant value of 100 mL of synthetic wastewater, 125 rpm shaking rotation at ambient temperature. Brunauer-Emmet-Teller (BET), Langmuir and Freundlich were tested for isotherm adsorption while pseudo-first order and pseudo-second order were examined in kinetic behavior investigation. The column study was run under constant bed height, flow rate, inlet metal concentration of 25 cm, 16 mL/min, 1000 mL (Cr(III)); 400 mg/L (Zn(II)) respectively at ambient temperature. Boehm titration indicated that ACS and ACP are classified as acidic AC. The highest iodine number value (528.63 mg/g) and BET surface area (591.25 m^2/g) were obtained by 20% v/v ACS and carbonized at 470°C. The highest iodine number value (1174.19 mg/g) and BET surface area (1272.38 m^2/g) were achieved by 20% v/v ACP and carbonized at 490°C. Textural analysis produced an average pore diameter of 4.46 nm for the ACS and 2.92 nm for the ACP respectively. Batch adsorption analysis resulted in an optimum condition occurring at pH 4.5, 0.1 g of ACS and ACP, 40 minute contact time and 1000mg/L for Cr(III) and pH 5.5, 0.1 g of ACS and ACP with a 40 min contact time and 400 mg/L for Zn(II). Cr(III) maximum removal was 83.49% using ACS and 88.88% using ACP respectively while Zn(II) maximum removal was 81.55% using ACS and 84.13% using ACP respectively. It was demonstrated that high metal removal was achieved due to high range of metal concentration used in the study. Column adsorption

demonstrated breakthrough of 70 min and 100 min for Cr(III) and Zn(II), respectively. The regeneration study achieved three (3) adsorption cycles of the spent ACP. The present study was able to prove that the honeydew rind impregnated activated carbon is a promising adsorbent in Cr(III) and Zn(II) removal from synthetic wastewater solution. This study has also therefore confirmed that a relatively lower heating rate in the course of carbonization may manage to convert the HDR into its AC. Ion exchange and complexation were suggested to be the metals sorption mechanism.

ABSTRAK

Pencemaran logam berat media berair dan hasil buangan industri adalah salah satu masalah alam sekitar yang ketara disebabkan oleh sifat toksik dan pengumpulan ion logam ini dalam rantai makanan. Kajian ini telah mengguna semula sisa pertanian, kulit tembikai susu (HDR) sebagai bahan pemula dalam penyediaan penjerap impregnasi karbon diaktifkan untuk penyingkiran Cr(III) dan Zn(II) daripada air sisa sintetik. Sifat kimia fizikal HDR terlebih dahulu telah dikaji menggunakan kaedah analisis XRF, FESEM, TGA and FTIR. Ujikaji pengoptimuman agen pengisitepuan asid sulfurik (H_2SO_4) dan asid fosforik (H_3PO_4) pada pencairan 10%–30% per unit isipadu air menghasilkan dua jenis karbon diaktifkan; karbon diaktifkan kulit tembikai susu ACS dan ACP. Analisis pengoptimuman suhu karbonisasi melibatkan julat suhu $430^\circ C$ – $490^\circ C$ untuk H_2SO_4 dan $450^\circ C$ – $510^\circ C$ untuk H_3PO_4 . Analisis penjerapan kelompok telah dijalankan pada suhu sekitar mengikut ketetapan berikut; 100 mL isipadu air sisa sintetik dan 125 rpm putaran goncang. Persamaan Brunauer-Emmet-Teller (BET), Langmuir dan Freundlich telah digunakan untuk menguji keseimbangan isoterma sementara model tertib pertama dan model tertib kedua digunakan untuk pengujian kinetik. Analisis penjerapan turus dijalankan pada suhu persekitaran mengikut ketetapan berikut; tinggi padatan penjerap 25 cm, kadar alir 16 mL/min dan kepekatan influen 1000 mg/L (Cr(III)); 400 mg/L (Zn(II)). Pentitratan Boehm menunjukkan ACS dan ACP dikelaskan sebagai karbon diaktifkan yang berasid. Untuk ACS, nilai iodin yang maksimum (528.63 mg/g) dan luas permukaan BET ($591.25\text{ m}^2/\text{g}$) telah diperolehi oleh ACS pengisitepuan asid sulfurik pada pencairan 20% dan karbonisasi pada $470^\circ C$. Untuk ACP, nilai iodin yang paling tinggi (1174.19 mg/g) dan luas permukaan BET ($1272.38\text{ m}^2/\text{g}$) telah dicapai oleh ACP pengisitepuan asid fosforik pada pencairan 20% dan karbonisasi pada $490^\circ C$. Analisis tekstur menghasilkan purata diameter liang 4.46 nm untuk ACS dan 2.92 nm untuk ACP. Analisis penjerapan berkelompok menunjukkan keadaan optimum berlaku pada pH 4.5, 0.1 g ACS dan ACP, masa sentuhan selama 40 min dan 1000 mg/L untuk Cr(III). Keadaan optimum berlaku pada pH 5.5, 0.1 g ACS dan ACP masa sentuhan selama 40 min dan 400 mg/L untuk Zn(II).

Penyingkiran Cr(III) maksimum didapati 83.49% menggunakan ACS dan 88.88% menggunakan ACP. Penyingkiran maksimum Zn(II) sebanyak 81.55% menggunakan ACS dan 84.13% menggunakan ACP. Penyingkiran logam yang tinggi diperolehi akibat penggunaan kepekatan logam yang digunakan di dalam kajian ini. Penjerapan turus menunjukkan takat muncul untuk Cr(III) ialah 70 min manakala 100 min untuk Zn(II). Analisis penjerapan-penyaherapan telah mencapai tiga (3) kitaran kebolegunaan ACP. Kajian menekankan bahawa karbon diaktifkan yang dihasilkan daripada pengisitepuan kulit tembikai susu adalah penjerap yang berpotensi dalam penyingkiran Cr(III) dan Zn(II) daripada larutan akueus. Selain itu kajian ini telah mengesahkan penggunaan suhu karbonisasi yang rendah dalam proses penghasilan karbon diaktifkan daripada kulit tembikai susu. Mekanisma pertukaran ion dan pengkompleksan telah dicadangkan dalam penjerapan logam-logam tersebut.

TABLE OF CONTENTS

	TITLE	i
	DECLARATION	ii
	DEDICATION	iii
	ACKNOWLEDGEMENT	iv
	ABSTRACT	v
	ABSTRAK	vii
	TABLE OF CONTENTS	ix
	LIST OF TABLES	xvi
	LIST OF FIGURES	xviii
	LIST OF SYMBOL AND ABBREVIATION	xxii
	LIST OF APPENDICES	xxiii
CHAPTER 1	INTRODUCTION	1
	1.1 Research background	1
	1.2 Problem statement	3
	1.3 The research objectives	5
	1.4 Scope of research	5
	1.5 Layout of thesis	6
CHAPTER 2	LITERATURE REVIEW	7
	2.1 Industrial wastewater	7
	2.2 Heavy metals	7
	2.3 Health effect of chromium to human	9
	2.4 Health effect of zinc to human	10
	2.5 Methods for removing heavy metals in wastewater	12
	2.6 Adsorption mechanism	15
	2.6.1 Physisorption	16
	2.6.2 Chemisorption	16

2.6.3	Ion exchange	16
2.6.4	Precipitation	17
2.6.5	Complexation	18
2.7	Factors affecting adsorption	18
2.7.1	pH of solution	20
2.7.2	Contact time	20
2.7.3	Mass of adsorbent	21
2.7.4	Metal concentration	22
2.8	Adsorption isotherm	23
2.8.1	Brunnauer, Emmett and Teller adsorption	23
2.8.2	Freundlich adsorption	24
2.8.3	Langmuir adsorption	25
2.9	Kinetics adsorption	27
2.10	Continuous adsorption	30
2.10.1	Breakthrough time	31
2.10.2	Column regeneration	31
2.11	Activated carbon	33
2.11.1	Agro waste	35
2.11.2	Honeydew melon rind as fruit waste activated carbon precursor	38
2.12	Preparation method in AC production	39
2.12.1	Chemical activation	41
2.12.2	Impregnation	42
2.12.2.1	Sulfuric acid	43
2.12.2.2	Phosphoric acid	45
2.12.2.3	Zinc chloride	46
2.12.2.4	Nitric acid	47
2.12.3	Carbonization	48
2.13	Properties of activated carbon	51
2.13.1	Porosity	51
2.13.2	Surface area	57
2.13.3	Adsorption capacity	57

2.13.4	Electrostatic potential	59
2.13.5	Mineral oxide content	60
2.13.6	Chemical functional groups in AC	60
2.13.7	Surface morphology	61
2.13.8	Thermal properties	62
2.14	Application of activated carbon	63
2.15	Concluding remarks	65
CHAPTER 3	METHODOLOGY	66
3.1	Framework of study	66
3.2	Materials	67
3.2.1	Sample preparation of raw material	67
3.2.2	Raw material pre-treatment	67
3.2.3	Chemicals	68
3.3	Equipment and method of analysis used in HDR and ACHDR characterization	68
3.3.1	Lignocellulosic analysis	69
3.3.1.1	Extraction of neutral detergent fibre (NDF)	69
3.3.1.2	Extraction of acid detergent fibre (ADF)	69
3.3.1.3	Extraction of acid detergent lignin (ADL)	70
3.3.2	Thermogravimetric analysis (TGA)	70
3.3.3	X-ray Florescence analysis (XRF)	70
3.3.4	Fourier transform-Infrared analysis (FTIR)	70
3.3.5	Field Emission-Scanning Electron Microscopy (FESEM)	71
3.3.6	Atomic Absorption Spectrometry (AAS)	71
3.3.7	Textural analysis	72
3.3.8	Iodine Number	72
3.3.9	pH _{pzc} of AC	73

3.3.10	Zeta potential	73
3.3.11	Ash content and yield percentage	74
3.3.12	Boehm titration analysis	74
3.4	Development of ACS and ACP production	75
3.4.1	Characterization of HDR	76
3.4.2	Observation on the effect of impregnation acid concentration and carbonization temperature on pore surface diameter of ACS and ACP	76
3.4.2.1	Observation on the effect impregnation acid concentration on pore surface diameter of ACS and ACP	76
3.4.2.2	Observation on the effect impregnation carbonization temperature on pore surface diameter of ACS and ACP	77
3.4.3	Washing step	78
3.5	Factors affecting metal removal in batch adsorption	79
3.5.1	Effect of pH of solution on Cr(III) on and Zn(II) removal	80
3.5.2	Effect of adsorbent mass on Cr(III) and Zn(II) removal	81
3.5.3	Effect of contact time on Cr(III) and Zn(II) removal	81
3.5.4	Effect of metal concentration on Cr(III) and Zn(II) removal	82
3.6	Cr(III) and Zn(II) removal under the best batch adsorption conditions	82
3.7	Determination of isotherm adsorption, kinetic adsorption and column adsorption	83
3.7.1	Isotherm adsorption	83

3.7.2	Kinetics adsorption	83
3.7.3	Column adsorption.	84
3.7.3.1	Determination of breakthrough time	86
3.7.3.2	Determination of adsorption cycle	86
3.8	Data analysis	87
CHAPTER 4	RESULT AND DISCUSSION	88
4.1	Physicochemical analysis of HDR as AC precursor	88
4.1.1	Lignocellulosic analysis	88
4.1.2	Thermal degradation of HDR	90
4.1.3	Mineral oxides in HDR	91
4.1.4	Chemical surface functional groups in HDR	92
4.1.5	Surface morphology of HDR	93
4.2	Observation the effect of impregnation agent concentration and carbonization temperature on surface morphology on of ACS and ACP	94
4.2.1	Effect of impregnation agent concentration on surface morphology of ACS and ACP	94 99
4.2.2	Effect of carbonization temperature on surface morphology on ACS and ACP	
4.3	Characterization of physicochemical properties of ACS and ACP	106
4.3.1	Thermal properties ACS and ACP	106
4.3.2	Chemical functional groups in ACS and ACP	107
4.3.3	Acidic and basic functional groups analysis	109
4.3.4	Textural analysis	111

4.3.4.1	Porosity	111
4.3.4.2	Surface area and adsorption capacity analysis	118
4.3.5	Ash content and yield analysis	120
4.3.6	pH at zero charge of ACS and ACP	121
4.4	Remarks of physiochemical analysis of optimized carbons	123
4.5	Batch adsorption	124
4.5.1	Effect of pH solution on metal adsorption	124
4.5.2	Effect of mass of ACS and ACP on metal adsorption	129
4.5.3	Effect of contact time on metals adsorption using ACS and ACP	131
4.5.4	Effect of metal concentrations on metals adsorption using ACS and ACP	133
4.6	Metal adsorption under the best condition	135
4.7	Surface morphology of ACS and ACP before and after metal adsorption	136
4.8	Chemical functional groups of the AC before and after metal adsorption	142
4.9	Determination of isotherm adsorption, kinetic adsorption and column adsorption	144
4.9.1	Isotherm adsorption	144
4.9.1.1	BET isotherm	145
4.9.1.2	Freundlich adsorption	146
4.9.1.3	Langmuir isotherm	147
4.9.2	Kinetic study	150
4.9.2.1	Pseudo-first order of Cr(III) adsorption	150
4.9.2.2	Pseudo-second order of	151

	Cr(III) adsorption	
4.9.2.3	Pseudo-first order of Zn(II) adsorption	152
4.9.2.4	Pseudo-second order of Zn(II) adsorption	152
4.9.3	Column adsorption study	156
4.9.3.1	Breakthrough study	156
4.9.3.2	Regeneration study	157
4.9.4	Surface morphology of spent ACP	160
CHAPTER 5	CONCLUSIONS AND RECOMMENDATIONS	162
5.1	Conclusions	162
5.2	Recommendations	163
	REFERENCE	165
	APPENDICES	187

LIST OF TABLE

TABLE	TITLE	PAGE
2.1	Heavy metals found in various industries	8
2.2	Toxicity heavy metals to human's health	9
2.3	Properties of chromium	10
2.4	Properties of zinc	11
2.5	Working principle, advantage and disadvantage of wastewater treatment methods	13
2.6	Factors affecting adsorption using agro waste AC from previous study.	19
2.7	Isotherm parameters of metal ions on various agricultural waste based-AC	27
2.8	Kinetic adsorption parameter of metal removal study	29
2.9	Performances of different types of agro waste based AC for heavy metals removal from aqueous solutions	37
2.10	Modification techniques used in activated carbon production and their advantages	41
2.11	Impregnation, carbonization temperature and heating rate in agro waste based-AC production	50
2.12	The IUPAC porosity classification of AC	51
2.13	Adsorption capacity, surface area, textural properties of agro waste-base AC	58
2.14	Electrostatic potential of various fruit waste based AC for cations removal	59
2.15	The use of agro waste based AC in liquid and gas application	64
3.1	List of equipment used in the characterization of HDR and ACHDR	69
3.2	Matrix design employed in optimization of concentration of impregnation acid and carbonization temperature experiments	78

3.3	Experimental conditions used for the adsorption of Cr(III) and Zn(II) onto honeydew rind activated carbon	80
3.4	Working condition under optimum study	82
3.5	Experimental design for isotherm adsorption of Cr(III) and Zn(II) using ACS and ACP	83
3.6	Experimental design of kinetic study for ACS and ACP	84
3.7	Physical design parameter for column adsorption	85
4.1	Cellulose, hemicellulose, lignin and ash content of honeydew rind and other fruits wastes	89
4.2	Analysis of chemical oxides compounds contained in HDR	91
4.3	Boehm analysis of ACS and ACP produced at various acid concentrations and carbonization temperatures	110
4.4	Volumes of micropore, mesopore and macropore in the AC that were produced at various concentrations of impregnation agents and carbonization temperatures	118
4.5	Physicochemical of optimized carbons	124
4.6	Metal uptake and removal values at optimized condition of ACS and ACP	136
4.7	Langmuir, Freundlich and BET parameter for Cr(III) and Zn(II) adsorption using ACS and ACP	149
4.8	Pseudo first-order and pseudo second-order parameter for Cr(III) and Zn(II) adsorption using agro waste based AC	155

LIST OF FIGURES

Figure	TITLE	PAGE
2.1	Method of activated carbon production	40
2.2	FESEM micrograph of surface morphology of agro waste based –AC before and after metal adsorption	52
2.3	N ₂ adsorption isotherm curve of type I – type VI	54
2.4	Hysteresis loop of H1-H4 in N ₂ adsorption-desorption isotherm	56
3.1	Flowchart of methodology	66
3.2	Dried honeydew rind	67
3.3	Impregnated honeydew rind	77
3.4	Activated honeydew rind	79
3.5	Schematic diagram of column set up for continuous metal adsorption	85
4.1	TGA and DTG of honeydew rind	90
4.2	FTIR spectra of honeydew rind	93
4.3	FESEM micrograph of honeydew rind (500x magnification)	94
4.4	The effect of 10% v/v H ₂ SO ₄ on pore surface diameter of ACS (10000x magnification)	95
4.5	The effect of 20% v/v H ₂ SO ₄ on pore surface diameter of ACS (10000x magnification)	96
4.6	The effect of 30% v/v H ₂ SO ₄ on pore surface diameter of ACS (10000x magnification)	96
4.7	The effect of 10% v/v H ₃ PO ₄ on pore surface diameter of ACS (10000x magnification)	98
4.8	The effect of 20% v/v H ₃ PO ₄ on pore surface diameter of ACS (10000x magnification)	98
4.9	The effect of 30% v/v H ₃ PO ₄ on pore surface diameter of ACS (10000x magnification)	99
4.10	The effect of 430°C carbonization temperature on pore surface	100

	diameter of ACS. (Impregnated at 20% v/v H ₂ SO ₄ ; 10000x magnification)	
4.11	The effect of 450°C carbonization temperature on pore surface diameter of ACS. (Impregnated at 20% v/v H ₂ SO ₄ ; 10000x magnification)	101
4.12	The effect of 470°C carbonization temperature on pore surface diameter of ACS. (Impregnated at 20% v/v H ₂ SO ₄ ; 10000x magnification)	101
4.13	The effect of 490°C carbonization temperature on pore surface diameter of ACS. (Impregnated at 20% v/v H ₂ SO ₄ ; 10000x magnification)	102
4.14	The effect of 450°C carbonization temperature on pore surface diameter of ACP. (Impregnated at 20% v/v H ₃ PO ₄ ; 10000x magnification)	103
4.15	The effect of 470°C carbonization temperature on pore surface diameter of ACP (Impregnated at 20% v/v H ₃ PO ₄ ; 10000x magnification)	103
4.16	The effect of 490°C carbonization temperature on pore surface diameter of ACP. (Impregnated at 20% v/v H ₃ PO ₄ ; 10000x magnification)	104
4.17	The effect of 510°C carbonization temperature on pore surface diameter of ACP. (Impregnated at 20% v/v H ₃ PO ₄ ; 10000x magnification)	104
4.18	TGA and DTG of honeydew rind after activation	107
4.19	FTIR spectra of (a) ACS at (10%–30%) v/v H ₂ SO ₄ concentrations (b) ACP at (10%–30%) v/v H ₃ PO ₄ . Carbonization temperature used was at 470°C (10000x magnification)	109
4.20	Nitrogen adsorption-desorption isotherm of ACS produced from various sulfuric acid concentrations and carbonization temperatures. A= adsorption, D= desorption	112
4.21	Nitrogen adsorption-desorption of ACP produced from various	115

phosphoric acid concentrations and carbonization temperatures.

A= adsorption, D= desorption

4.22	Adsorption capacity and S_{BET} of ACS and ACP produced at various acid concentrations and carbonization temperatures	120
4.23	Ash content of ACS and ACP produced at various acid concentrations and carbonization temperatures	121
4.24	pH of point zero charge of ACS and ACP	122
4.25	Physical transformation of honeydew rind into its activated carbon as final product; (a) fresh honeydew rind (b) pre-treated honeydew rind and (c) activated honeydew rind	123
4.26	Effect of pH of synthetic wastewater on (a) Cr(III) and (b) Zn(II) on uptake and removal	125
4.27	Effect of mass of ACS and ACP (a) Cr(III) and (b) Zn(II) on uptake and removal	130
4.28	Effect of contact time on (a) Cr(III) and (b) Zn uptake and removal using ACS and ACP	132
4.29	Effect of initial (a) Cr(III) concentration and (b) Zn (II) on metal uptake and removal	134
4.30	FESEM micrograph and EDX spectra of unloaded AC	137
4.31	FESEM micrograph and EDX spectra of ACSCr.	138
4.32	FESEM micrograph and EDX spectra of ACSZn.	139
4.33	FESEM micrograph and EDX spectra of ACPCr.	140
4.34	FESEM micrograph and EDX spectra of ACPZn	141
4.35	FTIR spectra of unloaded and metal loaded of (a) ACS and (b) ACP	144
4.36	BET isotherm of (a) ACSCr (b) ACPCr (c) ACSZn and (d) ACPZn	145
4.37	Freundlich adsorption of (a) ACSCr, (b) ACPCr (c) ACSZn and (d) ACPZn	146
4.38	Langmuir isotherm adsorption of (a) ACSCr (b) ACPCr, (c) ACSZn and (d) ACPZn	147
4.39	Pseudo-first order of (a) ACSCr and (b) ACPCr	151
4.40	Pseudo-second order of (a) ACSCr and (b) ACPCr	152

4.41	Pseudo-first order of (a) ACSZn and (b) ACPZn	153
4.42	Pseudo second order of (a) ACSZn and (b) ACPZn	153
4.43	Breakthrough curve for the simultaneous removal of metal ions	157
4.44	Breakthrough curve of (a) Cr(III) and (b) Zn(II) of each cycle	158
4.45	Surface morphology of ACP (a) Unoccupied pores before adsorption (present study) (b) Ruptures pores after three adsorption cycles (present study)	161

LIST OF SYMBOL AND ABBREVIATION

AC	-	activated carbonization
ACHDP	-	activated carbon honeydew rind
ACP	-	phosphoric acid activated carbon
ACS	-	sulfuric acid activated carbon
ACPCr	-	chromium bounded to phosphoric acid activated carbon
ACPZn	-	zinc bounded to phosphoric acid activated carbon
ACSCr	-	chromium bounded to sulfuric acid activated carbon
ACSZn	-	zinc bounded to sulfuric acid activated carbon
BET	-	Brunauer-Emmet-Teller
FESEM-EDX-		field emission electron microscopy-energy dispersive x-ray
FTIR	-	fourier transformed infrared spectroscopy
H	-	hysteresis
HDR	-	honeydew rind
N ₂	-	nitrogen
TGA	-	thermogravimetry analysis
XRF	-	x-ray florescence analysis
°C	-	degree Celcius
Cr(III)	-	trivalent chromium ion
EBCT	-	empty bed contact time
<i>b</i>	-	Langmuir isotherm constant
<i>g</i>	-	gram
IN	-	iodine number
H ₂ SO ₄	-	sulfuric acid
H ₃ PO ₄	-	phosphoric acid
<i>n</i>	-	affinity coefficient
mg/L	-	milligram per liter
mg/g	-	milligram per gram
minute		min

q_e		sorption capacity at equilibrium
q_{\max}		maximum sorption capacity
μm	-	micrometer
nm	-	nanometer
SD	-	standard deviation
pH	-	potential of hydrogen
pH_{pzc}	-	potential of hydrogen at point zero of charge
R^2	-	correlation coefficient
rpm	-	rotation per minute
t_b	-	breakthrough point
t_{exh}	-	exhausted point
Zn(II)	-	divalent zinc ion

LIST OF APPENDIX

Appendix	TITLE	PAGE
A1	Thermogravimetry	187
A2	X-ray Fluorescence (XRF)	187
A3	Fourier Transform Infrared (FTIR)	187
A4a	Field Emission Scanning Electron Microscope (FESEM)	188
A4b	Auto Fine Coater	188
A5	Atomic Absorption Spectroscopy (AAS)	189
A6	Muffle Furnace	189
B1	Preparation of 1000 mg/L metal stock solution	190
B2	Calculation for dilution of metal ion stock solution	191
C1	Batch Adsorption	192
C2	Column adsorption	192
D1	Results Of AAS Analysis for batch Studies on Synthetic Wastewater solution for Batch Study. Parameter: pH of solution	193
D2	Results Of AAS Analysis for Batch Studies on Synthetic Wastewater solution Batch Study. Parameter: Mass of adsorbent	195
D3	Results Of AAS Analysis for Batch Studies on Synthetic Wastewater solution Batch Study. Parameter: Contact Time	197
D4	Results Of AAS Analysis for Batch Studies on Synthetic Wastewater solution Batch Study. Parameter: Metal concentration	199
E1	Anova for effect of pH on ACSCr(III) removal	201
E2	Anova for effect of pH on ACPCr (III) removal	201
E3	Anova for effect of pH on ACSZn(II) removal	201
E4	Anova for effect of pH on ACPZn(II) removal	201

E5	Anova for effect mass of adsorbent on ACSCr(III) removal	202
E6	Anova for effect of adsorbent mass on ACPCr(III) removal	202
E7	Anova for effect of adsorbent mass on ACSZn(II) removal	202
E8	Anova for effect of adsorbent mass on ACPZn(II) removal	202
E9	Anova for effect of contact time on ACSCr (III) removal	203
E10	Anova for effect of contact time on ACPCr (III) removal	203
E11	Anova for effect of contact time on ACSZn(II) removal	203
E12	Anova for effect of contact time on ACPZn(II) removal	203
E13	Anova for effect of initial concentration on ACSCr(III) removal	204
E14	Anova for effect of initial concentration on ACPCr(III) removal	204
E15	Anova for effect of initial concentration on ACSZn(II) removal	204
E16	Anova for effect of initial concentration on ACPZn(II) removal	204
F1	Results Of AAS Analysis for Batch Studies on Synthetic Wastewater Solution at Optimized condition. (a) ACSCr (B) ACPCr	205
F2	Results Of AAS Analysis for Batch Studies on Synthetic Wastewater Solution at Optimized condition. (a) ACSZn (b) ACPZn	206
G	Results of Isotherm Study (a) ACSCr (b) ACSZn (c) ACPCr (d) ACPZn	207
H1	Calculation for BET Isotherm Parameter	211

H2	Calculation for Freundlich Isotherm Parameter	212
H3	Calculation for Langmuir Isotherm Parameter	213
I	Results of Kinetic Study	216
	(a) ACSCr (b) ACPZn (c) ACPCr (d) ACPZn	
J1	Calculation for pseudo first-order parameter	222
J2	Calculation for pseudo second-order parameter	223
K1	Breakthrough study for chromium removal	224
K2	Breakthrough study for zinc removal	225
L1	Regeneration study for adsorption cycles determination in chromium removal	226
L2	Regeneration study for adsorption cycles determination in zinc removal	227

CHAPTER 1

INTRODUCTION

1.1 Research background

The recent shift from an agricultural into a middle-income, knowledge-based economy observed in Malaysia has made its economy a role model for many developing countries. In its attempt to achieve the status of high-income and developed country by the year of 2020, the Malaysian government has clearly demonstrated its commitments towards stimulating a better growth in the manufacturing sector (Onundi *et al.*, 2011). Manufacturing in these industries involve producing electronic products, chemicals, fertilizers, drugs and pharmaceuticals, dyes and batteries (Abbaszadeh *et al.*, 2016).

Although each industry may have its own in-house waste management systems, releasing heavy metals in industrial discharge in huge amount into water drainage is deemed unavoidable. Some of them act as essential micronutrients for living things however at higher concentrations result in severe illness (Abbaszadeh *et al.*, 2016). Upon realizing that the heavy metals have potential in contributing adverse impact on the environment and consequently on human health, it is equally realize that such industries can be harmful at the same time. Therefore, industrial activities in Malaysia reportedly contribute to one of the key environmental problems in relation to contamination of water drainage with thousands of industrial chemical compounds. A recent study carried out by Othman *et al.*, (2014) reported the generation of waste containing heavy metals such as chromium, zinc, lead and nickel may originate from electroplating and metal treatment or fabrication industries which are located along the west coast of Peninsular Malaysia including major industrial areas like Klang Valley, Penang, Ipoh and Johor Bahru (Othman *et al.*, 2014).

Unlike the organic pollutants, the majority of which are susceptible to biological degradation, heavy metal ions do not degrade into harmless end products (Rahman *et al.*, 2014). Even though some of these heavy metals are essential in trace amounts, they may however turn highly lethal at higher concentrations as in such conditions, they are capable of causing some incurable diseases (Kaur *et al.*, 2013). Most of the metals are reported carcinogenic, teratogenic and may pose severe health problems like organ damage, reduced growth and development, nervous system impairments and oxidative stress (Lee *et al.*, 2012). For instance, chromium may possibly result in liver damage, pulmonary congestion, oedema and skin irritation resulting in ulcer formation and zinc toxic property is capable of producing general symptoms such as retardation of growth in plants, fever and oedema of lungs in human beings (Gupta, 2014). Therefore, the presence of heavy metals in aquatic ecosystems has in the last few decades received widespread attention among scholars around the world owing to their potential risks towards human health and harmful effects on living organisms in general (Barakat, 2011).

It is of utmost importance to remove these metals from wastewater in order to prevent contamination of natural water bodies by effluents containing toxic metals. The issues have convinced environmental engineer and researchers to carry out extensive investigations into identifying more suitable method which may assist in the removal of heavy metals from wastewater before it enters public water stream. As the result, numerous studies have in recent years been conducted aimed at the removal of heavy metals from waters and wastewaters (Díaz-Muñoz *et al.*, 2016; Kujundziski *et al.*, 2015; Kyzas & Kostoglou, 2014; Rahman *et al.*, 2014; Kikuchi & Tanaka, 2012). Various innovative treatment methods, namely ion exchange, reverse osmosis, electrolysis, oxidation and reduction, coagulation and flocculation, biodegradation, adsorption, membrane separations, and chemical precipitation are among some of the applications in wastewater treatment (Bilal *et al.*, 2013) but they are reportedly costly (Nguyen *et al.*, 2013). Other associated drawbacks are high sludge-production (coagulation and flocculation); high energy consumption and by-product formation (oxidation); adsorbent progressively deteriorating in capacity as number of cycles increases (adsorption) and the requirement of an optimal favourable environment (biodegradation) (Bilal *et al.*, 2013).

Adsorption has presently become one of popular treatment techniques over the abovementioned methods for wastewater laden with heavy metals. Adsorption mainly uses commercial activated carbon (AC); however it requires the incorporation of expensive technology. Conventional commercial AC is derived from wood and coconut shell and a non-renewable resource; commonly coal, and therefore it has to compete with the energy industry as it is presently considered as a diminishing commodity (Cheung *et al.*, 2012). Apart from that, its applications for multiple purposes have resulted in a steady rise observed in price of AC thus considered as an expensive. Hence, there is presently a need to employ waste materials as an alternative precursor to produce activated carbon.

Agricultural waste offers an effective, replacement for the non-renewable coal-based activated carbons due to their similar or better adsorption efficiency (Maheshwari & Gupta, 2016). Hence it has been considered as a better option for precursors of activated carbons from non-renewable source. Therefore, the need to find a new alternative precursor of AC has grown among the researchers by means of focusing on the use of alternative of non-conventional waste material. Adsorption was recently associated with new adsorbents such as biological origin, zeolites, industrial by-products, agricultural wastes, biomass, and polymeric materials as they have been proved to be a potentially feasible alternative (El Zayat & Smith, 2013). Some of its advantages over other conventional treatments include, the need for a smaller area compares to a biological system, relatively lower sensitivity to diurnal variation and operational flexibilities (Vargas *et al.*, 2011).

1.2 Problem statement

Agricultural waste was used as a precursor in various AC production (Anisuzzaman *et al.*, 2015; Köseoğlu & Akmil-Başar, 2015; Nurdin *et al.*, 2015; Angin, 2014; Mutah *et al.*, 2013; Amalenei *et al.*, 2012). However high concentration of chemical agents and high carbonization temperature was required during AC production to react with the lignocellulosic compounds in the material. Honeydew rind (HDR); a non-woody AC precursor contains cellulose (25.42%), hemicellulose (36.85%) and low lignin content (8.2%) thus requires lower acid concentration and lower carbonization

temperature. Therefore lower energy consumption in AC production from HDR (ACHDR) is an advantage.

A recent work has reported the potential of HDR biosorbent in lead, ferum and manganese removal from wastewater (Othman & Asharuddin, 2013). Hence, this study has carried out, in a way, a follow-up investigation and observation on upcycling of honeydew rind to its activated carbon. Cr(III) and Zn(II) which found in high concentration (150–450 mg/L) in effluent from tile and electroplating industries mining in Kluang and Ayer Hitam, Batu Pahat (Othman & Asharuddin, 2013) has embarked the selection in this study. Investigation of physicochemical properties has revealed both significant chemical compounds and physical behaviour are present in the native honeydew rind indicated its adsorption capacity. Hence previous study has triggered the potential of HDR with adsorption characteristic from a non-woody material.

By far, Cr(III) and Zn(II) removal in batch adsorption study at high range concentration (400 mg/L for chromium(III)) and (1000 mg/L for zinc(II) mg/L)) using ACHDR has not widely studied. Therefore, this study has provided an optimum experimental design and the affect of batch adsorption parameter on the metal removal from synthetic wastewater using ACHDR. Following from the investigation, determination of mechanism adsorption for chromium(III) and zinc(II) removal from the aqueous solution can be achieved for practical design and fundamental understanding of the adsorption systems (Foo & Hameed, 2012).

Previous studies have successfully proven the efficiency for non-woody agricultural waste-based AC from batch adsorption observations but unfortunately there is scant information on column application studies. Such arguments have sparked the interest to delve a deeper study. Therefore, assessing the performance of the ACs under the column apart is considered important for a wider range of applications. This has driven an operational model of activated carbon from honeydew rind bed-packed column for chromium(III) and zinc(II) removal in aqueous solution in order to manifest an extent of significant application of the carbon produced in this study.

In the present HDR or *Cucumis melo* rind was selected as a new alternative precursor for activated carbon adsorbent, specifically for chromium(III) and zinc(II) removal in wastewater. By means of selecting the waste material as a precursor to produce activated carbon, it may reduce the cost of waste disposal from its source (Umar *et al.*, 2015). Another contribution is it can be an alternative to overcome of

employing current commercial activated carbon which is estimated to increasing demand by 5-10% annually (Zaini *et al.*, 2014). As a conclusion remark, this study redounded to a number of significant contributions in the converting agricultural waste research area as an alternative AC precursor in wastewater application

1.3 The research objectives

The present study aims to utilize honeydew rind in wastewater application in order to produce its activated carbon. The objectives of the present study are:

- (a) To investigate adsorptive properties of HDR namely surface morphology, lignocellulosic compounds, thermal characteristic, mineral content and surface functional groups.
- (b) To observe the effect of impregnation agent concentration and carbonization temperature effect on surface morphology and characterize physicochemical properties of ACS and ACP.
- (c) To study factors affecting chromium(III) and zinc(II) removal in batch adsorption, namely pH of synthetic water solution, mass of AC, contact time and metals concentration.
- (d) To investigate the adsorption isotherms, adsorption kinetics in batch adsorption and the regeneration of honeydew rind acid impregnated activated carbon using column adsorption for chromium(III) and zinc(II) removal from synthetic wastewater by means of honeydew rind acid impregnated activated carbon.

1.4 Scope of research

HDR was used as the raw material in the preparation of sulfuric acid (H_2SO_4) and phosphoric acid (H_3PO_4) impregnated activated carbon adsorbent in the present study. The characterization and preparation of HDR as impregnated activated carbon precursor were carried out prior to the production of AC. H_2SO_4 was chosen because of its ability to produce high surface AC. H_3PO_4 was chosen due to its advantage in producing high thermal stability AC, user friendly and allow a low temperature

carbonization process. The process of carbonization was done in muffle furnace with limited oxygen supply to produce two types of activated carbon, namely honeydew rind H_2SO_4 impregnated activated carbon (ACS) and honeydew rind H_3PO_4 impregnated activated carbon (ACP). The study of chromium(III) and zinc(II) removal efficiency using the best ACS and ACP was done in batch adsorption parameter optimization. Determination of mechanism of the metal adsorption processes and adsorption kinetic were done. This was followed by the removal of heavy metals in synthetic wastewater using honeydew rind impregnation activated carbon in a continuous adsorption. In this experiment, a glass chromatography column was packed with only one AC based from removal efficiency result from batch adsorption study. Regeneration study of the exhausted carbon was attained for chromium(III) and zinc(II) removal. It is emphasized that throughout the present study, synthetic wastewater was utilized in all experiments.

1.5 Layout of thesis

This thesis is divided into five chapters and each chapter describes the sequence of this study. Chapter 1 consists of background, problem statement, objectives and scope of study. Chapter 2 reviews the affect of heavy metal, current wastewater treatment technology, agricultural waste based activated carbon, AC process and its relationship with the adsorbents performances, factors affecting batch adsorption. Isotherm and kinetic adsorption model investigation and previous column adsorption studies are also highlighted. Chapter 3 presents the methodology flow chart, description of honeydew rind collection, material preparation, instrumentation, chemicals preparation chromium(III) and zinc(II) stock solution and preparation of activated carbon from honeydew rind. The working condition range and experimental design in optimization of acids concentration and carbonization temperature, batch, isotherm, kinetic and column adsorption were included. Chapter 4 presents and discusses the analysis of data and result obtained from the experimental works. Chapter 5 presents the conclusions of the study.

CHAPTER 2

LITERATURE REVIEW

2.1 Industrial wastewater

Increased in industrial activities have generated of huge amount of polluted water containing a number of undesired products specifically harmful toxic matters which may potentially pollute the available fresh water (Gonzalez & Pliego-Cuervo, 2014). Small and medium enterprises involved in plating, polishing and metal-coating operations such as paint, motor vehicle parts and accessories manufacturing may significantly contribute to heavy metal water pollution (Issabayeva *et al.*, 2010).

In this regard, it has to be highlighted that the precise qualitative estimations can be hard to derive partly owing to poor environmental control provisions along with difficulties of carrying out technical monitoring for small, often family run enterprises (Hashim *et al.*, 2011). Due to the widely held belief and the findings of some recent studies that toxicants in water attributes affect living things, and the ecological lives as well as industrial activities. Therefore a huge concern in pollution control and industrial discharge management is now considered high priorities (Barakat, 2011). Although it is discharged through its own piping system, major concerns have been raised in relation to the safety of aquatics system and living things which may have to receive the wastewater from this source.

2.2 Heavy metals

Heavy metal is defined as elements with atomic weights of 63.5 g/mol–200.6 g/mol (Barakat, 2011). It is a chemical element in that has a relatively higher density; five times of specific gravity of water, classified toxic and harmful even in small amount

(Hashim *et al.*, 2011). Generally, most of the heavy metals includes cadmium, chromium, copper, plumbum, zinc, mercury, manganese can be found both from the earth's crust and oceanic sediments (Yus & Mashitah, 2014). Water stream is one of the transportation modes by means of which the heavy metals move from one place to another. Besides, heavy metals can be suspended by erosion and volcanic eruption sand ore exploitation. Anthropogenic sources are the resultant of activities of such rapid development in industrial activities, mineral combustible and waste dumps (Hashim *et al.*, 2011).

Some of the heavy metals such as cobalt, zinc, chromium, copper, manganese are considered essential for the biological function (Yus & Mashitah, 2014). However, they have tendency to gradually increase in quantity in both the environment and living organisms through deposition and settlement. The accumulation in human's bodies is carcinogenic and its consumption in excess may result in serious effects on inner organ damage, nervous system problems which eventually lead to the risk of death (Gautam *et al.*, 2014). Table 2.1 samples some of the heavy metals which can be found in local industries discharge residue.

Table 2.1: Heavy metals found in various industries
(Gautam *et al.*, 2014)

Industry	Al	As	Cd	Cr	Cu	Hg	Pb	Ni	Zn
Pulp & paper mills				x	x	x	x	x	x
Organic chemistry	x	x	x	x		x	x		x
Alcalies & Chlorine		x	x	x		x	x		x
Fertilizer	x	x	x	x		x	x	x	x
Petroleum refinery	x	x	x	x	x		x	x	x
Steelworks		x	x	x	x	x	x	x	x
Aircraft plating & finishing	x		x	x	x	x		x	
Flat glass & cement				x	x				
Textile mills				x					
Tanning				x					
Power plants				x					

Table 2.2 summarizes toxicity of several heavy metals which may adversely affect human's health.

Table 2.2: Toxicity heavy metals to human's health

Heavy metals	Toxicities	Maximum contaminant level (mg/L)
Arsenic	Skin malfunctions, visceral cancers & vascular disease	0.05 <i>Lo et al. (2012)</i>
Cadmium	Kidney damage, human & carcinogenic	0.005 <i>Lo et al. (2012)</i>
Chromium (IV)	Headache, nausea, diarrhea & vomit	0.05 <i>Miretzky & Cirelli (2010)</i>
Chromium (III)	Depression, lethargy, neurological signs such as seizures and ataxia	0.10 <i>Miretzky & Cirelli (2010)</i>
Cuprum	Linked to Alzheimer's disease, Parkinson's disease, and other neurodegenerative diseases with increased oxidative stress in the brain.	1.30 <i>Bilal et al. (2013)</i>
Lead	Abdominal pain, vomit, constipation	0.05 <i>Lo et al. (2012)</i>
Mercury	Rheumatoid arthritis, kidney failure, circulatory and nervous system damage.	0.006 <i>Gupta et al. (2014)</i>
Nickel	Dermatitis, nausea, chronic asthma, coughing	0.20 <i>Lo et al. (2012)</i>
Zinc	Headache, gastroenteritis, diarrhoea, vomit and increase thirst	5.0 <i>Maheshwari & Gupta (2016)</i>

2.3 Health effect of chromium to human

Property of chromium (Cr) is listed in Table 2.3. An oxide thin layer is formed to protect the metal below when exposes to oxygen. Cr is recognized as the important raw material in alloy industry such as stainless steel production, in chrome encrusting and in metal ceramics. The material plating was once widely applied in giving steel a polished silvery mirror glazing is widely used in dyes for plastic and to convey deterioration protection (*Wlibur et al., 2012*). Its salts are efficient for colouring glass in emerald green (*Huang et al., 2016*), producing synthetic rubies; as a catalyst in dyeing and in the tanning of leather and to make mold for the firing of bricks.

Table 2.3: Properties of chromium (*Devi & Manonmani, 2015*)

Colour	Atomic number	Atomic mass (g/mol)	Ionic radius (nm)	Density (g/cm ³)	Oxidation state	Electronegativity
Grey	24	52.00	0.069	7.16	+3	1.65

Chromium occurs in a number of oxidation states, but Cr(VI) and Cr(III) are of main environmental concern (Wlibur, 2012; Sud *et al.*, 2008). Forms of Cr(VI) are as chromate ion, HCrO_4^- predominant at $\text{pH} < 6.5$, or CrO_4^{2-} , prevalent at $\text{pH} > 6.5$. Dichromate, $\text{Cr}_2\text{O}_7^{2-}$, predominant at higher concentrations ($>10\text{mM}$) and at $\text{pH} 2-6$. The main forms of Cr(III) in freshwater are $\text{Cr}(\text{OH})^{2+}$, $\text{Cr}(\text{OH})_2$, $\text{Cr}(\text{OH})_4^-$ and they are generally stable and kinetically inert (Gupta *et al.*, 2014). Cr(III) is stable in acidic environment (Sulaymon *et al.*, 2011).

Cr(III) is important in element trace for human beings and participates in the metabolism of lipids and glucose. The level of concentration exceeding 0.01 mg/L Cr(III) found to be toxic to fish, cause more structural perturbation in the human erythrocyte membrane, change the biological membrane permeability, which affects the function of receptors, ion channels and enzymes found in the erythrocyte membranes (Maheshwari & Gupta, 2016, Pan *et al.*, 2013). Prolonged contact with high concentrations of Cr(III) can cause allergic skin reactions, cancer and DNA damage. Therefore, it is vital to ensure removal of Cr(III) from wastewater before disposal and amass in drainage. There have been only few reports on the Cr(III) removal in water treatment thus it is a huge concern on investigating an appropriate treatment method study of Cr(III) removal from wastewater (Pan *et al.*, 2013; Duran *et al.*, 2011; Miretzky *et al.*, 2010).

2.4 Health effect of zinc to human

Zinc (Zn) can be found in water, soil, air, and food items, and it is notably the most common trace in the earth's crust. Table 2.4 lists the properties of Zn. It is reportedly bluish in colour and shiny metal in the pure or metallic form. Zinc is considered essential to our body as one of the nutritional requirements in trace quantity as a physiological function of living tissues and biochemical processes. It is an indicative element in enzymes participating in the synthesis and degradation of carbohydrates,

lipids, protein and nucleic acid as well as in the metabolism of other micronutrients. Zn is also a significant nutrient to plants' growth.

Table 2.4: Properties of zinc (Sarkar, 2003)

Colour	Atomic number	Atomic mass (g/mol)	Ionic radius (nm)	Density (g/cm ³)	Oxidation state	Electronegativity
Bluish	30	65.38	0.074	7.13	+2	1.65

Dose recommendation of Zn for man, woman, children and infant on a daily basis is 15 mg, 12 mg, 10 mg and 5 mg, respectively (Roney & Osier, 2005). In the industrial sector, zinc has relatively wider applications such as steel and iron coating which helps preventing rust and corrosion during galvanizations; incorporate with other heavy metals to form brass and bronze alloys and in dry battery factories. Zinc sulfide and zinc oxide are recognized produce paints and ceramics (Sarkar, 2003).

A concentration level of higher than 5 mg/L zinc may cause a bitter, astringent taste to water, and it might precipitate as Zn(OH)₂ or Zn(CO)₃ in alkaline water to produce a milky turbidity. The toxicity is commonly warned by abnormal of growth in plants, zinc fever and edema of lungs in human beings (Moreno-Barbosa *et al.*, 2013). Zinc is a threat to biological system as it can travel through the food chain via bioaccumulation. Polluted water with zinc can be related to numerous industrial disposal such as cell production industry, leather metal coating, steel, paper and pulp, agrochemicals, petrochemicals and fertilizer industries (Yao *et al.*, 2016). It also enters water stream from the deterioration of galvanized iron pipes. Quite a number of studies have revealed these activities release zinc in high concentration from related industrial waste which in turn may result in the accumulation of zinc in the water bodies as untreated wastewater (Othman *et al.*, 2016; Moreno-Barbosa *et al.*, 2013; Othman *et al.*, 2012; Lalhruaitluanga *et al.*, 2011). Owing to these factors which appear to be threats, there is a necessity to eliminate Cr(III) and Zn(II) from untreated effluents in order to avoid the pollutants enter into natural water bodies.

2.5 Methods for removing heavy metals in wastewater

The necessity to employ suitable wastewater treatment to ensure it is safe before it is discharged to environment has widely been acknowledged among the researchers. Subsequently, numerous investigations with multiple degrees of success have been documented to date to manage water pollution as a result of serious and cooperative efforts among researchers in the field of wastewater treatment and management. Common methods for removing heavy metals from wastewater are physicochemical methods which include chemical precipitation (Maheshwari & Gupta 2016), chemical coagulation (Huang *et al.*, 2016), ion exchange (Lee *et al.*, 2016), electrochemical (Fu & Wang 2011), membrane filtration (Keng *et al.*, 2013), adsorption (Devi & Manonmani 2015; Mishra 2014; Kyzas & Kostoglou, 2014) and biological treatment (Hashim, 2011). A comprehensive review of literature indicates that leading experts have unanimously concluded that these methods were found to have their own shortcomings and limitations in terms of being either ineffective, not employed for all processes that generate heavy metals bearing wastewater or expensive (Table 2.5).

At present, adsorption is recognized as an effective and economic method for heavy metals wastewater treatment. Despite of its disadvantages such as product recovery possibly requiring a special, expensive distillation (or extraction), adsorbent progressively deteriorating in capacity as number of cycles increases, adsorbent regeneration requiring a steam or vacuum source (Bilal *et. al.*, 2013), adsorption is stated as notorious wastewater purification method for heavy metals removal. This method is preferably attributable on its advantage in low operational cost and spontaneous reaction during the remediation processes (Rahman *et al.*, 2014; Gupta 2013). This process offers flexibility in design and operation, high treatment capacity, high removal efficiency and fast kinetic (Abbaszadeh *et al.*, 2016). In addition, adsorption is occasionally reversible, reproducible and regenerated by suitable desorption process. It has wider applicability in the removal of diverse types of pollutants, environmental friendliness and exhibiting resistance to fouling from toxic pollutants and greater versatility (Barakat, 2011).

Table 2.5: Working principle, advantage and disadvantage of wastewater treatment methods

Technique	Working Principle	Advantage	Disadvantage
Chemical precipitation	<ul style="list-style-type: none"> • Involves the using of chemicals to cooperate with heavy metals ions with the purpose to form insoluble compound which can be separated from the water by sedimentation or filtration. • Ph value of 8 to 11 is essential to be retained in order to prolong the hydroxides precipitation in the medium. (Fu & Wang, 2011). 	<ul style="list-style-type: none"> • A simple and inexpensive operation that is effective and most widely used in wastewater application (El-Zayat & Smith, 2013). 	<ul style="list-style-type: none"> • Generates of huge quantity of relatively low-density sludge thus presents dewatering and disposal problems. • Insufficient treatment due to tedious in pH control for all types of metals contain in the polluted water (Keng <i>et al.</i>, 2013). • Not a suitable metal removal method when the pollutant concentration is low (Mishra, 2014).
Coagulation and flocculation	<ul style="list-style-type: none"> • Coagulation destabilize colloids by offsetting forces that keep them disassociated with the aid of coagulants. Impurities are removed by neutralizing the charge of the particulate to form precipitates. • Flocculation takes place where by the particles binds together into large agglomerates with the aids of flocculants (Fu & Wang, 2011) and removed or separated by filtration, straining or floatation. 	<ul style="list-style-type: none"> • Removes wastewater particulate and impurities efficiently (Hashim, 2011).. 	<ul style="list-style-type: none"> • Frequent maintenance and scrupulous chemical feed system monitoring to control the pH. • A careful operational routine is crucial by which overload dosing with coagulant to compensate for inefficient may produce a high amount of sludge. • Could result to uneconomical wastewater treatment in terms of chemical usage but it is expensive in terms of unwanted product (Drinan & Spellman, 2013).
Ion exchange	<ul style="list-style-type: none"> • Employs ion-exchange resin; either synthetic or natural solid resin in heavy metals removal application (Díaz-Muñoz <i>et al.</i>, 2016). 	<ul style="list-style-type: none"> • Specific ability to exchange its ionic species through the cationic metals in metal wastewater treatment. • Cheap natural resin, whilst the synthetic form has wider application and more effective in heavy metals removal in wastewater. (Huang <i>et al.</i>, 2014) 	<ul style="list-style-type: none"> • Zeolites and montmorillonites ion-exchanger resin are limited compared to the synthetic resins (Kim <i>et al.</i>, 2013). Generally applicable to remove heavy metals at low concentration due to the cost of replacing ion exchange resins prohibits the treatment of highly concentrated wastewater (Keng <i>et al.</i>, 2013).

(continued) Table 2.5: Working principle, advantage and disadvantage of wastewater treatment method

Membrane filtration	<ul style="list-style-type: none"> • Adopt ultra filtration (UF), reverse osmosis (RO), nanofiltration and electro dialysis technology. • Its operational technique based of pore size and molecular weight of suspended solids from organic solution pollutants; molecules with 5-20 nm and molecular weight of the separating compounds of 1000-100000 Dalton. • UF membrane has larger pore sizes than the dissolved metal ions thus the ions are able to pass through easily. RO comprises a semi-permeable membrane, which filtered out the fluid by rejecting the contaminants (Fu & Wang, 2011). 	<ul style="list-style-type: none"> • Easy operational, continuous throughput, low energy requirement, normal operating temperature, simple maintenance, flexible modular design and space saving technology. 	<ul style="list-style-type: none"> • Consumes high power to pump the pressure required and high maintenance cost due to its membrane to be restored after certain operational time and low permeate flux (Hubbe <i>et al.</i>, 2011).
Adsorption	<ul style="list-style-type: none"> • A process of accumulation of ions at the interface between a solid phase and an aqueous phase. • Involves mass transfer process, in which, pollutant in aqueous is transferred to the adsorbent solid surface bound by physical and chemical interactions. Pollutant in aqueous is known as adsorbate, while solid surface of adsorbent is known as adsorbent (Abdolali <i>et al.</i>, 2014) 	<ul style="list-style-type: none"> • Effective and economic method for heavy metals wastewater treatment. • Flexibility in design and operation, high treatment capacity, and fast kinetic (Abbaszadeh <i>et al.</i>, 2016). • Reversible, reproducible and regenerated by suitable desorption process. • Wider applicability in the removal of diverse types of pollutants, environmental friendliness and exhibiting resistance to fouling from toxic and pollutants (Barakat, 2011). 	<ul style="list-style-type: none"> • Product recovery possibly requiring a special, expensive distillation (or extraction), adsorbent progressively deteriorating in capacity as number of cycles increases, adsorbent regeneration requiring a steam or vacuum source (Hashim <i>et al.</i>, 2011)

2.6 Adsorption mechanism

Adsorption is a process of accumulation of ions at the interface between a solid phase and an aqueous phase. Pollutant in aqueous is known as adsorbate, while solid surface of adsorbent is known as adsorbent. Adsorption involves mass transfer process, in which, pollutant is transferred to the adsorbent solid surface bound by physical and chemical interactions (Abdolali *et al.*, 2014). Barakat (2011) highlighted three general steps involved in adsorption: (i) transportation of sorbate sorption to sorbent surface, (ii) adsorption on sorbent surface and (iii) transportation within the sorbent particles (Barakat, 2011).

Adsorption study concerns the adsorbent, which is reacted with solutions containing varying quantities of the metal(s) of interest for a specified period of time using either batch or column techniques. The concentration range of adsorbate study should be imbricated with the concentration of environmental interest (Abdolali *et al.*, 2014). The reaction time ought to approach an equilibrium, which is usually determined by kinetic experiment. The mixture of metal adsorbed adsorbent and solution is separated by centrifugation and/or filtration after a targeted contact time. The filtrate solution is analyzed by Atomic Absorption Spectroscopy (AAS) for the remaining metal ions while the metal adsorbed adsorbent is examined for its characteristic observation via various tools such as Field Emission Electron Microscopy (FESEM) and Fourier Transform Infrared (FTIR) spectroscopy. Batch adsorption and continuous adsorption are the two common types of adsorptions, which are employed in heavy metals metal (Gupta *et al.*, 2014).

The understanding on metal adsorption mechanisms is crucial for the development of adsorption in aqueous system. The removal of heavy metals using activated carbon could involve several mechanisms such as physical adsorption, chemical adsorption, ion exchange, complexation, and electrostatic interactions (Díaz-Muñoz *et al.*, 2016).

2.6.1 Physical adsorption

Physical adsorption, also called physisorption is based on intermolecular forces (Van der Waals) force between the adsorbate and functional groups on the carbon surface (Pyrzyńska & Bystrzejewski, 2010). The driving force for this type of adsorption is the affinity of the adsorbate to the adsorbent. However physisorption is independent of the electronic properties of the adsorbent. Ion exchange of electrons does not occur results in less strongly adsorbate attached to a specific site on the adsorbent and thus this mechanism is reversible. Van der Waals forces exist not only between adsorbates and adsorbent but also among adsorbates. Because the adsorbate-surface interaction is weak in physisorption lateral interactions are very important for physisorbed molecules and can be as strong as the adsorbate – adsorbent interaction. Physical adsorption involves multilayer formation if the pores are close to the size of molecules. Therefore physically adsorbed adsorbate is free to move within the interface (Cecen & Aktas, 2012).

2.6.2 Chemical adsorption

Chemical adsorption, also called chemisorption is based on a strong force that allows the adsorption to occur at active sites on the carbon surface (Pyrzyńska & Bystrzejewski, 2010). The forces of attraction that hold the metal ions onto the carbon surface are valence forces. Chemisorption involves exchange of electrons between specific surface sites and adsorbate, a chemical bond being formed. Chemically adsorbed adsorbates are not free to move on the surface or within the interface. It is irreversible and forms a specific interaction. Since the adsorbate is linked to the carbon surface by valence bonds, the adsorbate usually occupies certain adsorption sites on the surface thus monolayer adsorption is formed.

2.6.3 Ion exchange

Ion exchange is a chemical reaction in which free mobile ions on a carbon surface, the ion exchanger, are exchanged for different ions of similar charge in solution. Functional groups on carbon's network structure undergo hydrolysis in aqueous

solution and form positively or negatively charged ion depending on to the pH of solution (Kumar and Jain, 2009).



Cation exchanger containing negatively charged groups like sulphate, carboxylate, phosphate, benzoate and so forth are fixed to be the backbone materials and allow the passage of cations and rejects the anions. Anion exchanges contain basic functional groups, such as amine. There are also amphoteric exchangers that are able to exchange both cations and anions simultaneously (Kumar & Jain, 2013). The mechanism of ion exchange involves replacement of protons, alkali, alkali earth or other cations present on the carbon surface by the heavy metal ions in the solutions as represented by the following equation (Kumar & Jain, 2013):



Evidence presented by numerous researches on metal adsorption using AC has proven that this replacement phenomenon is taking place (Abdolali *et al.*, 2014, El Zayat *et al.*, 2013; Pan *et al.*, 2013; Ahmaruzzaman, 2011; Miretzky *et al.*, 2010; Sud *et al.*, 2008). In such cases, it has been seen that the surface groups such as carboxyl, lactones and phenols render the AC surface polar and hydrophilic thereby facilitating the cationic species of metal ions (Gupta *et al.*, 2014). Nguyen *et al.* (2013) reported that ion exchange might be the dominant mechanism in the removal of Cu(II), Zn(II) and Pb(II) using orange peel. A review on removal of Cd(II) from chemically modified plant waste AC has documented that ion-exchange was considered as a predominant mechanism in Cd(II) removal (Abdolali *et al.*, 2014).

2.6.4 Precipitation

Precipitation occurs when cations and anions are combined to form insoluble ionic solid called precipitate. In metal removal from aqueous solution, metal precipitation is dependant closely to the pH value of the solution. This is to allow metal hydrolysis formation ($\text{M}(\text{OH})^+$ which then will combine with negatively hydroxide ion (OH^-))

from the solution. Research on the removal of Co(II) from aqueous solutions by green vegetable waste AC found that the adsorption favored precipitation of metal ions (Sabela *et al.*, 2016). Runtti *et al.* (2014) observed removal of Fe(II), Cu(II) and Ni(II) via precipitation in addition to adsorption using chemically activated residue adsorbent at pH 6-8. The pH of solution was optimized in order to allow metal hydroxides formation ($\text{Cu}(\text{OH})_2$ at pH 9; $\text{Ni}(\text{OH})_2$ at pH 7.5) thus promoting the occurrence of metal precipitation. Co-precipitation of Cr(III) with $\text{Fe}(\text{OH})_3$ was reported in a study of Cr(III) removal from oil palm AC which occur at the value of pH 9 (Rahman *et al.*, 2011).

2.6.5 Complexation

Metal ions removals from the solution take place through complex formation on the carbon surface after the interaction between metal ion and functional groups. The removal of metal sorbate from solution may also happen through complex formation on the carbon surface after the interaction between sorbate species and active groups (Hashim *et al.*, 2011). This mechanism was found uses polymeric nano-adsorbent whereby its exterior shell can be tailored (e.g., hydroxyl or amine-terminated) for adsorption of heavy metals. The interaction is responsible for the uptake of Cr(III) from aqueous solution (Qu *et al.*, 2013). Nguyen *et al.* (2013) reported metal-carboxylate complexes formation in Cr(III) and Cu(II) removal using *Cupressus lusitanica* bark adsorbent as one of the interactions during adsorption. The other mechanisms are ion-exchange and precipitation.

2.7 Factors affecting adsorption

The adsorbate-adsorbent interaction is influenced by some parameters namely, operating parameters pH of solution, mass of adsorbent, contact time and metal concentration (Othman *et al.*, 2012). In order to describe the response of the sorption systems to the changes caused by the variations in experimental conditions and the properties of the sorbents, batch sorption modelling is deemed pivotal (Patel, 2012; Ngah & Hanafiah, 2008). Table 2.6 compiles the affect of adsorption parameter on metal removal and adsorption capacity.

Table 2.6: Factors affecting adsorption using agro waste AC from previous study.

Activated carbon	Metal	pH of solution	Mass of adsorbent (g/L)	Contact time (minute)	Metal concentration (mg/L)	Metal removal (%)	Adsorption capacity(mg/g)	Reference
Tea waste	Cr(III)	1-8 (5)	0.1-2.5 (1.0)	1-240 (120)	0.02	95	61.6	Duran (2011)
Tobacco dust	Cu(II)	4-5	1.0	1440	-	-	36	Bilal <i>et al.</i> (2013)
Papaya peel	Pb(II)	3-7 (5)	0.01-2 (0.1)	10-180 (120)	10-200 (120)	90-70.7		Abbaszadeh <i>et al.</i> (2016)
Banana peel	Cu(II)	5	5	60	10	-	4.08	Hossain <i>et al.</i> (2012)
Water melon shell	Zn(II)	4.5	0.2	240	10-500 (10)	80	6.08	Moreno-Barbosa <i>et al.</i> (2013)
Oil palm shell	Ni(II)	5	1.0	40	6.06	50.9	15.97	Rahman <i>et al.</i> (2014)
Green vegetable	Cu(II)	2-8 (3.5)	0.1-0.6 (0.6)	0-120 (90)	1.5-5.0 (18)	97.36	75.93	Sabela <i>et al.</i> (2016)
<i>Tamarix hispida</i>	Zn(II)	2-10 (6)	1-20(10)	2-80 (50)	20-100 (100)	95.75	188.7	Khademi <i>et al.</i> (2012)
Tunisian date	Cu(II)	2-7 (5)	0.5	100	100	30	31.25	Bouhamed <i>et al.</i> (2012)
Crop straw	Cr(III)	2.5-5.0 (3.5)	0.1	120	5-35 (10)	-	330.0	Pan <i>et al.</i> (2013)
Rice husk	Pb(II)	2.5-6.5 (5.5)	-	0-150 (90)	40-140 (80)	45	143.45	Yao <i>et al.</i> , 2016
Orange peel	Cu(II)	5	2	480	5-150	-	86.73	Bilal <i>et al.</i> (2013)
Grape seed	Cu(II)	5	25	120	25-1000	-	95	Bilal <i>et al.</i> (2013)
Palm date stone	Cr(III)	3.5	1	180-	-	-	120.5	Ahmed <i>et al.</i> (2016)

Optimum value in bracket

2.7.1 pH of solution

Adsorbate-adsorbent interaction in aqueous solution system is influenced greatly by the pH value of the solution (Gundogdu *et al.*, 2013). A number of research has been carried out on the effect of pH on metal adsorption using AC as adsorbent (Nowicki *et al.*, 2015; Gundogdu *et al.*, 2013; Sych *et al.*, 2012) . The pH was found to control the ionic activities including functional groups ionization and ionic state of metals species. Duran (2012) in a study revealed that the tea waste activated carbon adsorbent pH values fell in the acidic region and this shows dominance of acidic groups over basic groups. This is also related to Boehm titration, which proposed that the surfaces of adsorbents were rich in acidic groups. Cr(II) adsorption by using palm date stone AC was found best at 3.5 (Ahmed *et al* 2016; Pan *et al.*, 2013). Therefore, the knowledge on this value may help in deciding at which pH value one should work during adsorption studies.

A study carried out on palm shell activated carbon to remove Cu(II) in aqueous solutions concluded that the pH affected (Issabayeva *et al.*, 2008) the metal ion removal. Adsorption at pH 5 was found relatively higher than pH 3. Such negative effect of acidic was assumed to be related with clogged pores due to the complex compound, hence the number of adsorption sites available for copper ions decreased.

2.7.2 Contact time

Contact time is also the significant factor that affects metals adsorption. According to Hossain *et al.* (2012), the influence of contact time on Cu(II) adsorption marked a swift rate of Cu(II) adsorption during the first 30 minutes, before Cu(II) removal became steady (Hossain *et al.*, 2012). Abbaszadeh *et al.* (2016) studied Pb(II) removal using papaya peel AC with increasing time from 10 to 120 minutes. It was found that greater amount of adsorption as the contact time increased with maximum (93.22%) removal and it eventually became constant after 2 hours. The uptake trend became downward and steady after 2 hours indicating adsorption equilibrium has achieved.

In other study, in the beginning of the adsorption, a big number of empty active binding sites available during the early part of experiment and enormous of Cu(II) were rapidly attached on banana peel at a quick adsorption rate. Eventually, the amount of binding site decreased and the remaining empty surface sites were hardly adsorbed

by Cu(II) due to the formation of repellent between the Cu(II) on the adsorbent surface and the aqueous phase (Zaini *et al.*, 2014). This finding shows that optimal contact time is of utmost importance in order to obtain maximum adsorption interaction.

2.7.3 Mass of adsorbent

A study of Cu(II) adsorption using banana peel activated carbon has included adsorbent mass optimization experiments and revealed that the percentage removal was proportional to the mass of banana peel AC. At higher mass of AC, Cu(II) removal was observed to be decreasing. The highest Cu(II) removal (88%) was obtained through the initial Cu(II) concentration of 10 mg/L and dose of 5 g/L. Cu(II) adsorption onto banana peel was retarded when the incomplete aggregation among the available active binding sites were at higher doses and the shortage of active binding site at lower amount of adsorbent (Hossain *et al.*, 2012).

The influence of adsorbent mass on the adsorption process of Zn (II) was proven using *Tamarix hispida* AC (Khademi *et al.*, 2015). The removal of Zn(II) at a dose of 1 g/L was 21.7% improved to 95.75% when the adsorbent dosage was increased to 10 g/L. The author mentioned that adsorption efficiency with increasing adsorbents dose can be explained by the fact that the higher the dose of adsorbents in the solution, greater the availability of exchangeable sites for Zn(II) and greater the surface area would be. An adsorbent mass dependent experiment of 0.1 – 0.6 g adsorbent conducted in a Cu(II) removal study using green vegetable waste AC stated that increase of AC surface area and availability of more adsorption site that gradually improved the adsorption. However at higher dose the metal adsorbed per unit weight of adsorbent decreased means at higher adsorbent dose the solution ion concentration decreases to a lower value of q_e , (amount adsorbed) indicating that adsorption sites remained unsaturated (Sabela *et al.*, 2016). Based from the review, mass of AC in heavy metals removal from aqueous solution is one of the important adsorption parameter.

3.7.4 Metal concentration

Previous research have proved the influence of initial metal ion concentration in metal adsorption (Khademi *et al.*, 2012; Wahi & Senghie, 2011; Moreno-barbosa *et al.*, 2013; Ibrahim *et al.*, 2010). Zn(II) adsorption onto the *Tamarix hispida* AC study at metal ions concentration of 20–100 mg/L resulted that degree of Zn(II) removal was decreased from 79% to 57% at respective concentration. The increase of initial Zn(II) concentrations resulted in a reduction of its adsorption percentage due to the limitation of available free sites for the adsorption of Zn(II). In fact, when the Zn(II) concentration was higher, the ratio of Zn(II) to the AC was greater, and therefore the percentage of Zn(II) removal was lower. Sorption capacity of Zn(II) at the selected conditions increased from 36.4 to 188.7 mg/g AC when the concentration of Zn(II) was increased from 20 to 100 mg/L. The enhancement of mass transfer rates occurs due to a higher Zn(II) gradient concentration at a higher initial Zn(II) (Khademi *et al.*, 2012).

The influent of Pb(II) and Zn(II) concentration was investigated with different concentrations of 10–500 mg/L at constant 0.5 g of AC. The study concluded that at higher concentration (200–500 mg/L), the efficiency of adsorption process became poor confirming that initial concentration had an influence in the adsorption process. An assumption had been made that the saturation of micropores and mesopores of the watermelon shell and walnut shell AC could be attributed to the result (Moreno-Barbosa *et al.*, 2013). Heavy metals removal using palm oil kernel shell AC resulted that the percentage of metal removal increased with the increase in metal initial concentration. It was found that at lower metal initial concentration (5 mg/l), Ni(II), Cu(II), and Cr(IV) removal were 12%, 26% and 10%, respectively. A pronounce increase in Cr(IV) removal (48%) was found at 35 mg/L. This study has resulted that more metal ions were left in the solutions at higher concentrations, and indicated smaller amount of available sites at higher concentration of metal ions in the aqueous solution (Wahi & Senghie, 2011).

2.8 Adsorption isotherm

Adsorption isotherm is a well-known instrument to comprehend the behavior of the adsorbent surface. It is an equation, which concerns with the quantity of pollutant

adsorbed onto the adsorbent surface and the equilibrium concentration of the solute in a solution at a given temperature (Kyzas & Kostoglou, 2014).

Brunnauer, Emmett and Teller, Freundlich and Langmuir are equilibrium isotherm model equations that are used to explain adsorption data in batch mode (Othman *et al.*, 2012). It is of utmost importance to test the most suitable isotherm in order to assess the success of the adsorbent in constructing appropriate real application adsorption system designs. Isotherms BET portrayed the process more precisely if the adsorbent's pores are filled with several layers of adsorbate (Lakovleva & Sillanpää, 2013). It is worth to try Freundlich isotherm since this isotherm is widely employed despite its rough approximation from a thermodynamical point of view. The Langmuir isotherm assumes that adsorption happens at specific homogeneous sites within the adsorbent at the exclusion of any interaction between the adsorbed substances. These two isotherms employed reduced concentration approach, which contributes to the coverage of parameter equal to one as far as the pores are filled. Nevertheless, it is quite common for the data to not properly fit with the linear equation (Lakovleva & Sillanpää, 2013).

2.8.1 Brunnauer, Emmett and Teller adsorption

Adsorbate molecules often form multilayer, in which, some are adsorbed on already adsorbed molecules and thus, the Langmuir isotherm is not valid. In 1938, Stephan Brunnauer, Paul Emmett and Edward Teller developed an isotherm model that took this possibility into consideration. Hence, their model is known as the BET isotherm model (Lakovleva & Sillanpää, 2013).

Each additional layer of adsorbate molecules above the monolayer is assumed to equilibrate with the layer below it and layers of different thickness are allowed to coexist and take the following form (Othman *et al.*, 2016):

$$\frac{C}{(C_S - C_{eq}) q_m} = \frac{1}{K_B \cdot q_m} + \frac{K_B - 1}{K_B \cdot q_m} \frac{C}{C_S} \quad (2.3)$$

In comparison with linear equation, $y = mx + c$;

$$y = \frac{C}{(C_S - C_{eq})q_m} \quad x = \left[\frac{C}{C_S} \right] \quad m = \left[\frac{K_B - 1}{K_B \cdot q_m} \right] \quad c = \frac{1}{K_B \cdot q_m} \quad (2.4)$$

Where q is the amount of metal ions adsorbed per specific amount of adsorbent ($\mu\text{g/g}$), C is the equilibrium concentration ($\mu\text{g/l}$), q_m is the maximum amount of metal ions required to form a monolayer ($\mu\text{g/g}$), and K_B is the constant BET adsorption (Danish *et al.*, 2011).

2.8.2 Freundlich adsorption

The Freundlich isotherm is among the widely employed isotherm in the explanation of adsorption equilibrium as it is regarded as an empirical equation (Pan *et al.*, 2013; Bello *et al.*, 2010). In addition, the Freundlich model assumes that the adsorbent surface energy is heterogeneous and hence, the stronger binding sites are first occupied and the binding strength decreases with the increasing degree of site occupation. The following equation specifies the Freundlich isotherm (Giwa *et al.*, 2012):

$$q_e = K_F C_e^{\frac{1}{n}} \quad (2.5)$$

To linearize the equation, logarithms are taken.

$$\log q_e = \log K_F + n_F \log C_e \quad (2.6)$$

where q_e = quantity adsorbed per unit mass mol/g; C_e = equilibrium solution concentration mol/L; K_F = L/g and $1/n = n_F$ = is empirical Freundlich constant. K_F ($\text{mg/g (L/mg)}^{1/n}$) is defined as the adsorption capacity of the adsorbent. $1/n$ is a measure of adsorption intensity or surface heterogeneity, which may become more heterogeneous as its value gets closer to zero (Albadarin *et al.*, 2011).

It is stated that once the surface is covered, additional adsorbed species may still be accommodated. In this regard, multilayer adsorption is predicted. It should be noted that small organic molecules in water may distribute themselves between the

REFERENCES

- Abbaszadeh, S., Alwi, S.R.W., Webb, C., Ghasemi, N. (2016). Treatment of lead-contaminated water using activated carbon adsorbent from locally available papaya peel biowaste. *J. Clean. Production*, 118, 210–222.
- Abdolali, A., Ngo, H.H., Guo, W.S., Lee, D.J., Tung, L.L., Wang, X.C. (2014). Typical lignocellulosic wastes and by-products for biosorption process in water and wastewater treatment: A critical review. *Bioresour. Technol.*, 160, 57–66.
- Abdullah, L.C. Muhammad, Shima, S.J., Choong, T.S.Y. (2010). Modelling of single and binary adsorptions of heavy metals onto activated carbon - Equilibrium studies. *Pertanika J. Sci. Technol.*, 18(1), 83–93.
- Achaw, Osei-Wusu (2012). A Study of the Porosity of Activated Carbons Using the Scanning Electron Microscope, Scanning Electron Microscopy, Dr. Viacheslav Kazmiruk (Ed.), InTech, doi: 10.5772/36337. Available from: <http://www.intechopen.com/books/scanning-electron-microscopy/a-study-of-the-porosity-of-activated-carbons-using-the-scanning-electron-microscope>
- Adinaveen, T., Kennedy, J., Vijaya, J. (2014). Surface and porous characterization of activated carbon prepared from pyrolysis of biomass (rice straw) by two-stage procedure and its applications in supercapacitor electrodes. *J. Mat. Cycles Waste Manage.*, 17(4), 736–747.
- Ahmad, M.A. & Alrozi, R. (2010). Optimization of preparation conditions for mangosteen peel-based activated carbons for the removal of Remazol Brilliant Blue R using response surface methodology. *Chem. Eng. J.*, 165(3), 883–890.
- Ahmaruzzaman, M. (2011). Industrial wastes as low-cost potential adsorbents for the treatment of wastewater laden with heavy metals. *Adv. Coll. Interface Sci.*, 166(1-2), 36–59.

- Ahmed, M. (2016). Preparation of activated carbon from date (*Phoenix dactylifera* L) plm stones and application for wastewater treatment: Review. *Process Safety Environ. Protection*, 102, 168-182.
- Albadarin, A.B. Al-Muhtaseb, A., Gavin, M. (2011). Retention of toxic chromium from aqueous phase by H₃PO₄-activated lignin: Effect of salts and desorption studies. *Desal.*, 274(1-3), 64–73.
- Alkhatib, M.F., Muyibi, S. & Amode, J.O. (2011). Optimization of activated carbon production from empty fruit bunch fibers in one-step steam pyrolysis for cadmium removal from aqueous solution. *The Environmentalist*, 31(4), 349–357.
- Alvarez-Torrellas, S., Garcia-Lovera, R., Rodriguez, A., Garcia, J. (2015). Removal of methylene blue by adsorption on mesoporous carbon from peach stone, *Chem., Sci., Transaction*, 43, 1963-1968.
- Al-Lagtah, N., Al-Muhtaseb, A., Ahmad, M.N.M. (2016). Chemical and physical characteristics of optimal synthesised activated carbon s from grass-derived sulfonated lignin versus commercial activated carbons. *Microporous & Mesoporous Mat.*, 225, 504-514.
- Al-Swidan, H., Ahmad, A. (2011) Synthesis and characterization of activated carbon from Saudi Arabian dates tree's fronds. *3rd Intern. Conf. Chem. Biol. Environ. Eng.* 20, 25-31.
- Amalenei, R.L.M., Miron, A., Volf, I., Paduraru, C., Tofan, L. (2012). Investigations on the feasibility of Romanian pine bark wastes conversion into a value-added sorbent. *Bioresource*, 7(1), 148–160.
- Anastopoulos, I., Kyzas, G. Z. (2014). Agricultural peels for dyes adsorption: A review of recent literature. *J. Mol. Liq.* <http://dx.doi.org/10.1016/j.molliq.2014.11.006>.
- Anderson, S.M. (2010). *Characterization and Remediation of Toxic Metals in Wastewater Reuse for Agricultural Irrigation*. University of Illionis, Urbana-Champaign. MSc Thesis.
- Angin, D., (2014). Production and characterization of activated carbon from sour cherry stones by zinc chloride. *Fuel*, 115, 804–811.
- Angin, D., Köse, T.E. & Selengil, U. (2013). Production and characterization of activated carbon prepared from safflower seed cake biochar and its ability to absorb

- reactive dyestuff. *Appl. Surface Sci.*, 280, 705–710.
- Anirudhan, T. S., Sreekumari, S. S (2011) Adsorptive removal of heavy metals ions from industrial effluents using activated carbon derived from waste coconut buttons, *J. Environ., Sci.*, 23(12), 1989-1998.
- Anisuzzaman, S.M. Collin, G., Daud, W. M. A. W., Krishnaiah, D, Yee, H. S. (2015.) Preparation and characterization of activated carbon from *Typha orientalis* leaves. *Intern. J. Ind. Chem.*, 6(1), 9–21.
- ASTM Committee on Standards. *Standard Test Method for Determination of Iodine Number of Activated Carbon*. ASTM D 4607-94; ASTM: Philadelphia, PA, USA. 2006
- Azizul-Rahman, M.F.H., Mohd Suhaimi, A.A. & Othman, N. (2015). Biosorption of Zn(II) in High and Low Strength Synthetic Wastewater by Watermelon Rind (*Citrullus lanatus*). *Appl. Mech. Mat.*, 773-774 (January 2015), 1286–1290.
- Bajpai, K. S & Jain, A. (2013) History, introduction and kinetics of ion exchange materials, *J. Chem.*, 2013, vol. 2013, Article ID 957647. doi:10.1155/2013/957647. Accepted manuscript.
- Banerjee, K., Ramesh, S., Gandhimathi, R., Nidheesh, P.V., Bharathi, K.S (2012). A novel agricultural waste, watermelon shell for the removal of Copper from aqueous solution, *Iranica J. Energy & Environ.*, 3(20), 143-156
- Barakat, M.(2011). New trends in removing heavy metals from industrial wastewater. *Arabian J. Chem.*, 4(4), 361–377.
- Beh, C.L., (2012). Removal of Heavy Metals from Steel Making Waste Water by Using Electric Arc Furnace Slag. *E-J. Chem.*, 9(4), 2557–2564.
- Bello, O.S., Oladipo, M.A. & Olatunde, A.M. (2010). Sorption studies of lead ions onto activated carbon produced from oil-palm fruit fibre, *Stem Cell*, 1(1), 14–30.
- Bernado, G. R., Rene, R. J., Catalina A. T. M. (2009). Chromium (III) uptake by agro-waste biosorbents: Chemical characterization, sorption-desorption studies, and mechanism. *J. Hazard. Mat.*, 170, 845-854.
- Bhatnagar, A. Hignand, W., Marques, M., Sillampaa, M. (2013). An overview of the modification methods of activated carbon for its water treatment applications. *Chem. Eng. J.*, 219, 499–511.

- Bhatnagar, A. & Sillanpää, M. (2010). Utilization of agro-industrial and municipal waste materials as potential adsorbents for water treatment—A review. *Chem. Eng. J.*, 157(2-3), 277–296.
- Bilal, M., Shah, J.A.S., Gardazi, S. M. H., Tahir, A., Pervez, A., Haroon, H., Mahomood, Q. (2013). Waste biomass adsorbents for copper removal from industrial wastewater-A review. *J. Hazard. Mat.*, 263 Pt 2, 322–33.
- Birbas, D. *Preparation of Activated Carbon : Forest residues activated with Phosphoric Acid and Zinc Sulfate*. Ph.D Thesis. Royal Institute of Technology, Sweden; 2011.
- Boehm, H.P.(2002). Surface oxides on carbon and their analysis : a critical assessment. *Carbon*, 40, 145–149.
- Bories, C., Borredon, M., Vedrenne, E., Vilarem, G., Agamuthu, P. (2009). Challenges and oppportunities in agro-waste management: An Asian perspective. *J. Environ. Manage.*, 143, 186-196.
- Bouhamed, F., Elouer, Z., Bouzid, J. (2012). Adsorptive removal of copper(II) from aqueous solutions on activated carbon prepared from Tunisian date stones: Euilibrium, kinetics and thermodynamics. *J. Taiwan Inst. Chem. Eng.*, 43, 741-749.
- Borhan, A., Abdullah, N. A., Rashidi, A. A., Taha, M. F. (2016). Removal of Cu²⁺ and Zn²⁺ from single metal aqueous solution using rubber-seed shell based activated carbon. 4th Intern. Conf. Process Eng. Advanced Mat., *Proc. Eng.*, 148, 694-710.
- Byamba-Ochir, N., Shim, W. G., Balathanigaimani, M. S., Moon, H. (2016). Highly porous activated carbon prepared from carbon rich Mongolian anthracite by direct NaOH activation, *App. Surf. Sci.*, 379, 331-337
- Carrier, M., Loppnet-Serani, A., Denux, D., Lasnier, J., Ham-Pichavant, F., Cansell, A. (2011). Thermogravimetric analysis as a new method to determine the lignocellulosic composition of biomass. *Biomass and Bioenergy*, 35(1), 298–307.
- Cazes, J (2005). *Ewing's Analytical Instrumentation Handbook*, 3rd. New York: Marcell Dekker, USA.
- Ceballus, D.C.C. *Production of Bio-coal and Activated Carbon from Biomass*. Ph.D Thesis. The University Of Western Ontario. P.D; 2013.
- Cecen, F., Aktas, O. (2011). *Integration of activated carbon adsorption and biological process in wastewater treatment, In activated carbon for water and wastewater*

treatment, Germany, WileyVCH Verlag GmbH.

- Chandane, V., Singh, V. K. (2014). Adsorption of safranin dye from aqueous solutions using a low cost agro waste material soya beana hull, *Desal. & Wastewater Treatment*, 57 (9), 1-13.
- Chen, Y., Zhai, S., Liu, N., Song, Y., An, Q, Song X. (2013). Dye removal of activated carbons prepared from NaOH-pretreated rice husks by low-temperature solution-processed carbonization and H₃PO₄ activation. *Bioresour. Technol.*, 144, 401–409.
- Cheung, W.H., Lau, S.S.Y. Leung, S.Y., Ip, A.W.M., McKay, G.(2012). Characteristics of Chemical Modified Activated Carbons from Bamboo Scaffolding. *Chinese J. Chem. Eng.*, 20(3), 515–523.
- Chun-Hisen H, Ruey-An HD (2012) Sugarcane bagasse as the scaffold for mass production of hierarchically porous carbon monoliths by surface self-assembly. *Micro Meso Mater.* 147, 47–52.
- Cooney, D. O. (1999). *Adsorption design for wastewater treatment*. U.S.A.: Lewis Publisher.
- Daniel, N.O., Chima, E.S. & Chinedu, M.T. (2014). Comparative study of the Bioadsorbtion of Cadmium and lead from industrial waste water using melon (*Citrullus colocynthis*) husk activated with sulphuric acid. *American J. Environ. Protection*, 3, 1–8.
- Danish, M., Hashim. R., Ibrahim, M.N.I., Rafatullah, M., Ahmad. T., Sulaiman, O. (2011). Characterization of Acacia Mangium wood based activated carbons prepared in the presence of basic activating agents. *Bioresour.*, 6(3), 3019–3033.
- Danish, M. Hashim, R., Ibrahim, M. N. M. (2013). Optimized preparation for large surface area activated carbon from date (*Phoenix dactylifera* L.) stone biomass. *Biomass and Bioenergy*, 35217(320), 2–13.
- Depci, T., Kul, A.R. & Önal, Y. (2012). Competitive adsorption of lead and zinc from aqueous solution on activated carbon prepared from Van apple pulp: Study in single- and multi-solute systems. *Chem. Eng. J.*, 200-202, 224–236.
- Department of Agricultural, Ministry of Agricultural. (2017). Retrieved on January, 2017 from http://www.data.gov.my/data/ms_MY/dataset/keluasan-dan-pengeluaran-tanaman
- Dermibas, A.(2008). Heavy metals adsorption onto agro-based waste materials: a

- review. *J. Hazard Mat.*, 157 (2-3), 220-209.
- Devi, M.M. & Manonmani, S. (2015). Removal of Hexavalent Chromium Ions from Aqueous Solution by Adsorption Using Activated Carbon Prepared from Cucumis Melo Peel Activated carbon. *Oriental J. Chem.*, 31(1), 531–539.
- Díaz-Muñoz, L.L. Bonilla-Petriciolet, A., Reynel-Avila, H. E., Mendoza-Castillo, D.J. (2016). Sorption of heavy metal ions from aqueous solution using acid-treated avocado kernel seeds and its FTIR spectroscopy characterization. *Journal of Molecular Liquids*, 215, 555–564.
- Dong, L., Liu, W., Jiang, R., Wang, Z. (2014). Physicochemical and porosity characteristics of thermally regenerated activated carbon polluted with biological activated carbon process. *Bioresour. Technol.*, 171, 260–264.
- Drinan, J. E., Spellman, F.R. *Water and wastewater treatment: A guide for the nonengineering professional*. 2nd Ed. New York. CRC Press; 2013.
- Duran, C., Ozdes, D., Gundogdu, A., Imamoglu, M., Senturk, H. B. (2011). Tea-industry waste activated carbon, as a novel adsorbent, for separation, preconcentration and speciation of chromium. *Anal. Chim. Acta*, 688, 75-83.
- Eckenfelder, Jr. W. W., Ford, D. L., Englande, Jr., A. J. *Industrial water quality*. 4th Ed. USA. WEF Press ;2009.
- Ekpete, O.A. & Horsfall, M.J. (2011). Preparation and Characterization of Activated Carbon derived from Fluted Pumpkin Stem Waste (*Telfairia occidentalis* Hook F). *Res. J. Chem. Sci.*, 1(3), 10–17.
- El Zayat. M., Smith, E. (2013). Heavy metals removal from aqueous solution using activated carbon produced from cotton stalk, *Wat. Sci. & Technol.*, 67(7), 1612-1619.
- Foo, K.Y. & Hameed, B.H. (2012). Coconut husk derived activated carbon via microwave induced activation: Effects of activation agents, preparation parameters and adsorption performance. *Chem. Eng. J.*, 184, 57–65.
- Foo, K.Y. & Hameed, B.H. (2012) Preparation of activated carbon by microwave heating of langsat (*Lansium domesticum*) empty fruit bunch waste. *Bioresour. Technol.*, 116, 522–525.
- Fu, F. & Wang, Q. (2011). Removal of heavy metal ions from wastewaters: a review. *J.*

- Environ. Manage.*, 92(3), 407–18.
- Gautam, R.K., Mudhoo, A., Lofrano, G., Chattopadhyaya. (2014). Biomass-derived biosorbents for metal ions sequestration: Adsorbent modification and activation methods and adsorbent regeneration. *J. Environ.Chem. Eng.*, 2(1), 239–259.
- Ghorbani F, Sanati, A.M., Younesi, H., Ghoreyshi, A. A. (2012). The potential of date palm leaf ash as low-cost adsorbent for the removal of Pb(II) ion from aqueous solution, *Intern. J. Eng.*, 25(4), 269-278.
- Ghosh, P. K., Philip, L.(2005). Performance of evaluation of waste activated carbon on atrazine removal from contaminated water, *J. Environm. Health Part B*, 40 , 425-441.
- Giraldo, L. & Moreno-Pirajan, J.C. (2012). Synthesis of Activated Carbon Mesoporous from Coffee Waste and Its Application in Adsorption Zinc and Mercury Ions from Aqueous Solution. *E-J. Chem.*, 9(2), 938–949.
- Giwa, A.A.Bello, I. A., Oladipo, Adeoye, D.O. (2013). Removal of Cadmium from Waste - water by Adsorption Using the Husk of Melon (*Citrullus lanatus*) Seed 1. *Intern. J. Bas. Appl. Sci.*, 2(1), 110–123.
- Goertzen, K., Theriault, S. L., Oickle, A., Tarasuk, A.M., Andreas, H. (2010). Standardization of the Boehm titration. Part I. CO₂ expulsion and end pint determination, *Carbon*, 48-4), 1252-1262.
- Goldstein, J., Newbury, D. E., Joy, D. C., Lyman, C. E., Echlin, P., Sawyer, L., Micheal, J. R. (2003). *Scanning Electron Microscopy and X-ray Microanalysis*, 3rd Ed., US., Springer.
- Gonzalez, P.G. & Pliego-Cuervo, Y.B. (2014). Adsorption of Cd(II), Hg(II) and Zn(II) from aqueous solution using mesoporous activated carbon produced from *Bambusa vulgaris striata*. *Chem. Eng. Res. Design*, 92(11), 2715–2724.
- González-Domínguez, J.M., Fernandez-Gonzalez, Alexandre-Franco, M. (2011). The influence of the impregnation method on yield of activated carbon produced by H₃PO₄ activation. *Mat. Lett.*, 65(9), 1423–1426.
- Gottipati, R. *Preparation and Characterization of Microporous Activated Carbon from Biomass and its Application in the Removal of Chromium (VI) from Aqueous Phase*. Thesis Ph.D. National Institute of Technology, Rourkela, India; 2012.

- Gottipati R., Mishra, S. (2016). Preparation of microporous activated carbon from Aegle Marmelos fruit shell and its application in removal of chromium(IV) from aqueous phase. *J. Ind. Eng. Chem.*, 36, 355-363.
- Gundogdu, A., Duran, C., Senturk, H. B., Soylak, M. (2013). Physicochemical characteristics of a novel activated carbon produced from tea industry waste. *J. Anal. Appl. Pyrolysis*, 104, 249–259.
- Guo, W., Ngo, H.H. & Liu, C. (2012). Watermelon Rind: Agro-waste or Superior Biosorbent, *Appl. Biochem. Biotechnol.*, 167(6), 1699–1715.
- Guo, Y., Rockstraw, D. A. (2007). Physical properties of carbons prepared from pecan shell by phosphoric acid activation, *Bioresour. Technol.*, 98(1513-1521).
- Gupta, V.K., Nayak, A., Bhushan, B., Agarwal, S. (2014). A Critical Analysis on the Efficiency of Activated Carbons from Low-Cost Precursors for Heavy Metals Remediation. *Crit. Rev. Env. Sci. Technol.*, 45(6), 613–668.
- Haro, M., Andrade, M., Mestre, A.S., Parra, J.B., Carvalho, A.P., Ania, C.O. (2012). Dual role of copper on the reactivity of activated carbons from coal and lignocellulosic precursors. *Microporous and Mesoporous Mat.*, 154, 68–73.
- Hadoun, H., Sadaoui, Z., Souami, N., Sahel, D., Toumert, I.(2013). Characterization of mesoporous carbon prepared from date stems by H₃PO₄ chemical activation. *App. Surf. Sci.*, 280, 1-7.
- Hashim, M.A., Mukhopadhyay, S., Sahu, J. N., Sengupta, B. (2011). Remediation technologies for heavy metal contaminated groundwater. *J. Environ. Manage.*, 92(10), 2355–2388.
- Hashemian, S., Salari, K., Yazdi, Z. A. (2014). Preparation of activated carbon from agricultural waste (alond shell and orange peel) for adsorption of 2-pic from aqueous solution, *J. Ind. Eng. Chem.*, 20, 1892-1900.
- Hayashi, J., Kazehaya, A., Muroyama, K., Paul Watkinson, A. (2000). Preparation of activated carbon from lignin by chemical activation. *Carbon*, 38, 1873-1878.
- Hazourli, S., Ziati, M., Hazourli, A.(2009). Characterization of activated carbon prepared from lignocellulosic natural residue:-Example of date stone, *Phy. Proc.* 2, 1039-1043.
- Hernández-Montoya, V., Mendoza-CastilloBonilla-Petriciolet, A. (2011). Role of the

- pericarp of *Carya illinoensis* as biosorbent and as precursor of activated carbon for the removal of lead and acid blue 25 in aqueous solutions. *J. Anal. Appl. Pyrolysis*, 92(1), 143–151.
- Hossain, M.A., Ngo, H.H., Gaa, W., Nguyen, T.V. (2012). Biosorption of Cu (II) from water by banana peel based biosorbent: experiments and models of adsorption and desorption. *J. Wat. Sustain.*, 2(1), 87–104.
- Hsi, H.-C., Horng, R., Pan, T., Lee, S. (2011). Preparation of Activated Carbons from Raw and Biotreated Agricultural Residues for Removal of Volatile Organic Compounds. *J. Air Waste Manage. Assoc.*, 61(5), 543–551.
- Huang, Y., Li, S., Linn, H., Chen, J. (2014). Fabrication and characterization of mesoporous activated carbon from *Lemna minor* using one-step H_3PO_4 activation for Pb(II) removal. *Appl. Surf. Sci.*, 317, 422–431.
- Hubbe, M.A., Hassan, S.H. & Ducoste, J.J. (2011). Cellulosic Substrate For Removal Of Pollutants From Aqueous Systems: A Review 1. Metals. *Bioresour.*, 6(2), 2161–2287.
- Húmpola, P., Odetti, H., Moreno-Pirajan, J. C., Giraldo, L. (2016). Activated carbons obtained from agro-industrial waste: textural analysis and adsorption environmental pollutants. *Adsorption*, 22(1), 23–31.
- Ibrahim, M.N.M., Ngah, W.S.W., Norliyaa, M.S., Daud, W.R.W. (2010). A novel agricultural waste adsorbent for the removal of lead (II) ions from aqueous solutions. *J. Hazard. Mat.*, 182(1-3), 377–85.
- Idris, S., Yisa, J., Muhammaed, N., Anyichukwu, C. 2013. Equilibrium and adsorption studies of Malachite Green onto melon seed shell activated carbon, *Intern., J. Mod. Chem.*, 4(2), 90-103).
- Ilhan, U. & Fuat, G., 2000. Adsorption of Some Heavy Metal Ions from Aqueous Solution by Activated Carbon and Comparison of Percent Adsorption Results of Activated Carbon with those of Some Other Adsorbents. *Turkish J. Chem.*, 24(3), 291–297.
- Isa, M.H. Kutty, S.R.M., Hussin, S.R.M., Daud, N. M., Malakhmad, A. (2012). Cadmium (Cd) Removal from Aqueous Solution Using Microwave. *Pertanika J. Sci. & Technol.*, 20(2), 339–346.

- Issabayeva, G., Aroua, M.K., Sulaiman, N.M.(2010). Study on palm shell activated carbon adsorption capacity to remove copper ions from aqueous solutions. *Desalination*, 262(1-3), 94–98.
- Jassim, A. N., Amlah, L. K., Ali, D. F., Aljabar, A. T., (2012). Preparation and characterization of activated carbon from Iraqi apricots stones, *Canadian J. Chem. Eng. & Technol.*, 3(3) 20. 60-65.
- Jun, T.Y., Arumugam, S.D., Latip, A.H.A., Abdullah, A. M., Latif, A.P. (2010). Effect of Activation Temperature and Heating Duration on Physical Characteristics of Activated Carbon Prepared from Agriculture Waste. *Environ. Asia*, 3, 143–148.
- Kaąomierczak, J., Nowicki, P., Pietrzak, R. (2013). Sorption properties of activated carbons obtained from corncobs by chemical and physical activation, *Adsorption*, 19(2-4), 273-281.
- Kalijadis, A.M., Vukcevic, A., Jovanovic, Z.M., Lausevic, A.V., Lausevic, M.D. (2011). Characterization of surface oxygen groups on different carbon materials by the Boehm method and temperature programmed desorption. *J. Serbian Chem. Soc.*, 76(5), 757–768.
- Kamaruddin, M., Yusoff, M. & Ahmad, M. (2011). Optimization of durian peel based activated carbon preparation conditions for ammoniacal nitrogen removal from semi-aerobic landfill leachate. *J. Sci. Ind. Res.*, 70, 554–560.
- Kanchi, S., Bisetty, K., Gopalakrishnan, K., Lin, C., Chin, T. (2014). Development of green energy waste activated carbon for removal of trivalent chromium: Equilibrium and kinetic modelling. *Sep. Sci. Technol.*, 49(4)513-522.
- Kaouah, F., Boumaza, S., Berrama, T., Trari, M. (2013). Preparation and characterization of activated carbon from wild olive cores (oleaster) by H₃PO₄ for the removal of Basic Red 46. *J. Clean. Prod.*, 54, 296–306.
- Karimi, K., Taherzadeh, M. J. (2016). A critical review on analysis method in pre-treatment of lignocellulose: Composition, imaging and crystallinity. *Bioresour. Technol.*, 200, 1080-1018.
- Karnib, M., Kabbani, A., Holail, H., Olama, Z. (2014). Heavy metals removal using activated carbon, silica and silica activated carbons composite. *Energy Procedia*, 50, 113-120.