

MODIFICATION OF BANANA STEM FIBERS FOR EFFICIENT MERCURY(II)  
ADSORPTION

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MODIFICATION OF BANANA STEM FIBERS FOR EFFICIENT MERCURY(II)  
ADSORPTION

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requirements for the award of the degree of  
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***For Mak and Abah,***

Thank you for always being there; your endless love, faith, and encouragement  
never fail to strengthen me

***To my beloved siblings, family and family-in laws,***

Your continuous helps, cares, motivations, and supports can never be repaid

***and specially for my husband, Eddie Zawira Nordin,***

Thank you for always standing next to me, lifting me up whenever I couldn't reach

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## ABSTRACT

The potential of banana stem fiber (BSF) and its modifications as a low cost adsorbent for Hg(II) adsorption was evaluated. In this study, three types of adsorbents were prepared; chemically treated BSFs, grafted BSFs and amine functionalized grafted BSFs. Chemically-treated BSFs were modified by HCl and NaOH pre-treatments. Grafted BSFs were prepared by grafting methacrylic acid (MAA) onto BSF using  $\beta$ -radiation, microwave-radiation and conventional chemical initiation grafting methods. Subsequently, the grafted BSF was further functionalized using three types of amine, namely ethylenediamine (EDA, primary amine), *N,N'*-methylenebisacrylamide (MBA, secondary amine) and triethylamine (TEA, tertiary amine). Prior to adsorption, all the adsorbents were activated *in vacuo* at 373 K. The adsorbents were characterized using X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy, nitrogen physisorption, thermogravimetric analysis (TGA), field emission scanning electron microscopy-energy dispersive X-ray (FESEM-EDX), electron spin resonance (ESR) spectroscopy and  $\text{pH}_{\text{zpc}}$ . Results of the study showed that HCl pre-treatment on BSF increased the cellulose accessibility, while activation process generated a large amount of structural defects on the BSF. Moreover, BSF grafted via  $\beta$ -radiation (BSF- $\beta$ ) was proved to have a higher grafting yield, which led to a higher Hg(II) adsorption capacity. In addition, the introduction of amines into BSF- $\beta$  significantly enhanced the Hg(II) uptake due to the stronger affinity towards Hg(II) ions. The functionalization of ethylenediamine onto BSF- $\beta$  (EDA-BSF) showed the highest Hg(II) adsorption capacity followed by MBA-BSF and TEA-BSF. These results indicate that the position of amine functional groups on BSF plays an important role in the adsorption process. Fitting of the adsorption data with the non-linear Langmuir isotherms produced the maximum adsorption capacity of 372, 484 and 843  $\text{mg g}^{-1}$  for activated BSF-HCl, BSF- $\beta$  and EDA-BSF, respectively. Besides, activation of BSF-HCl altered the activation energy from 3.5 to 76.9  $\text{kJ mol}^{-1}$ , which showed the increasing of Hg(II) chemisorption. On the other hand, the adsorption of Hg(II) onto BSF- $\beta$  and EDA-BSF were mainly via ion-exchange process, where their activation energy falls in the range of 13.7 to 19.2  $\text{kJ mol}^{-1}$ . It should be noted that BSF-HCl, BSF- $\beta$  and EDA-BSF adsorbents were effectively regenerated with 0.1 M HCl solution and exhibited good recyclability and reusability for a few cycles of Hg(II) adsorption. Furthermore, BSF- $\beta$  and EDA-BSF possessed an excellent adsorption capacity for cationic heavy metals ( $\text{Hg}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$ ), offering potential applications in the recovery of cationic heavy metals from multi-metal aqueous systems. This study demonstrates an inexpensive yet effective material such as BSF from agricultural waste, has a great potential as adsorbent for the removal and recovery of Hg(II) ions from aqueous solutions.

## ABSTRAK

Potensi serat batang pisang (BSF) dan pengubahsuaianya sebagai penjerap kos rendah untuk penjerapan Hg(II) telah dinilai. Dalam kajian ini, tiga jenis penjerap telah disediakan; BSF yang dirawat secara kimia, cangkukan BSF dan pemfungsian amina pada cangkukan BSF. BSF terawat secara kimia telah diubahsuaikan dengan pra-rawatan HCl dan NaOH. Cangkukan BSF telah disediakan dengan mencantumkan asid metakrilik (MAA) ke atas BSF menggunakan kaedah sinaran- $\beta$ , sinaran gelombang mikro dan pemulaan cantuman kimia konvensional. Kemudian, cangkukan BSF telah difungsikan selanjutnya dengan menggunakan tiga jenis amina, iaitu etilenadamina (EDA, amina primer), *N,N'*-metilenabisakarilamida (MBA, amina sekunder) dan trietilamina (TEA, amina tertier). Sebelum dilakukan penjerapan, kesemua penjerap telah diaktifkan *in vacuo* pada 373 K. Penjerap telah dicirikan menggunakan kaedah pembelauan sinar-X (XRD), spektroskopi inframerah transformasi Fourier (FTIR), fizijerapan nitrogen, analisis termogravimetri (TGA), mikroskopi elektron pengimbasan pancaran medan-penyebarkan tenaga sinar-X (FESEM-EDX), spektroskopi resonans putaran elektron (ESR) dan  $pH_{zpc}$ . Keputusan kajian menunjukkan bahawa pra-rawatan HCl ke atas BSF meningkatkan ketercapaian selulosa, manakala proses pengaktifan menghasilkan sejumlah besar kecacatan pada struktur BSF. Selain itu, BSF yang telah dicangkukkan melalui sinaran- $\beta$  (BSF- $\beta$ ) terbukti mempunyai hasil cangkukan yang lebih tinggi yang membawa kepada kapasiti penjerapan Hg(II) yang lebih tinggi. Tambahan lagi, kemasukan amina dalam BSF- $\beta$  meningkatkan pengambilan Hg(II) dengan ketara disebabkan oleh tarikan yang lebih kuat terhadap ion Hg(II). Pemfungsian etilenadamina ke atas BSF- $\beta$  (EDA-BSF) menunjukkan kapasiti penjerapan Hg(II) tertinggi diikuti oleh MBA-BSF dan TEA-BSF. Keputusan ini menandakan bahawa kedudukan kumpulan berfungsi amina di BSF memainkan peranan yang penting dalam proses penjerapan. Pemadanan data penjerapan menggunakan isoterma Langmuir bukan linear menghasilkan kapasiti penjerapan maksimum iaitu masing-masing 372, 484 dan 843 mg g<sup>-1</sup> untuk BSF-HCl yang diaktifkan, BSF- $\beta$  dan EDA-BSF. Selain itu, pengaktifan BSF-HCl mengubah tenaga pengaktifan dari 3.5 kepada 76.9 kJ mol<sup>-1</sup>, yang menunjukkan peningkatan pengkimierapan Hg(II). Sebaliknya, penjerapan Hg(II) pada BSF- $\beta$  dan EDA-BSF adalah tertumpu melalui proses pertukaran ion di mana tenaga pengaktifannya tergolong dalam lingkungan 13.7 hingga 19.2 kJ mol<sup>-1</sup>. Perlu diperhatikan bahawa penjerap BSF-HCl, BSF- $\beta$  dan EDA-BSF dapat dijanakan semula secara berkesan dengan menggunakan larutan HCl 0.1 M dan mempamerkan kitaran semula dan kebolegunaan yang baik untuk beberapa kitaran penjerapan Hg(II). Tambahan pula, BSF- $\beta$  dan EDA-BSF memiliki kebolehan penjerapan yang sangat baik untuk logam berat kationik (Hg<sup>2+</sup>, Pb<sup>2+</sup> dan Cd<sup>2+</sup>), yang menawarkan potensi penggunaan dalam pemulihan logam berat kationik dari sistem akueus berbilang logam. Kajian ini menunjukkan bahawa bahan yang murah lagi berkesan seperti BSF daripada sisa pertanian mempunyai potensi besar sebagai bahan penjerap bagi penyingkiran dan pemulihan Hg(II) dari larutan akueus.

## TABLE OF CONTENT

CHAPTER	TITLE	PAGE
	DECLARATION	ii
	DEDICATION	iii
	ACKNOWLEDGEMENT	iv
	ABSTRACT	v
	ABSTRAK	vi
	TABLE OF CONTENTS	vii
	LIST OF TABLES	xii
	LIST OF FIGURES	xiv
	LIST OF SCHEME	xviii
	LIST OF ABBREVIATIONS	xix
	LIST OF SYMBOLS	xxi
	LIST OF APPENDICES	xxiii
<b>1</b>	<b>INTRODUCTION</b>	<b>1</b>
	1.1 Research Background	1
	1.2 Problem Statement and Hypothesis	5
	1.3 Objectives of Study	7
	1.4 Scopes of Study	8
	1.5 Significance of Study	10
	1.6 Thesis Outline	11

<b>2</b>	<b>LITERATURE REVIEW</b>	<b>12</b>
	2.1 Overview of Mercury	12
	2.2 Treatment Technologies	14
	2.3 Adsorption	18
	2.4 Agricultural Waste Materials	19
	2.5 Cellulose Substrates	21
	2.6 Modification of Cellulose	23
	2.6.1 Direct Chemical Modification	24
	2.6.1.1 Esterification	24
	2.6.1.2 Halogenation	25
	2.6.1.3 Acidic Treatment	26
	2.6.2 Grafting Monomer	26
	2.6.2.1 Chemical Initiation Grafting	28
	2.6.2.2 Microwave Radiation Grafting	30
	2.6.2.3 Photochemical Grafting	30
	2.6.2.4 High Energy Radiation Grafting	31
	2.7 Subsequent Functionalization	32
	2.8 Mechanism of Adsorption	33
	2.9 Adsorption of Equilibrium	34
	2.9.1 Two Parameters Isotherm	35
	2.9.2 Three Parameters Isotherm	37
	2.10 Adsorption Kinetic Study	38
	2.10.1 Pseudo-First Order	39
	2.10.2 Pseudo-Second Order	40
	2.10.3 Intraparticle Diffusion	41
	2.11 Thermodynamic Study	42
<b>3</b>	<b>METHODOLOGY</b>	<b>45</b>
	3.1 Preface	45
	3.2 Chemicals, Materials and Instrumentations	47



3.3	Preparation of Adsorbents	48
3.3.1	Preparation of Treated BSF	49
3.3.2	Preparation of Grafted BSF	49
3.3.2.1	Grafting by $\beta$ -radiation method	49
3.3.2.2	Grafting by Microwave- Radiation Method	50
3.3.2.3	Grafting by Conventional Chemical Initiation Method	50
3.3.3	Preparation of Amine Functionalized on Grafted BSF	51
3.4	Characterization of Adsorbents	52
3.4.1	Determination of Cellulose, Hemicellulose and Lignin Contents	52
3.4.2	X-Ray Diffraction (XRD) Analysis	53
3.4.3	Fourier Transform Infrared (FTIR) Spectroscopy	53
3.4.4	Surface Area Analysis	54
3.4.5	Thermal Gravimetric Analysis (TGA)	54
3.4.6	Electron Spin Resonance (ESR) Spectroscopy	54
3.4.7	Field Emission Scanning Electron Microscopy-Energy Dispersive X-Ray (FESEM-EDX)	55
3.4.8	Determination of $\text{pH}_{\text{zpc}}$	55
3.5	Preparation of Metal Stock Solution	56
3.6	Adsorption of Hg(II) onto Adsorbents	56
3.6.1	Effect of pH	57
3.6.2	Isotherms Study	57
3.6.3	Kinetics Study	58
3.6.4	Thermodynamics Study	58

3.7	Reuse and Regeneration of Adsorbents	59
3.9	Adsorption of Hg(II) in Multi-Metals Aqueous System	59
<b>4</b>	<b>RESULTS AND DISCUSSION</b>	<b>61</b>
4.1	Preface	61
4.2	Preparation and Characterization of Adsorbents	61
4.2.1	Crystallinity, Phase and Structural Studies	62
4.2.2	Vibrational Spectroscopy	65
4.2.3	Study of Textural Properties	69
4.2.4	Thermal Properties	72
4.2.5	Surface Defects Determination	75
4.2.6	Topological Properties	78
4.2.7	Surface Charge of Adsorbents	80
4.3	Adsorption Studies	81
4.3.1	Effect of Chemical Pre-treatments on BSF	81
4.3.2	Effect of Grafting Modification Methods	82
4.3.3	Effect of Amine functionalization	86
4.3.4	Effect of pH	88
4.3.5	Equilibrium Isotherms Studies	90
4.3.6	Kinetics Studies	98
4.3.6	Thermodynamic Studies	102
4.4	Regeneration and Reusability Studies	107
4.5	Effect of Hg(II) Adsorption in the Presence of Other Metal Ions	110
<b>5</b>	<b>CONCLUSION</b>	<b>113</b>
5.1	Conclusion	113

5.2 Recommendations for Future Work	115
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<b>REFERENCES</b>	<b>116</b>
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Appendices A - B	134-136
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**LIST OF TABLES**

<b>TABLE NO.</b>	<b>TITLE</b>	<b>PAGES</b>
2.1	Treatment technologies for the removal of heavy metals and its advantages and disadvantages (O'Connel <i>et al.</i> , 2008)	17
2.2	Adsorption of Hg onto various agricultural waste adsorbents	20
3.1	List of chemicals	47
3.2	List of Instruments	48
3.3	List of adsorbents	48
4.1	Chemical composition of BSF-raw, BSF-NaOH and BSF-HCl	62
4.2	Peak area of C=O form Gaussian curve fitting	68
4.3	The textural properties of the BSF, grafted BSF and amine functionalized on grafted BSF adsorbents	71
4.4	Thermogravimetric data of BSF, grafted BSF and amine functionalized on grafted BSF	74
4.5	Isotherm parameters for Hg(II) adsorption onto BSF-HCl, BSF- $\beta_{40}$ and EDA-BSF	95
4.6	Comparison with other adsorbents	96
4.7	Parameters of kinetic and intraparticle diffusion study for the Hg(II) adsorption on activated BSF-HCl, BSF- $\beta_{40}$ and EDA-BSF at different temperatures	101

4.8	Thermodynamic parameters for the Hg(II) adsorption on activated BSF-HCl, BSF- $\beta_{40}$ and EDA-BSF at different temperatures	105
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## LIST OF FIGURES

FIGURE NO.	TITLE	PAGES
2.1	Schematic representation of cellulose structure	22
2.2	Schematic of goals of pretreatment on lignocellulosic material (Mosier <i>et al.</i> , 2005)	24
2.3	Methods for synthesis of graft copolymers (Kang <i>et al.</i> , 2015)	28
2.5	Plausible mechanism of adsorption (Sud <i>et al.</i> , 2008)	34
3.1	Research flow chart	46
3.2	Schematic procedure for the preparation of amine functionalized on grafted BSF	52
4.1	XRD patterns of (a) BSF-raw, (b) BSF-NaOH and (c) BSF-HCl	63
4.2	XRD patterns of (a) BSF-HCl, (b) BSF- $\beta$ , (c) BSF-MW, (d) BSF-C and (e) Hg loaded on BSF- $\beta$	64
4.3	XRD patterns of (a) BSF- $\beta$ , (b) EDA-BSF, (c) MBA-BSF, (d) TEA-BSF and (e) Hg-EDA-BSF	65
4.4	(A) FTIR spectra of (a) BSF-raw, (b) BSF-NaOH and (c) BSF-HCl and (B) FTIR spectra of (a) fresh BSF-HCl, (b) Hg adsorbed on fresh BSF-HCl, (c) activated BSF-HCl and (d) Hg adsorbed on activated BSF-HCl	66
4.5	FTIR spectra of (a) BSF-HCl, (b) BSF- $\beta$ , (c) BSF-MW, (d) BSF-C and (e) Hg loaded on BSF- $\beta$	67

4.6	Gaussian curve-fitting peaks of C=O for BSF based adsorbents	68
4.7	FTIR spectra of (a) BSF- $\beta$ , (b) EDA-BSF, (c) MBA-BSF, (d) TEA-BSF and (e) Hg-EDA-BSF	69
4.8	(A) N <sub>2</sub> adsorption-desorption isotherm and (B) pore size distribution of all adsorbents	70
4.9	TG curves of activated BSF-HCl and Hg-BSF-HCl	72
4.10	TG curves of BSF, BSF- $\beta$ , BSF-MW and BSF-C	73
4.11	TG curves of BSF- $\beta$ , EDA-BSF, MBA-BSF and TEA-BSF	75
4.12	ESR spectra of fresh BSF-HCl, activated BSF-HCl and Hg loaded on activated BSF-HCl	76
4.13	(A) ESR spectra of BSF based adsorbents and their (B) variations in the intensity of the ESR signal at $g=1.98$	77
4.14	ESR spectra of BSF- $\beta$ , EDA-BSF, MBA-BSF and TEA-BSF	78
4.15	FESEM images of (A) activated BSF-HCl, (B) BSF- $\beta$ , (C) EDA-BSF, (D) Hg adsorbed on activated BSF-HCl, (E) Hg adsorbed on BSF- $\beta$ and (F) Hg adsorbed on EDA-BSF	79
4.16	EDX analysis of Hg adsorbed on (A) activated BSF-HCl, (B) BSF- $\beta$ and (C) EDA-BSF	80
4.17	Isoelectric point ( $\text{pH}_{\text{zpc}}$ ) of (A) activated BSF-HCl, (B) BSF- $\beta_{40}$ and (C) EDA-BSF	81
4.18	Effect of pre-treatment and activation of BSF on the adsorption of Hg(II)	82
4.19	Effect of adsorbed dose of $\beta$ -radiation on the degree of grafting and Hg(II) adsorption capacity	84
4.20	Effect of microwave power on the degree of grafting and Hg(II) adsorption capacity	85

4.21	Effect of chemical initiator concentration on the degree of grafting and Hg(II) adsorption capacity	86
4.22	Effect of different amine precursors on Hg(II) adsorption	87
4.23	Effect of EDA concentration on Hg(II) adsorption	88
4.24	Effect of pH on Hg(II) adsorption onto (A) activated BSF-HCl, (B) BSF- $\beta_{40}$ and (C) EDA-BSF	89
4.25	Non-linear plots of isotherm models for Hg(II) adsorption onto (A) fresh BSF-HCl and (B) activated BSF-HCl	91
4.26	Non-linear plots of isotherm models for Hg(II) adsorption onto (A) BSF- $\beta_{40}$ and (B) EDA-BSF	94
4.27	Non-linear plots of kinetics models for Hg(II) adsorption onto (A) activated BSF-HCl, (B) BSF- $\beta_{40}$ and (C) EDA-BSF	99
4.28	Intra-particle diffusion model for Hg(II) adsorption onto (A) activated BSF-HCl, (B) BSF- $\beta_{40}$ and (C) EDA-BSF	100
4.29	Plot of $\ln K_c$ versus $1/T$ for estimation of thermodynamic parameters for the adsorption of Hg(II) onto (A) fresh BSF-HCl, (B) activated BSF-HCl, (C) BSF- $\beta_{40}$ and (D) EDA-BSF	103
4.30	Plot of $\ln k$ versus $1/T$ for estimation of activation energy for the adsorption of Hg(II) onto (A) fresh BSF-HCl, (B) activated BSF-HCl, (C) BSF- $\beta_{40}$ and (D) EDA-BSF	106
4.31	Regeneration of activated BSF-HCl for Hg(II) adsorption	108
4.32	(A) Regeneration of BSF- $\beta_{40}$ for Hg(II) adsorption and (B) FTIR spectra for (a) BSF- $\beta_{40}$ , (b) Hg loaded on	109



	BSF- $\beta_{40}$ , (c) BSF- $\beta_{40}$ after desorbed and (d) Hg loaded on BSF- $\beta_{40}$ after six cycles	
4.33	Regeneration of EDA-BSF for Hg(II) adsorption	110
4.34	Performance of BSF- $\beta_{40}$ for various heavy metal pollutants in single, binary and quaternary mixtures	111
4.35	Performance of EDA-BSF, MBA-BSF and TEA-BSF on single (pattern bar) and multi-metals (solid bar) aqueous systems	112

**LIST OF SCHEME**

<b>SCHEME NO.</b>	<b>TITLE</b>	<b>PAGES</b>
2.1	A simplified mechanism for the graft polymerisation of cellulose in the presence of $K_2S_2O_8$ as a free radical polymerisation catalyst (Roy <i>et al.</i> , 2008)	29

**LIST OF ABBREVIATIONS**

BET	-	Brunauer Emmet Teller
BJH	-	Barrett, Joyner, and Halenda
BSF	-	Banana Stem Fibers
BSF-C	-	Grafted BSF by Conventional Chemical Initiation Method
BSF-HCl	-	BSF treated with Hydrochloric Acid
BSF-MW	-	Grafted BSF by Microwave-Radiation Method
BSF-NaOH	-	BSF treated with Sodium Hydroxide
BSF- $\beta$	-	Grafted BSF by $\beta$ -Radiation Induced Method
Cd	-	Cadmium
DG	-	Degree of Grafting
EDA	-	Ethylenediamine
EDA-BSF	-	Functionalization of EDA on BSF- $\beta$
EDX	-	Energy Dispersive X-Ray
ESR	-	Electron Spin Resonance
FESEM	-	Field Emission Scanning Electron Microscopy
FG	-	Functional Groups
FTIR	-	Fourier Transform Infrared
FDT	-	Final Decomposition Temperature
Hg	-	Mercury
IDT	-	Initial Decomposition Temperature
IPA	-	Isopropyl Alcohol
IUPAC	-	International Union of Pure and Applied Chemistry
MAA	-	Methacrylic Acid
MBA	-	N,N-methylenebisacrylamide
MBA-BSF	-	Functionalization of MBA on BSF- $\beta$
MP-AES	-	Microwave Plasma-Atomic Emission Spectrometer
MPSD	-	Marquadt's Percent Standard Deviation

MW	-	Microwave
Pb	-	Lead
TEA	-	Triethylamine
TEA-BSF	-	Functionalization of TEA on BSF- $\beta$
TGA	-	Thermal Gravimetric Analysis
XRD	-	X-Ray Diffraction
ZPC	-	Zero Point of Charge

## LIST OF SYMBOLS

$\%G$	-	Grafting percentage
$A_{RP}$	-	Redlich-Peterson constant
$B_{RP}$	-	Redlich-Peterson constant
$C_e$	-	Concentration at equilibrium time ( $\text{mg L}^{-1}$ )
$C_f$	-	Final Concentration ( $\text{mg L}^{-1}$ )
$C_i$	-	Thickness of the boundary layer ( $\text{mg g}^{-1} \text{min}^{-1/2}$ )
$C_o$	-	Initial concentration ( $\text{mg L}^{-1}$ )
$C_t$	-	Concentration at time $t$ of reaction ( $\text{mg L}^{-1}$ )
$E_a$	-	Activation energy ( $\text{kJ mol}^{-1}$ )
$g$	-	Redlich-Peterson exponent
$k_1$	-	Pseudo-first order rate constant ( $\text{min}^{-1}$ )
$k_2$	-	Pseudo-second order rate constant ( $\text{g mg}^{-1} \text{min}^{-1}$ )
$K_F$	-	Freundlich constant ( $\text{L}^{1/n_F} \text{mg}^{(1-1/n_F)} \text{g}^{-1}$ )
$k_{id}$	-	intraparticle diffusion constant ( $\text{mg g}^{-1} \text{min}^{-1/2}$ )
$K_L$	-	Langmuir constant ( $\text{L mg}^{-1}$ )
$K_T$	-	Temkin constant
$M$	-	Molecular Weight ( $\text{g mol}^{-1}$ )
$n_F$	-	Heterogeneity factor
$\text{pH}_f$	-	Final pH
$\text{pH}_i$	-	Initial pH
$\text{pH}_{zpc}$	-	pH at Zero Point of Charge
$q_e$	-	Adsorption uptake at equilibrium conditions ( $\text{mg g}^{-1}$ )
$q_m$	-	Maximum adsorption capacity ( $\text{mg g}^{-1}$ )
$q_t$	-	Adsorption uptake at time $t$ ( $\text{mg g}^{-1}$ )
$R$	-	Gas constant ( $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ )
$R_L$	-	Dimensionless equilibrium constant
$T$	-	Absolute temperature (K)

$t$	-	Time (min)
$V$	-	Volume of solution (L)
$W_g$	-	Weight of grafted BSF (g)
$W_i$	-	Weight of ungrafted BSF (g)
$X_c$	-	Crystallinity index (%)
$\Delta G^\circ$	-	Gibbs free energy ( $\text{kJ mol}^{-1}$ )
$\Delta H^\circ$	-	Enthalpy ( $\text{kJ mol}^{-1}$ )
$\Delta S^\circ$	-	Entropy ( $\text{J mol}^{-1} \text{K}^{-1}$ )

**LIST OF APPENDICES**

<b>APPENDIX</b>	<b>TITLE</b>	<b>PAGES</b>
A	Standard calibration curves	134
B	List of publication and proceedings	136

## CHAPTER 1

### INTRODUCTION

#### 1.1 Research Background

Heavy metals are very toxic toward living organisms, even if only present in low concentration. This arises from their enormous potential to accumulate in the environment and in the food chain. Among those heavy elements mercury is the most toxic and non-biodegradable metal that brings no beneficial effects on human (Sun *et al.*, 2013; Syversen and Kaur, 2012). Mercury can be entered to the environment by several sources, resulting in contamination of atmospheric and aquatic systems. The presence of mercury in the aquatic environment is known to cause severe health problems in both animals and humans. Mercury and its compounds act as dangerous and insidious poisons, with the possibility of adsorption not only through the gastrointestinal tract but also through the skin and lungs. After adsorption, mercury circulates in the blood and is stored in the liver, kidneys, brain, spleen and bone, thereby leading to several health problems such as paralysis, serious intestinal and urinary complexations, and dysfunction of the central nervous system and, in more severe cases of intoxications, death. The soluble compounds of mercury are particularly toxic because their adsorption is very fast. Ingesting a dose of less than 0.5 g can prove to be fatal (Wajima *et al.*, 2011). Although mercury is being less and less used in process industry, its overall emissions are still a serious health hazard and in the last 20 years, anthropogenic sources were found to be comparable to natural sources, accounting for around 2000 tonnes per year. In the last 50 years, largest part of the mercury contamination arise from gaseous emissions of fossil fuel combustion, industrial processes (mainly chloro-alkali productions, pharmaceutical and cosmetic



preparations, electrical instruments) and municipal solid waste treatment plants (Ismail *et al.*, 2015; Wang *et al.*, 2004).

Mercury is included in the list of priority pollutants by all environmental agencies worldwide. To reduce mercury pollution phenomena in waters, severe environmental regulations were applied all over the world to define the maximum allowable concentration of mercury in liquid emissions. In the United States of America, the permitted discharge limit of wastewater for total mercury is  $10 \mu\text{g L}^{-1}$  and the limit for drinking water is  $2 \mu\text{g L}^{-1}$ . On the other hand, in Japan the established values are much more restrictive with corresponding limits of  $5 \mu\text{g L}^{-1}$  and  $0.5 \mu\text{g L}^{-1}$ , respectively. The World Health Organization (WHO) recommends a maximum uptake of 0.3 mg per week and  $1 \mu\text{g L}^{-1}$  as the maximum acceptable concentration of mercury in drinking water (Wajima *et al.*, 2011).

The conventional techniques for Hg(II) removal from wastewater include chemical precipitation (González-Muñoz *et al.*, 2006), solvent extraction (Deligöz *et al.*, 2008), membrane separation (Pejic *et al.*, 2009), ion-exchange (Oehmen *et al.*, 2014) and adsorption (Anirudhan *et al.*, 2008). Apart from being economically expensive, some of these techniques have disadvantages of incomplete metal removal, high reagent and energy requirements, and generation of toxic sludge or other waste products (Zhang *et al.*, 2010; Lisha *et al.*, 2008; Mangold *et al.*, 2014; Pejic *et al.*, 2009). Among these techniques, adsorption is the most useful and economical technique that has been widely used for the treatment of trace-Hg(II)-contaminated wastewater (Huang *et al.*, 2009). Adsorption is a well-known equilibrium separation process and an effective method for water decontamination applications and has been found to be superior to other techniques for water reuse in terms of initial cost, flexibility and simplicity of design, ease of operation and insensitivity to toxic pollutants. This technique also does not result in the formation of harmful substances and the organic sorbents can be used as fuel for power generation or as ferment substrate (Achak *et al.*, 2009).

A large number of different adsorbent materials containing a variety of attached chemical functional groups have been reported for this purpose. Activated

carbon, ion exchange resins and other adsorbents have been used for the adsorptive removal of Hg(II) from wastewater. Nonetheless, the cost and regeneration of adsorbents are the key factors influencing their application in practice, especially for the treatment of large volume of wastewater. So, it is necessary to develop low-cost, efficient and reusable adsorbents for the adsorptive removal of Hg(II). In general, an adsorbent is assumed to be 'low-cost' when it requires little processing, is abundant in nature or is a by-product or waste material from other industries. A wide range of adsorbent based on low cost agricultural by-products been used for removing Hg(II) from wastewaters which included rice straw (Rocha *et al.*, 2009), sugarcane bagasse (Hoi and Martincigh, 2013), coconut coir pith (Anirudhan *et al.*, 2008), saw dust (Meena *et al.*, 2008) and banana pith (Pillai *et al.*, 2013; Nada *et al.*, 2010). In recent years, lignocellulosic fibers have attracted the attention of many research groups that are considering their use for industrial purposes and the reinforcement of polymers. These fibers have many advantages compared to glass fibers, such as low density and low cost, and they are recyclable and biodegradable. Moreover, there is a high production of fibrous plants in tropical countries such as Malaysia and some of them, for instance, banana, are agricultural crops. The use of banana fibers is of particular interest because they originate from agricultural waste, being extracted from the pseudo stem which would be abandoned in the farming practice for natural decomposition after the harvesting of the fruits (Merlini *et al.*, 2011). Banana is one of the largest consumed fruit in the world and therefore, creates one of the major agro-waste problems.

Banana stem fiber (BSF) is principally composed of cellulose, hemicellulose and lignin (Gabhane *et al.*, 2014). These biopolymers have abundant and specific functional group such as hydroxyl (OH) groups (Liu *et al.*, 2006), which have affinities for heavy metal ions. The cellulosic surface becomes partially negatively charged when immersed in water and, therefore, possess coulombic interaction with cationic species in water (Laszlo and Dintzis 1994; McKay *et al.*, 1987; Weixing *et al.*, 1998). Although shown to be effective adsorbent for a wide range of solutes, particularly divalent metals cations, crop residues suffer from at least two major drawback: low exchange or sorption capacity, and poor physical stability (partial solubility) (Laszlo and Dintzis, 1994). In order to overcome these problems, chemical modification and/or

activation of the raw adsorbents are required (Kumar, 2013). Consequently, more active binding sites are provided, better ion-exchange properties are obtained, and new functional groups are formed. There is less report available on the chemical modification of banana stem to enhance the quality and acceptability of banana stem product. Previously, Anirudhan *et al.* (2007) synthesized a strong cation exchange resin which was fabricated through the hydrolysis of graft copolymer of banana stem (BS) with acrylonitrile for removal of Hg(II) from aqueous solution. However, the maximum adsorption capacity obtained is still low compared to other available adsorbent with 90.88 mg g<sup>-1</sup>.

One of the widely used methodologies for the preparation of adsorbent material is the graft polymerization technique followed by functionalization; resulting surface modification. Graft copolymerization is a well-established and commonly used technique for modification of polymer surface and it is an important tool in order to modify the physical or chemical properties of polymers (Wojnarovits *et al.*, 2010). In graft copolymer synthesis, there are various techniques that have been used to activate or initiate the backbone of cellulose polymer. Conventional chemical free radical initiators (Anirudhan and Shainy, 2015), high energy radiation (gamma rays or electron beam) (Goel *et al.*, 2015), UV rays in the presence of photo sensitizers or microwave radiation are used for this purpose (Kang *et al.*, 2015; Singh *et al.*, 2010). Conventional chemical free radical initiators essentially require an inert atmosphere and control of the percentage grafting and reproducibility is quite low (Mishra *et al.*, 2011). Microwave-based synthesis of graft copolymers has the inherent advantage of being fast, simple, highly reproducible and providing a great degree of control over percentage grafting. However, Mishra *et al.* (2011) reported that grafting reaction initiated by a combination of microwave radiation and conventional method will yield grafted products with a higher percentage of grafting. Thus, in the microwave-based synthesis method, it is also necessary to utilize a chemical free radical initiator to enhance the formation of radical sites on the backbone of cellulose. Among different innovative techniques used for the production of sorption-active materials, the application of economical and ecologically clean radiation technologies is now under the attention of researches. In particular, the utilization of the  $\beta$ -radiation-induced graft polymerization technique allows the inert polymeric matrix and the chains of a

monomer with desirable functional groups to be introduced, or the chains of a precursor-monomer to be grafted, which can be subsequently modified.

Further functionalization of various adsorbents for the removal of heavy metal ions from water or wastewater has attracted great research interest in recent years due to the advantages of achieving high efficiency and good selectivity. Among the various studies, amine-functionalized adsorbents are perhaps the most common, arising from the strong chelation properties of amine to heavy metals, specifically Hg ions due to stronger affinity toward Hg ions. Researchers have reported the functionalization of polymeric materials with amine-groups increased the chelation between metal ions and adsorbent surface, resulting in enhanced Hg(II) uptake (Ma *et al.*, 2009a; Ma *et al.*, 2009b; Atia *et al.*, 2007).

However, as the best to our knowledge, detailed studies on introduction of amine functional groups onto banana stem fibers via radiation method as well as their subsequent application to Hg(II) adsorption is still scanty. Therefore, the aim of this study is to prepare amine functionalized on grafted BSFs and to explore their feasibility for removal of Hg(II) ions from aqueous solution. Herein, we report the preparation of BSF by chemical treatment and activation process. The graft modification on treated BSF by several free radical generation methods was also performed. Then, further functionalization of grafted BSF with a series of amine functional groups was conducted to enhance the performance on adsorption of Hg(II). Lastly, the potential of the adsorbents on practical applications were studied.

## **1.2 Problem Statement and Hypothesis**

Mercury and its derivatives are considered as priority pollutants due to their neurological toxicity, volatility, persistence, and bioaccumulation through food chain, which pose a great threat to both human health and organism security (Miretzky and Cirelli, 2009). The main anthropogenic path way through which Hg(II) enters the water bodies is through wastes from industrial processes like chloralkali, paper and pulp, oil

refinery, mining, electroplating, paint, pharmaceutical and battery manufacturing. Consequently, removal of mercury ions from wastewaters is a very important issue. For this reason, various technological methods are available, including lime softening, chemical precipitation, coagulation, reverse osmosis, ion exchange and membrane filtration (Shamsijazeyi and Kaghazchi, 2010). However, the application of such processes is often restricted because of technical and/or economic constraints. Thus, among these techniques, adsorption is the most useful and economical technique that has been widely used for the treatment of heavy metals.

Activated carbon, ion exchange resins and other adsorbents have been used for the adsorptive removal of Hg(II) from wastewater. Nonetheless, the cost and regeneration of adsorbents are the key factors influencing their application in practice, especially for the treatment of large volume of wastewater. So, it is necessary to develop low-cost, efficient and reusable adsorbents for the adsorptive removal of Hg(II) (Huang *et al.*, 2009). Therefore, the search for a low-cost and easily available adsorbent has led to the investigation of materials of biological origin as potential metal adsorbents.

The low cost agricultural by product having lignocellulosic materials were found to have good adsorption capacity due to substances inherently associated with cellulose such as lignin, tannin and pectin, which contains polyphenolic and aliphatic hydroxyl groups (Demirbas *et al.*, 2008; Ngah and Hanafiah, 2008; Sud *et al.*, 2008). However, these materials have several disadvantages due to low exchange or sorption capacity, and poor physical stability (partial solubility). Thus, several chemical modifications have been thought in order to improve the physical and chemical properties and also increase the adsorption potential. Simple and inexpensive acids or bases treatment were commonly used to increase the capacity of lignocellulosic fibers to remove heavy metals. However, the adsorption capacity is still low and needs further modification to improve the exchange/sorption properties.

One of the widely used methodologies for the preparation of adsorbent material is the graft polymerization technique followed by functionalization process; resulting in surface modification. Combination of these techniques is possible for tuning the

chemical composition of the well-defined cellulosic copolymers by appropriately selecting the reactive agents for use in many emerging fields; especially in adsorption. Unfortunately, the detail studies on the introduction of amine functional groups onto treated BSF via radiation method as well as their subsequent application to Hg(II) adsorption is still scanty. Therefore, it is desirable to explore the effect of chemical and activation treatment on BSF, graft modification on treated BSF by several free radical generation methods and functionalization of grafted BSF with a series of amine functional groups, which play a significant roles in enhancing the Hg(II) adsorption capacity.

Amine functionalized on grafted BSF is expected to enhance adsorption activity in term of the adsorption capacity, rate of adsorption and its selectivity towards wide range of heavy metals. The chemical pre-treatment along with the activation process was estimated to increase cellulose accessibility and structural defect sites which will enhanced the Hg(II) adsorption capacity. The graft copolymerization of BSF with methacrylic acid (MAA); having  $-\text{COOH}$  functional groups, by using an environmental benign radiation-induced grafting process will transformed BSF into a high capacity and strong cationic polymeric adsorbent. Lastly, the functionalization with amine functional groups on the grafted BSF was expected to increase the chelation properties and selectivity due to the stronger affinity toward Hg ions.

### **1.3 Objectives of Study**

The objectives of this study are:

1. To prepare and characterize chemically treated banana stem fibers (BSF), grafted BSF and amine functionalized on grafted BSF adsorbents.
2. To determine the effect of chemical pre-treatment, grafting modification methods and amine functionalization on BSF towards their performance on Hg(II) adsorption.

3. To study the equilibrium isotherms, kinetics, and thermodynamics of all the adsorbents on Hg(II) adsorption.
4. To study the potential of adsorbents for practical application in wastewater treatment.

#### 1.4 Scopes of Study

The scope of this study consists of four parts, which are:

1. Preparation and characterization of banana stem fibers (BSF), grafted BSF and amine functionalized on grafted BSF adsorbents.

BSFs were prepared by chemical pre-treatment using acid and base media and were denoted as BSF-HCl and BSF-NaOH, respectively. Then BSF was copolymerized with MAA using various free radical generation methods ( $\beta$ -radiation, microwave-radiation and conventional chemical initiation which denoted as BSF- $\beta$ , BSF-MW and BSF-C, respectively). In  $\beta$ -radiation method, the irradiation dose used was 20 to 80 kGy (Dong *et al.*, 2016; Kaur *et al.*, 2013). Meanwhile in microwave-radiation method, the microwave power usage was in the range of 300 to 800 W (Likhita *et al.*, 2014; Kumar *et al.*, 2013). Lastly, for conventional chemical initiator, potassium peroxydisulphate ( $K_2S_2O_8$ ) was used and the concentration was varied from  $0.02 \times 10^{-2}$  to  $0.09 \times 10^{-2}$  mol L<sup>-1</sup> (Xing and Wang 2009; Liu and Sun, 2008; Donia *et al.*, 2012). Further functionalization of amine on grafted BSF were prepared by  $\beta$ -radiation grafting of MAA onto BSF, followed by functionalization with ethylenediamine (EDA-BSF, primary amine), *N,N'*-methylenebisacrylamide (MBA-BSF, secondary amine) and triethylamine (TEA-BSF, tertiary amine).

All the adsorbents were characterized using X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), N<sub>2</sub> physisorption, thermal gravimetric

analysis (TGA), Electron spin resonance (ESR) and field emission scanning electron microscopy with energy dispersive X-ray (FESEM/EDX). The functional and surface chemistry of the grafted fibers were analyzed.

2. Determination of the effect of chemical pre-treatment, grafting modification methods and amine functionalization on BSF towards the performance on Hg(II) adsorption.

The performances of all of the adsorbents were executed towards the adsorption of Hg(II) in aqueous solution. The adsorption process is carried out in a batch system under varying pH (2-11), contact time (5-300 min), initial Hg(II) concentration (5-200 mg L<sup>-1</sup>) and temperature (303-333 K). The range of pH used should be significant for the adsorption process. At low pH, low affinity for Hg(II) ions were anticipated, due to competition with H<sup>+</sup> ions for the active sites. However, at higher pH values, precipitation of Hg(II) were favorable (Gupta *et al.*, 2014). Anirudhan and Shainy (2015) conducted the Hg(II) adsorption for 240 min, whereas Sun *et al.* (2013) needed 480 min for the Hg(II) adsorption to reach equilibrium. The contact time was varied based on the type of adsorbent used. An initial Hg(II) concentration up to 500 mg L<sup>-1</sup> were used by Gupta *et al.* (2014). The adsorption data were then evaluated in the equilibrium isotherm studies. Generally, the temperature used were in the range of 303 to 333 K. Higher temperature values were not recommended due to high cost in adsorption process. Prior to adsorption, the adsorbents were activated (*vacuo* pre-treatment at 373 K). Microwave Plasma-Atomic Emission Spectrometer (MP-AES) was used to determine the level of Hg(II) content in the aqueous solution after treatment.

3. Study the isotherm, kinetic and thermodynamic behaviors of adsorbents on the adsorption of Hg(II).

The equilibrium data were analyzed using non-linear regression method of two- and three-parameter isotherm models in order to examine the relationship between adsorption and aqueous concentration at equilibrium. The two-parameter isotherm



models were Langmuir, Freundlich and Temkin; whereas the three-parameter model was Redlich-Peterson. In order to clarify the adsorption kinetics of Hg(II) onto the adsorbents, three conventional kinetic models, namely Lagergren pseudo-first order, Ho pseudo-second order and Weber and Morris Intraparticle diffusion models have been used. Lastly, the adsorption enthalpy ( $\Delta H^\circ$ ), entropy ( $\Delta S^\circ$ ) and Gibbs free energy ( $\Delta G^\circ$ ) were calculated using the thermodynamic functions. Activation energy ( $E_a$ ) was calculated based on the Arrhenius equation.

#### 4. Study the potential of adsorbents for practical application in wastewater.

The potential of the best adsorbent was studied for adsorption of multi-metal aqueous system which contained of four types of toxic heavy metals, including mercury, lead, cadmium and arsenic. For economic purpose, the reusability and regeneration of the adsorbents were investigated to indicate the robustness of the adsorbents towards the adsorption process.

### 1.5 Significance of Study

This study is conducted to prepare low cost based-adsorbents derived from banana stem fibers (BSF) for adsorption of Hg(II). The adsorbents were characterized and the adsorptive ability of the adsorbents were studied in details to elucidate the relationship of their physicochemical properties with the performance. Besides, the modification of BSF for further enhanced Hg(II) adsorption capacity was investigated. It is well known that BSF possesses abundant source of cellulose, which is prone to various chemical modifications. Thus, it is worth to explore the surface modification on BSF for efficient Hg(II) adsorption. From this study, efforts have been made to convert this agricultural waste into an inexpensive yet effective material for water treatment technologies.

## 1.6 Thesis outline

This thesis was divided into five chapters. In Chapter 1, an introduction is given about the toxicity of Hg(II) which caused severe problems to human and environment and the importance of heavy metals removal. The conventional removal techniques of Hg(II) were also mentioned. Besides that, the potential of low cost agricultural wastes as adsorbent was highlighted. The problem of the current research was stated to give the clear objectives of the present study, while the scopes of study cover the research work done to meet these objectives.

Chapter 2 which is the literature review covers the details on previous studies that have been done in order to get the clear view in the type of adsorbent used, modification of adsorbent and their adsorption ability towards heavy metals, especially Hg(II).

Chapter 3 or experimental methodology describes in details on the materials and chemical reagents used in the present work, the procedure for adsorbent preparation, characterization and adsorption studies which includes experimental setup and analysis calculation.

Chapter 4 discusses the experimental results performed in this study. First part explains the physicochemical properties of all adsorbents by XRD, N<sub>2</sub> physisorption, FTIR, TGA, FESEM-EDX and ESR. Next, their performances towards adsorption of Hg(II) were observed. In this section, the effect of pH, initial Hg(II) concentration and temperature were studied, in line with the equilibrium isotherm, kinetic and thermodynamic view of the adsorption. The last part is the regeneration study and the capability study of the adsorbents towards various heavy metals.

Finally, Chapter 5 consists of the conclusions about the study. The recommendation for future studies were also given in this final chapter.

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