UNIVERSITI PUTRA MALAYSIA

FABRICATION AND CHARACTERIZATION OF ION-IMPRINTED POLYMER FOR REMOVAL OF MERCURY

SITI KHADIJAH BT AB. RAHMAN

FS 2017 75

FABRICATION AND CHARACTERIZATION OF ION-IMPRINTED POLYMER FOR REMOVAL OF MERCURY

By

SITI KHADIJAH BT AB. RAHMAN

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfilment of the Requirements for the Degree of Doctor of Philosophy

May 2017

DEDICATION

To my lovely husband, Fardiyuz bin Abdul Mutalib, who has encouraged me all the way, and whose encouragement has made sure that I give it all it takes to finish my Ph.D. study in Universiti Putra Malaysia;

To my children Ahmad Asyraf and Ahmad Ameen, the symbol of love and giving. Both of you have been my best cheerleaders;

To my loving parents, family members and friends for their endless support;

To all the people in my life who touch my heart;

... I dedicate this research.

Thank you.
My love for you all can never be quantified. God bless you.

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirements for the degree of Doctor of Philosophy

FABRICATION AND CHARACTERIZATION OF ION IMPRINTED-POLYMER FOR REMOVAL OF MERCURY

By

SITI KHADIJAH BT AB. RAHMAN

May 2017

Chair : Professor Nor Azah Yusof, PhD
Faculty : Science

Mercury (Hg) is a natural trace component found in the petroleum reservoir. The presence of Hg is detrimental to petroleum production facilities as it forms corrosion induced through Hg amalgamates. Moreover, it has an effect on human beings if it is discharged into the waterways and atmosphere leading to severe, acute and chronic poisoning. Ion imprinted polymer (IIP) being one of the latest adsorbents which is alternative technique that is more selective and effective than the conventional removal method of Hg.

IIP is synthetic polymers having a predetermined selectivity for a template ion, which makes them ideal materials to be used in removal processes. In this study, the IIP was developed for the removal of Hg(II) ions from aqueous solutions and actual samples. The IIP particles and monoliths was prepared by thermal polymerization technique with Hg(II) as a template ions, [2-(methacryloyloxy)ethyl] trimethylammonium cysteine (MAETC) as a ligand, methacrylic acid (MAA) as a functional monomer, 2-hydroxyethyl methacrylate ethylene glycol (HEMA) as a co-monomer, dimethacrylamide (EGDMA) as a cross-linker, benzoyl peroxide (BPO) as an initiator and methanol or acetonitrile as a porogen. The IIP-20A monolith was selected as the best monolithic IIP due to its high adsorption capacity and good physical properties.

The prepared IIP-particle and all of the monolithic IIPs were characterized using Fourier transform infrared (FTIR), thermal gravimetric analysis (TGA), field emission scanning electron microscope (FESEM) and Brunauer Emmet-Teller (BET) for determining the polymerization and imprinting process occurred. In the down-flow technique of IIP-20A monolith, pH, dosage, initial concentration, reusability, selectivity and kinetic study were investigated.

Removal of Hg(II) of pH dependent was found maximum at pH 4.7. The removal percentage of Hg(II) increased with increasing of adsorbent dose and the total uptake of Hg(II) increased with increasing initial concentration of Hg(II) ions. The kinetic study of Hg(II) adsorption by IIP-20A monolith was fit well with Adam's Bohart model. The adsorbents have very good selectivity towards Hg(II) ions even in the presence of other metals (Pb(II), Cd(II), As(II) and Cr(III)) and can be reusable up to fifteen cycles.

The comparison of removal test of Hg(II) ions for up-flow column technique (pilot plant-scale) showed that the IIP-20A monolith having good adsorption capacities compared with IIP-particle (packed in a coffee filter). Other than that, the IIP-20A monolith has been successfully applied for the recovery of trace Hg(II) in actual samples (river water, wastewater and condensate).

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia
sebagai memenuhi keperluan untuk ijazah Doktor Falsafah

FABRIKASI DAN PENCIRIAN POLIMER CETAKAN ION UNTUK PENYINGKIRAN MERKURI

Oleh

SITI KHADIJAH BT AB. RAHMAN

Mei 2017

Pengerusi : Profesor Nor Azah Yusof, PhD
Fakulti : Sains

Mercury (Hg) adalah kesan komponen semulajadi yang terdapat dalam takungan petroleum. Kehadiran Hg mendatangkan keburukan dalam fasiliti penghasilan petroleum, kerana ia akan merangsang pembentukan hakisan melalui pencantuman Hg. Selain itu, ia mempunyai kesan ke atas manusia jika ia dilepaskan ke dalam laluan air dan atmosfera kerana membawa kepada keracunan yang amat teruk dan kronik. Polimer cetakan ion (IIP) ialah salah satu daripada penjerap terkini yang merupakan teknik alternatif yang lebih selektif dan berkesan jika di bandingkan dengan kaedah penyingkiran Hg yang konvensional.

IIP adalah polimer sintetik yang mempunyai selektiviti terhadap ion tertentu. Justeru, ia menjadikan IIP sebagai bahan yang ideal untuk digunakan dalam proses penyingkiran. Dalam kajian ini, IIP telah dikembangkan bagi penyingkiran Hg(II) ion dari larutan akueus dan sampel sebenar. IIP dalam bentuk serbuk dan monolit telah disintesis menggunakan teknik pempolimeran haba dengan menggunakan Hg(II) ion sebagai acuan, [2- (metakriloiloksi) etil] trimetilammonium cysteine (MAETC) sebagai ligan, asid metakrilik (MAA) sebagai monomer berfungsi, 2-hidrosietil metakrilat etilena glikol (HEMA) sebagai monomer-bersama, etilena glikol dimetakrilat (EGDMA) sebagai penggabung, benzoil peroksida (BPO) sebagai pemula dan metanol atau asetonitril sebagai *porogen.* IIP-20A monolit telah dipilih sebagai polimer monolitik yang terbaik kerana kapasiti penjerapannya yang tinggi dan sifat-sifat fizikalnya yang baik.

IIP dalam bentuk serbuk dan monolit yang telah dihasilkan telah dicirikan menggunakan Fourier inframerah (FTIR), analisis terma gravimetrik (TGA), medan pengimbas mikroskopi elektron (FESEM) dan Brunauer Emmet-Teller (BET) bagi menentukan proses pempolimeran dan pencetakan ion itu telah berlaku. Dalam kajian menggunakan teknik aliran ke bawah bagi IIP-20A monolit, kajian bagi kesan pH, dos penjerap, kepekatan awal, kemampuan kitar semula, ujian selektiviti dan kinetik telah dikaji. Penyingkiran maksimum Hg(II) bagi kesan pH telah dicapai pada pH 4.7. Manakala, peratusan penyingkiran Hg(II) meningkat dengan peningkatan dos bahan penjerap dan penjerapan bagi ion Hg(II) meningkat dengan peningkatan kepekatan awal bagi ion Hg(II). Ujian kinetik bagi penjerapan Hg(II) oleh IIP-20A monolit adalah sesuai dengan model Adam's Bohart. Penjerap ini mempunyai selektiviti yang sangat baik kepada Hg (II) ion walaupun dengan kehadiran ion logam lain seperti Pb (II), Cd(II), As(II) dan Cr (III) dan penjerap ini juga boleh dikitar semula sehingga lima belas kali kitaran.

Perbandingan ujian penyingkiran Hg(II) bagi teknik kolum aliran ke atas menunjukkan bahawa IIP-20A monolit mempunyai kapasiti jerapan yang sangat baik berbanding dengan IIP-serbuk yang dibungkus dalam penapis kopi. Selain itu, IIP-20A monolit telah berjaya diaplikasikan bagi menyingkirkan Hg(II) dalam sampel yang sebenar (air sungai, air kumbahan dan kondensat).

ACKNOWLEDGEMENTS

All praise to Allah S.W.T. who has showered me with kindness and affection during the course of my study. His endless grace and love have provided me the strength to finish this study.

I would like to express my sincere gratitude to my main supervisor, Prof. Dr. Nor Azah Yusof for her continuous support, supervision, patience, motivation, invaluable guidance, and immense knowledge throughout the phase of my Ph.D. study. Her guidance has greatly helped me during the time of research and writing of this thesis. I could not have imagined having a better advisor and mentor for my Ph.D. study. Besides my main supervisor, I would like to thank my co-supervisors, Assoc. Prof. Dr. Abdul Halim Abdullah and Prof. Dr. Azni Idris for their encouragement, constructive comments, constant advice and useful suggestions.

I also would like to express my gratitude to all my lab mates for their help and support to finish my Ph.D. study. My special thanks to the staff of *Jabatan Kimia, Jabatan Sains Alam Sekitar, Jabatan Pengurusan Tanah, Institut Biosains* and *Institut Teknologi Maju* Universiti Putra Malaysia for their invaluable assistance, help, information, and co-operation. Last but not least, a special note of appreciation is extended to Ministry of Higher Education (MOHE) for their fully financial support in the form of My Brain15 (My Phd).

This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfilment of the requirement for the degree of Doctor of Philosophy. The members of the Supervisory Committee were as follows:

Nor Azah bt Yusof, PhD
Professor
Faculty of Science
Universiti Putra Malaysia
(Chairman)

Abdul Halim bin Abdullah, PhD
Associate Professor
Faculty of Science
Universiti Putra Malaysia
(Member)

Azni bin Idris, PhD
Professor
Faculty of Engineering
Universiti Putra Malaysia
(Member)

ROBIAH BINTI YUNUS, PhD
Professor and Dean
School of Graduate Studies
Universiti Putra Malaysia

Date:

Declaration by Members of Supervisory Committee

This is to confirm that:

- the research conducted and the writing of this thesis was under our supervision;
- supervision responsibilities as stated in the Universiti Putra Malaysia (Graduate Studies) Rules 2003 (Revision 2012-2013) are adhered to.

Signature: ____________________________
Name of Chairman of Supervisory Committee: Prof. Dr. Nor Azah Bt Yusof

Signature: ____________________________
Name of Member of Supervisory Committee: Assoc. Prof. Dr. Abdul Halim Bin Abdullah

Signature: ____________________________
Name of Member of Supervisory Committee: Prof. Dr. Azni Bin Idris

TABLE OF CONTENTS

3 MATERIALS AND METHODS

4 RESULTS AND DISCUSSION

5 CONCLUSION AND RECOMMENDATIONS

LIST OF TABLES

LIST OF FIGURES

LIST OF SCHEMES

LIST OF ABBREVIATIONS

AC	Activated carbon
AFS	Atomic fluorescence spectrometry
BET	Brunauer Emmett Teller
BJH	Barret-Joyner-Halenda
CNTs	Carbon nano-tubes
CP	Control polymer
CVAAS	Cold vapor atomic absorption spectrometry
DTG	Differential thermogravimetric analysis
FAAS-CVAAS	Flame atomic absorption spectrometric-Cold vapor atomic absorption spectrometry
FESEM	Field emission scanning electron microscope
FTIR	Fourier transform infrared
HPLC	High performance liquid chromatography
ICP-AES	Inductively coupled plasma- atomic emission spectroscopy
ICP-MS	Inductively coupled plasma- mass spectroscopy
ICP-OES	Inductively coupled plasma- optical emission spectroscopy
IIP	Ion imprinted polymer
IIP-10A	Ion imprinted polymer monolith - 10 mL of acetonitrile
IIP-10M	Ion imprinted polymer monolith -10 mL of methanol
IIP-20A	Ion imprinted polymer monolith - 20 mL of acetonitrile
IIP-20M	Ion imprinted polymer monolith -20 mL of methanol
IIP-30A	Ion imprinted polymer monolith - 30 mL of acetonitrile
IIP-30M	Ion imprinted polymer monolith -30 mL of methanol
IIP-5A	Ion imprinted polymer monolith - 5 mL of acetonitrile
IIP-5M	Ion imprinted polymer monolith -5 mL of methanol
IIP-monolith	Ion imprinted polymer monolith
IIP-particle	Ion imprinted polymer particle
IIP-WP	Ion imprinted polymer monolith – without porogen
LNG	Liquefied natural gas
MAC	N-Methacrylol- (L)-cysteine
MAETC	[2-(Methacryloyloxy)ethyl] trimethylammonium cysteine
MBT	2-mercaptobenzothiazole
MIIP	Metal ion imprinted polymer
MIONPs	Magnetic iron oxide nanoparticles
MIPs	Molecularly imprinted polymers
MOTAC	Methacryloyl(oxyethyl)trimethyl ammonium chloride
MRS	Mercury removal systems
MRU	Mercury removal unit
MSS-AC	Mango seeds shells-activated carbon
MWCNTs	Multi-walled carbon nanotubes
NIPs	Non imprinted polymers
NMOs	Nanosized metal oxides
PEG	Polyethylene glycol
PEI	Poly(ethyleneimine)

PHEMA	Poly(2-hydroxyethylmethacrylate)
ppb	Part per billion
ppm	Part per million
ppt	Part per trillion
PVP	Polyvinylpyrrolidone
SE	Southeast
SPE	Solid phase extraction
TAR	4-(2-thiazolylazo) resorcinol
TGA	Thermal gravimetric analysis
UATR	Universal attenuated total reflectance
VGAAAS- GTA-AAS	Vapour generation accessory-atomic absorption spectrometer-76 -graphite tube atomizer-atomic Absorption spectrometer- 96
WHO	World health organization

CHAPTER 1

INTRODUCTION

1.1 Background of Research

Mercury (Hg) is considered as a global pollutant due to its toxicity, persistence, long range of transport potential and bioaccumulation (Yun *et al.,* 2013). Emission and distribution of Hg to the environment can occur from natural, anthropogenic and re-emitted sources (Zheng *et al.,* 2012, Wang *et al.,* 2012). Petrochemical industries (Gaulier *et al.,* 2015), urban discharges, agricultural materials, mining and coal combustion, industrial discharges (Rodríguez *et al.,* 2012), metal refining and manufacturing and chloralkali production (Wang *et al.,* 2012) are the principal anthropogenic sources of Hg pollution in the environment.

Petroleum is one of the most important energy sources for the modern society, along with the raw material form any industrial products such as chemical fertilizer, plastics and more (Yun *et al.,* 2013). Hg is a natural contaminant commonly found as traces in all fossil fuels including natural gas, gas condensates, crude oil, coal, tar sands and other bitumens that are processed in the petrochemical industries (Gaulier *et al.,* 2015, de Jesus *et al.,* 2013). A total of approximately 2000 tons per year of Hg are estimated to be released from petrochemical industries (fossil fuel combustion) and metal production combined. For instance, natural gas and liquid production frequently generate hydrocarbon streams containing trace levels of Hg, especially in Southeast (SE) Asia where Hg concentration can reach up to 1200 µg/L (wt) which is the highest value in the world (Sainal *et al.,* 2007). Table 1.1 shows the hydrocarbons from different geological locations containing Hg in microgram levels. The values shown are estimations and may change from time to time, depending on geological factors and production practices (Sainal *et al.,* 2007).

The effects of Hg in feeds on processing systems include equipment degradation, toxic waste generation, and poisoning of catalysts, which all tend to reduce the quality of the final products and increase the risk to the health and safety of the workers (Wilhelm and Bloom, 2000). Besides that, in the production of offshore oil and gas, water becomes contaminated with elemental, organic and inorganic Hg. The amount of components that are exposed to the environment increases with the volume of wastewater, condensate and produced water due to high petroleum demand and maturity of oil and gas wells. The wastewater, condensate and produced water shall be treated before being discharged to the environment or re-injected into the original reservoir, depending on its quality and environmental constraints (Chaturabul *et al.,* 2015).

Table 1.1: Estimated world levels of mercury in natural gas and liquids

Location	Mercury Concentration	
	Gas (µg/m^3)	Liquid (µg/L)
Europe	100-150	-
South America	50-120	50-100
Gulf of Mexico (USA)	0.02-0.4	-
Overthrust Belt (USA)	5-15	1-5
Africa	80-100	500-1000
North Africa	50-80	20-50
Indonesia	200-300	10-500
Gulf of Thailand	100-400	400-1200
Malaysia	1-200	10-100

The toxic contaminants from these activities can enter into the environmental cycle and food chains easily, through emission during processing stages or unregulated disposal of wastes or accidents (Sainal *et al.,* 2007). When Hg(II) solution is deposited in the sea, lakes or streams, the anaerobic bacteria convert it into methyl-mercury (CH_3Hg^+) (Wilcox *et al.,* 2012). The toxicity of CH_3Hg^+ is associated with its bioaccumulation in the fish, which then enters the food chain, thereby influencing human health (Wilcox *et al.,* 2012, Rodríguez *et al.,* 2012). Symptoms of Hg poisoning can be numerous and may occur either rapidly or over long periods of time. High exposures of elemental Hg can cause kidney malfunction, respiratory failure, and death (Ganjali *et al.,* 2011). According to the World Health Organization (WHO) guideline values, the limitation of Hg inside water is 1µg/L for the total Hg and 1µg/kg Hg in the air. In addition, WHO estimated a tolerable concentration of 0.2 µg/kg for long-term inhalation exposure to elemental Hg vapour and a tolerable intake of a total Hg of 2 µg/kg body weights per day (WHO, 2007).

From the above considerations, it has been proven that the removal of Hg(II) from actual samples is very important to protect the people and the environment. Various available commercial methods are available in petrochemical industries for mercury removal systems (MRS) in hydrocarbon streams such as impregnated activated carbon, adsorption on activated carbon by amalgamation with a metal (such as silver impregnated alumina, silver zeolites, metal sulphides, gold and metal oxides) (UK Essays, 2015), ion-exchange resin material, membrane filtration, electrochemical treatment technologies (Fu and Wang, 2011, Purkayastha *et al.,* 2014), sulphur-containing molecular sieve, and ionic salt containing activated carbon (Sainal *et al.,* 2007). However, these available commercial methods have several advantages and disadvantages. For instance, chemisorption on sulphur impregnated activated carbon is cheap and mostly used in the oil and gas industry. However, it has some disadvantages such as disposal problems when the adsorbent is contaminated with Hg and it is not efficient when treating hydrocarbon gas with the moisture content of more than 50% because the moisture can be adsorbed into the pore spaces of the activated carbon. Other than that, adsorption by amalgamation with a metal such as silver and gold has a high removal capacity of Hg but this adsorbent is very expensive (UK Essays, 2015).

For these reasons, the basic requirements for a successful MRS are the economics of the process and the removal medium needs to be capable of reducing Hg concentrations to extremely low and acceptable levels. Besides that, the selection of the MRS has been done as per the following criteria and considerations such as proven and reliable technology, process effectiveness for the removal of Hg, stable and robust (physically and chemically), has the ability to integrate with existing facilities (minimal modification to the existing facilities), and the removal agent should be inexpensive and easy to get (Sainal *et al.,* 2007).

1.2 Problem Statement

Mercury removal systems (MRS) for both gas and processed liquid hydrocarbon streams are commercially available. The available MRS deals excellently with gas hydrocarbon because natural gases are normally present as elemental Hg at a bulk concentration. However, the conventional MRS for hydrocarbon liquid or hydrocarbon waste (such as produced water, wastewater and condensate) has not selective to target ion and may still render high Hg(II) content in the hydrocarbon waste above the environmental discharge limit (not greater than 0.005 mg/L).

Nowadays, the ion imprinted polymer (IIP) which is a suitable method for the removal of Hg(II) in actual sample due to high sample load capacity, high selectivity to target ion, easy preparation and reusable in repeated cycles. Generally, many IIP for the removal of Hg(II) from previous researchers were prepared IIP in particles formed. Unfortunately, when IIP in particles formed packed in the column it will increase the pressure of column, slow water transport and increase of risk of bubble formation. Therefore, IIP-particle packed column is not suitable to commercialize and apply to the industrial column.

In view of this, the suitable physical of the IIP was proposed as an alternative approach that to overcome the disadvantages and weaknesses of the conventional IIP-particle packed column. The present work proposes the determination of the performance of IIP for the removal of Hg(II) ions in aqueous solution and actual samples. Here, we scaled up the preparation of IIP in particles and monoliths form by bulk radical polymerization using [2-(Methacryloyloxy)ethyl] trimethylammonium cysteine (MAETC) as the metal complexing monomer. The physical form of the IIP-particle was optimized using extruded, tableting and packaging techniques for improving the pressure of column, and decreasing the risk of bubble formation in the column. The performances of IIP towards Hg(II) ions from aqueous solution were determined using the batch and column technique. Mercury removal unit (MRU) which was designed as well as a mimic with the actual of the petrochemical industry set up was used in the column technique. Besides that, the application of the developed IIP in the recovery of Hg(II) ions from actual samples was also studied. The commercialization of IIP as sorbents in MRU is very promising, considering the reducing of Hg(II) ions concentrations to extremely low and acceptable levels that can be achieved.

1.3 Objectives of this Research

The general objective of this research is to prepare an ion imprinted polymer (IIP) for the efficient and selective removal of Hg.The following specific objectives are designed to achieve the general objective:

i. To scale-up and optimize the preparation of ion imprinted polymer (IIP).
ii. To obtain the suitable physical form of IIP
iii. To carry out spectroscopic, morphological and thermal stability for the prepared IIP.
iv. To determine the performance of IIP in the down-flow technique based on the pH, dosage, initial concentration, kinetic, reusability and selectivity study.
v. To determine the performance of IIP using the up-flow column technique based on pH, dosage and flow rate.
vi. To evaluate the performance of the IIP on the analysis of actual samples (wastewater, condensate (from oil and gas industry) and river water).

REFERENCES

Albroomi, H. I., Elsayed, M. A., Baraka, A., and Abdelmaged, M. A. (2017). Batch and fixed-bed adsorption of tartrazine azo-dye onto activated carbon prepared from apricot stones. *Applied Water Science*, 7(4), 2063-2074.

Alijani, H., Shariatinia, Z., and Mashhadi, A. A. (2015). Water assisted synthesis of MWCNTs over natural magnetic rock: An effective magnetic adsorbent with enhanced mercury (II) adsorption property. *Chemical Engineering Journal*, 281, 468-481.

Alizadeh, T., Ganjali, M. R., and Zare, M. (2011). Application of an Hg^{2+} selective imprinted polymer as a new modifying agent for the preparation of a novel highly selective and sensitive electrochemical sensor for the determination of ultratrace mercury ions. *Analytica Chimica Acta*, 689(1), 52-59.

Andaç, M., Mirel, S., Şenel, S., Say, R., Ersöz, A., and Denizli, A. (2007). Ion-imprinted beads for molecular recognition based mercury removal from human serum. *International Journal of Biological Macromolecules*, 40(2), 159-166.

Anirudhan, T. S., and Sreekumari, S. S. (2011). Adsorptive removal of heavy metal ions from industrial effluents using activated carbon derived from waste coconut buttons. *Journal of Environmental Sciences*, 23(12), 1989-1998.

Anirudhan, T. S., Divya, L., and Ramachandran, M. (2008). Mercury (II) removal from aqueous solutions and wastewaters using a novel cation exchanger derived from coconut coir pith and its recovery. *Journal of Hazardous Materials*, 157(2), 620-627.

Beng, Y.B. 2015. *Preparation and Evaluation of Aqueous Phase Molecularly Imprinted Polymers for Shikimic Acid*, Phd Thesis, Universiti Putra Malaysia.

Branger, C., Meouche, W., and Margaillan, A. (2013). Recent advances on ion-imprinted polymers. *Reactive and Functional Polymers*, 73(6), 859-875.

Büyüktiryaki, S., Say, R., Denizli, A., and Ersöz, A. (2007). Mimicking receptor for methylmercury preconcentration based on ion-imprinting. *Talanta*, 71(2), 699-705.

Cain, A., Vannela, R., and Woo, L. K. (2008). Cyanobacteria as a biosorbent for mercuric ion. *Bioresource Technology*, 99(14), 6578-6586.

Chaturabul, S., Srirachat, W., Wannachod, T., Ramakul, P., Pancharoen, U., and Kheawhom, S. (2015). Separation of mercury (II) from petroleum produced water via hollow fiber supported liquid membrane and mass transfer modeling. *Chemical Engineering Journal*, 265, 34-46.

Chaturabul, S., Wannachod, T., Leepipatpiboon, N., Pancharoen, U., and Kheawhom, S. (2015). Mass transfer resistance of simultaneous extraction and stripping of mercury (II) from petroleum produced water via HFSLM. *Journal of Industrial and Engineering Chemistry*, 21, 1020-1028.

Christian, G.D. (1994). *Analytical Chemistry*. 5th ed. USA: John Wiley and sons, Inc.

Common, A., Sauceau, M., Rodier, E., Letourneau, J. J., and Fages, J. (2015). Capillary rheometry of a binary mixture polymer/CO_2 in a single screw extruder. *Chemical Engineering and Processing: Process Intensification*, 93, 21-26.

Cormack, P. A., and Elorza, A. Z. (2004). Molecularly imprinted polymers: synthesis and characterisation. *Journal of Chromatography B*, 804(1), 173-182.

Dai, C., Zhang, J., Zhang, Y., Zhou, X., and Liu, S. (2013). Application of molecularly imprinted polymers to selective removal of clofibric acid from water. *PloS One*, 8(10), e78167.

Dakova, I., Karadjova, I., Georgieva, V., and Georgiev, G. (2009). Ion-imprinted polymethacrylic microbeads as new sorbent for preconcentration and speciation of mercury. *Talanta*, 78(2), 523-529.

de Jesus, A., Zmozinski, A. V., Vieira, M. A., Ribeiro, A. S., and da Silva, M. M. (2013). Determination of mercury in naphtha and petroleum condensate by photochemical vapor generation atomic absorption spectrometry. *Microchemical Journal*, 110, 227-232.

Dekhil, A.B., Hannachi, Y., Ghorbel, A. and Baubaker. (2011). Comparative study of the removal of cadmium from aqueos solution by low cost adsorbents. *Journal Environmental Science and Technology*. 4, 520-533.

DiNatale, F., Erto, A., Lancia, A., and Musmarra, D. (2011). Mercury adsorption on granular activated carbon in aqueous solutions containing nitrates and chlorides. *Journal of Hazardous Materials*, 192(3), 1842-1850.

dos Santos, V. C. G., Grassi, M. T., and Abate, G. (2015). Sorption of Hg (II) by modified K10 montmorillonite: influence of pH, ionic strength and the treatment with different cations. *Geoderma*, 237, 129-136.

Eitzlmayr, A., and Khinast, J. (2015). Co-rotating twin-screw extruders: Detailed analysis of conveying Elements based on smoothed particle Hydrodynamics. part 1: Hydrodynamics. *Chemical Engineering Science*, 134, 861-879.

El-Shafey, E. I. (2010). Removal of Zn (II) and Hg (II) from aqueous solution on a carbonaceous sorbent chemically prepared from rice husk. *Journal of Hazardous Materials*, 175(1), 319-327.

Ferreira, S. L., Lemos, V. A., Silva, L. O., Queiroz, A. F., Souza, A. S., da Silva, E. G., dos Santos, W.N., and das Virgens, C. F. (2015). Analytical strategies of sample preparation for the determination of mercury in food matrices-a review. *Microchemical Journal*, 121, 227-236.

Firouzzare, M., and Wang, Q. (2012). Synthesis and characterization of a high selective mercury (II)-imprinted polymer using novel aminothiol monomer. *Talanta*, 101, 261-266.

Fu, F., and Wang, Q. (2011). Removal of heavy metal ions from wastewaters: a review. *Journal of Environmental Management*, 92(3), 407-418.

Ganjali, M. R., Alizadeh, T., Azimi, F., Larjani, B., Faridbod, F., and Norouzi, P. (2011). Bio-mimetic ion imprinted polymer based potentiometric mercury sensor composed of nano-materials. *International. Journal Electrochemical Science,* 6(11), 5200-5208.

Gaulier, F., Gibert, A., Walls, D., Langford, M., Baker, S., Baudot, A., Porcheron, F., and Lienemann, C. P. (2015). Mercury speciation in liquid petroleum products: Comparison between on-site approach and lab measurement using size exclusion chromatography with high resolution inductively coupled plasma mass spectrometric detection (SEC-ICP-HR MS). *Fuel Processing Technology*, 131, 254-261.

González, P. G., and 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. *Chemical Engineering Research and Design*, 92(11), 2715-2724.

Gupta, A., Vidyarthi, S. R., and Sankararamakrishnan, N. (2014). Thiol functionalized sugarcane bagasse - A low cost adsorbent for mercury remediation from compact fluorescent bulbs and contaminated water streams. *Journal of Environmental Chemical Engineering*, 2(3), 1378-1385.

Hadi, P., To, M. H., Hui, C. W., Lin, C. S. K., and McKay, G. (2015). Aqueous mercury adsorption by activated carbons. *Water Research*, 73, 37-55.

Ho, Y. S., and Wang, C. C. (2008). Sorption equilibrium of mercury onto ground-up tree fern. *Journal of Hazardous Materials*, 156(1), 398-404.

Hu, Y., Pan, J., Zhang, K., Lian, H., and Li, G. (2013). Novel applications of molecularly-imprinted polymers in sample preparation. *TrAC Trends in Analytical Chemistry*, 43, 37-52.

Ismaiel, A. A., Aroua, M. K., and Yusoff, R. (2013). Palm shell activated carbon impregnated with task-specific ionic-liquids as a novel adsorbent for the removal of mercury from contaminated water. *Chemical Engineering Journal*, 225, 306-314.

Jing, T., Gao, X. D., Wang, P., Wang, Y., Lin, Y. F., Zhou, Y. K., and Mei, S. R. (2007). Preparation of high selective molecularly imprinted polymers for tetracycline by precipitation polymerization. *Chinese Chemical Letters*, 18(12), 1535-1538.

Khairi, N. A. S., Yusof, N. A., Abdullah, A. H., and Mohammad, F. (2015). Removal of Toxic Mercury from Petroleum Oil by Newly Synthesized Molecularly-Imprinted Polymer. *International Journal of Molecular Sciences*, 16(5), 10562-10577.

Khan, S. B., Lee, J. W., Marwani, H. M., Akhtar, K., Asiri, A. M., Seo, J., and Han, H. (2014). Polybenzimidazole hybrid membranes as a selective adsorbent of mercury. *Composites Part B: Engineering*, 56, 392-396.

Khoramzadeh, E., Nasernejad, B., and Halladj, R. (2013). Mercury biosorption from aqueous solutions by sugarcane bagasse. *Journal of the Taiwan Institute of Chemical Engineers,* 44(2), 266-269.

Khorrami, A. R., and Narouenezhad, E. (2011). Synthesis of molecularly imprinted monolithic fibers for solid-phase microextraction of acetaldehyde from head-space of beverages stored in PET bottles. *Talanta*, 86, 58-63.

Kolya, H., Das, S., and Tripathy, T. (2014). Synthesis of starch-g-poly-(N-methylacrylamide-co-acrylic acid) and its application for the removal of mercury (II) from aqueous solution by adsorption. *European Polymer Journal*, 58, 1-10.

Komiyama, M., Takeuchi, T., Mukawa, T. and Asanuma, H. (2003). *Molecular Imprinting From Fundamentals to Applications.* Weinheim: Wiley-VCH verlag GmbH & Co. KGaA.

Kyzas, G. Z., and Matis, K. A. (2015). Nanoadsorbents for pollutants removal: a review. *Journal of Molecular Liquids*, 203, 159-168.

Laatikainen, K., Udomsap, D., Siren, H., Brisset, H., Sainio, T., and Branger, C. (2015). Effect of template ion–ligand complex stoichiometry on selectivity of ion-imprinted polymers. *Talanta*, 134, 538-545.

Li, G., Shen, B., Wang, Y., Yue, S., Xi, Y., An, M., and Ren, K. (2015). Comparative study of element mercury removal by three bio-chars from various solid wastes. *Fuel*, 145, 189-195.

Li, H., and Li, D. (2015). Preparation of a pipette tip-based molecularly imprinted solid-phase microextraction monolith by epitope approach and its application for determination of enkephalins in human cerebrospinal fluid. *Journal of Pharmaceutical and Biomedical Analysis*, 115, 330-338.

Lin, Z., Lin, Y., Sun, X., Yang, H., Zhang, L., and Chen, G. (2013). One-pot preparation of a molecularly imprinted hybrid monolithic capillary column for selective recognition and capture of lysozyme. *Journal of Chromatography A*, 1284, 8-16.

Lin, Z., Yang, F., He, X., Zhao, X., and Zhang, Y. (2009). Preparation and evaluation of a macroporous molecularly imprinted hybrid silica monolithic column for recognition of proteins by high performance liquid chromatography. *Journal of Chromatography A*, 1216(49), 8612-8622.

Liu, Y., Chang, X., Yang, D., Guo, Y., and Meng, S. (2005). Highly selective determination of inorganic mercury (II) after preconcentration with Hg (II)-imprinted diazoaminobenzene–vinylpyridine copolymers. *Analytica Chimica Acta*, 538(1), 85-91.

Lorenzo, R. A., Carro, A. M., Alvarez-Lorenzo, C., and Concheiro, A. (2011). To remove or not to remove? The challenge of extracting the template to make the cavities available in molecularly imprinted polymers (MIPs). *International Journal of Molecular Sciences*, 12(7), 4327-4347.

Ma, C., Chen, H., Sun, N., Ye, Y., and Chen, H. (2012). Preparation of molecularly imprinted polymer monolith with an analogue of thiamphenicol and application to selective solid-phase microextraction. *Food Analytical Methods*, 5(6), 1267-1275.

McMurry, J. (2004). *Organic Chemistry*. 6th ed. USA: Brooks/cole-Thomson Learning, Inc.

Miretzky, P., and Cirelli, A. F. (2009). Hg (II) removal from water by chitosan and chitosan derivatives: a review. *Journal of Hazardous Materials*, 167(1), 10-23.

Mohan, D., and Pittman, C. U. (2006). Activated carbons and low cost adsorbents for remediation of tri-and hexavalent chromium from water. *Journal of Hazardous Materials*, 137(2), 762-811.

Mondal, D. K., Nandi, B. K., and Purkait, M. K. (2013). Removal of mercury (II) from aqueous solution using bamboo leaf powder: equilibrium, thermodynamic and kinetic studies. *Journal of Environmental Chemical Engineering*, 1(4), 891-898.

Munusamy, K., Somani, R. S., and Bajaj, H. C. (2015). Breakthrough adsorption studies of mixed gases on mango (Mangifera indicaL.) seed shell derived activated carbon extrudes. *Journal of Environmental Chemical Engineering*, 3(4), 2750-2759.

Namasivayam, C., and Sangeetha, D. (2006). Recycling of agricultural solid waste, coir pith: removal of anions, heavy metals, organics and dyes from water by adsorption onto $ZnCl_2$ activated coir pith carbon. *Journal of Hazardous Materials*, 135(1), 449-452.

Nema, T., Chan, E. C., and Ho, P. C. (2014). Applications of monolithic materials for sample preparation. *Journal of Pharmaceutical and Biomedical Analysis*, 87, 130-141.

Otero-Romaní, J., Moreda-Piñeiro, A., Bermejo-Barrera, P., and Martin-Esteban, A. (2008). Synthesis, characterization and evaluation of ionic-imprinted polymers for solid-phase extraction of nickel from seawater. *Analytica Chimica Acta*, 630(1), 1-9.

Pan, S., Shen, H., Xu, Q., Luo, J., and Hu, M. (2012). Surface mercapto engineered magnetic Fe_3O_4 nanoadsorbent for the removal of mercury from aqueous solutions. *Journal of Colloid and Interface Science*, 365(1), 204-212.

Parham, H., Zargar, B., and Shiralipour, R. (2012). Fast and efficient removal of mercury from water samples using magnetic iron oxide nanoparticles modified with 2-mercaptobenzothiazole. *Journal of Hazardous Materials*, 205, 94-100.

Pavia, Lampman and Kriz (2001). *Introduction Spectroscopy*. 3rd ed. USA: Brooks/cole-Thomson Learning, Inc.

Pelden, T., Thammaknet, C., Thavarungkul, P., and Kanatharana, P. (2014). Tea bag filter paper as a novel protective membrane for micro-solid phase extraction of butachlor in aqueous samples. *Journal of Environmental Science and Health, Part B*, 49(7), 480-490.

Pelden, T., Thammaknet, C., Thavarungkul, P., and Kanatharana, P. (2014). Tea bag filter paper as a novel protective membrane for micro-solid phase extraction of butachlor in aqueous samples. *Journal of Environmental Science and Health, Part B*, 49(7), 480-490.

Phothitontimongkol, T., Siebers, N., Sukpirom, N., and Unob, F. (2009). Preparation and characterization of novel organo-clay minerals for Hg (II) ions adsorption from aqueous solution. *Applied Clay Science*, 43(3), 343-349.

Pillay, K., Cukrowska, E. M., and Coville, N. J. (2013). Improved uptake of mercury by sulphur-containing carbon nanotubes. *Microchemical Journal*, 108, 124-130.

Praveena, S. M., De Burbure, C., Aris, A. Z., and Hashim, Z. (2013). Mini review of mercury contamination in environment and human with an emphasis on Malaysia: status and needs. *Reviews on Environmental Health*, 28(4), 195-202.

Purkayastha, D., Mishra, U., and Biswas, S. (2014). A comprehensive review on Cd (II) removal from aqueous solution. *Journal of Water Process Engineering*, 2, 105-128.

Ramstron, O. and Yan, M. 2005. *Molecularly Imprinted Materials: Science and Technology*. New York: Marcel Dekker.

Reddy, S., Das, P., Das, H., and Ghosh, A. (2011). MUPS (multiple unit pellet system) tablets-a brief review. *Journal of Pharmaceutical and Biomedical Sciences*, 12(12).

Rodríguez, O., Padilla, I., Tayibi, H., and López-Delgado, A. (2012). Concerns on liquid mercury and mercury-containing wastes: A review of the treatment technologies for the safe storage. *Journal of Environmental Management*, 101, 197-205.

Rodríguez-Reino, M. P., Rodríguez-Fernández, R., Peña-Vázquez, E., Domínguez-González, R., Bermejo-Barrera, P., and Moreda-Piñeiro, A. (2015). Mercury speciation in seawater by liquid chromatography-inductively coupled plasma-mass spectrometry following solid phase extraction pre-concentration by using an ionic imprinted polymer based on methyl-mercury-phenobarbital interaction. *Journal of Chromatography A*, 1391, 9-17.

Roushani, M., Abbasi, S., and Khani, H. (2015). Synthesis and application of ion-imprinted polymer nanoparticles for the extraction and preconcentration of mercury in water and food samples employing cold vapor atomic absorption spectrometry. *Environmental Monitoring and Assessment*, 187(9), 1-13.

Sainal, M. R., Shafawi, A., Mohamed, H., and Jabar, A. (2007). Mercury removal system for upstream application: experience in treating mercury from raw condensate. In *E&P Environmental and Safety Conference.* Society of Petroleum Engineers.

Saman, N., Johari, K., Song, S. T., Kong, H., Cheu, S. C., and Mat, H. (2016). High removal efficiency of Hg (II) and MeHg (II) from aqueous solution by coconut pith—Equilibrium, kinetic and mechanism analyses. *Journal of Environmental Chemical Engineering*, 4(2), 2487-2499.

Singh, D. K., and Mishra, S. (2010). Synthesis and characterization of Hg (II)-ion-imprinted polymer: Kinetic and isotherm studies. *Desalination*, 257(1), 177-183.

Suedee, R., Srichana, T., and Martin, G. P. (2000). Evaluation of matrices containing molecularly imprinted polymers in the enantioselective-controlled delivery of β-blockers. *Journal of Controlled Release*, 66(2), 135-147.

Sun, X., He, X., Zhang, Y., and Chen, L. (2009). Determination of tetracyclines in food samples by molecularly imprinted monolithic column coupling with high performance liquid chromatography. *Talanta*, 79(3), 926-934.

Svec, F. (2010). Porous polymer monoliths: amazingly wide variety of techniques enabling their preparation. *Journal of Chromatography A*, 1217(6), 902-924.

Svenson, J., and Nicholls, I. A. (2001). On the thermal and chemical stability of molecularly imprinted polymers. *Analytica Chimica Acta*, 435(1), 19-24.

Tamayo, F. G., Turiel, E., and Martín-Esteban, A. (2007). Molecularly imprinted polymers for solid-phase extraction and solid-phase microextraction: recent developments and future trends. *Journal of Chromatography A*, 1152(1), 32-40.

Tan, J., Jiang, Z. T., Li, R., and Yan, X. P. (2012). Molecularly-imprinted monoliths for sample treatment and separation. *TrAC Trends in Analytical Chemistry*, 39, 207-217.

TEPPFA. Production Processes. N.d. Retrieved 14 December 2016 from http://www.teppfa.eu/

Thakur, S., Kumari, S., Dogra, P., and Chauhan, G. S. (2014). A new guar gum-based adsorbent for the removal of Hg (II) from its aqueous solutions. Carbohydrate Polymers, 106, 276-282.

Tumin, N. D., Chuah, A. L., Zawani, Z., and Rashid, S. A. (2008). Adsorption of copper from aqueous solution by Elais Guineensis kernel activated carbon. *Journal of Engineering Science and Technology*, 3(2), 180-189.

UK Essays, 2015. Mercury Problems in Oil and Gas Industries Environmental Sciences Essay. https://www.ukessays.com/essays/environmental-sciences/mercury-problems-in-oil-and-gas-industries-environmental-sciences-essay.php. Retrieved 23 October 2016.

United Nations Environment Programme. *Global Mercury Assessment 2013: Sources, Emissions, Releases and Environmental Transport;* UNEP Chemicals Branch: Geneva, 2013.

Vinod, V. T. P., Sashidhar, R. B., Sivaprasad, N., Sarma, V. U. M., Satyanarayana, N., Kumaresan, R., T. N. Rao., and Raviprasad, P. (2011). Bioremediation of mercury (II) from aqueous solution by gum karaya (Sterculia urens): A natural hydrocolloid. *Desalination*, 272(1), 270-277.

Walsh, R. 2010. *Development and Characterisation of Molecularly Imprinted Suspension Polymers*, Phd Dissertation, Waterford Institute of Technology.

Wang, J., Feng, X., Anderson, C. W., Xing, Y., and Shang, L. (2012). Remediation of mercury contaminated sites - a review. *Journal of Hazardous Materials,* 221, 1-18.

Wang, T., Sun, H., Mao, H., Zhang, Y., Wang, C., Zhang, Z., Wang, B., and Sun, L. (2014). The immobilization of heavy metals in soil by bioaugmentation of a UV-mutant Bacillus subtilis 38 assisted by NovoGro biostimulation and changes of soil microbial community. *Journal of Hazardous Materials*, 278, 483-490.

Wang, X., Deng, W., Xie, Y., and Wang, C. (2013). Selective removal of mercury ions using a chitosan–poly (vinyl alcohol) hydrogel adsorbent with three-dimensional network structure. *Chemical Engineering Journal*, 228, 232-242.

Wilcox, J., Rupp, E., Ying, S. C., Lim, D. H., Negreira, A. S., Kirchofer, A., Feng, F., and Lee, K. (2012). Mercury adsorption and oxidation in coal combustion and gasification processes. *International Journal of Coal Geology*, 90, 4-20.

Wilhelm, S. M., and Bloom, N. (2000). Mercury in petroleum. *Fuel Processing Technology*, 63(1), 1-27.

Wilhelm, S. M., Naamani, M. N., Towell, W. J., Code, P., and Goddard, M. P. (2003). Health, Safety and Environmental Policy Guideline.

World Health Organisation. *Exposure to Mercury: A Major Public Health Concern;* WHO Document Production Services: Geneva, 2007.

Xu, S., Chen, L., Li, J., Guan, Y., and Lu, H. (2012). Novel Hg^{2+}-imprinted polymers based on thymine–Hg^{2+}–thymine interaction for highly selective preconcentration of Hg^{2+} in water samples. *Journal of Hazardous Materials*, 237, 347-354.

Yahya, M. A., Al-Qodah, Z., and Ngah, C. Z. (2015). Agricultural bio-waste materials as potential sustainable precursors used for activated carbon production: a review. *Renewable and Sustainable Energy Reviews*, 46, 218-235.

Yan, H., and Row, K. H. (2006). Characteristic and synthetic approach of molecularly imprinted polymer. *International Journal of Molecular Sciences*, 7(5), 155-178.

Yang, J., Li, Y., Wang, J., Sun, X., Cao, R., Sun, H., Huang, C., and Chen, J. (2015). Molecularly imprinted polymer microspheres prepared by Pickering emulsion polymerization for selective solid-phase extraction of eight bisphenols from human urine samples. *Analytica Chimica Acta*, 872, 35-45.

Ye, L., Mosbach, K., Spivak, D. A., and Sibrian-Vazquez, M. (2002). Molecularly imprinted materials: towards the next generation. In *MRS Proceedings* (Vol. 723, pp. M3-1). Cambridge University Press.

Yilmaz, V., Arslan, Z., Hazer, O., and Yilmaz, H. (2014). Selective solid phase extraction of copper using a new Cu (II)-imprinted polymer and determination by inductively coupled plasma optical emission spectroscopy (ICP-OES). *Microchemical Journal*, 114, 65-72.

Yoshimoto, N., Takaoka, M., Fujimori, T., Oshita, K., Sakai, N., and Kdir, S. A. S. A. (2016). Substance flow analysis of mercury in Malaysia. *Atmospheric Pollution Research*.

Yun, Z., He, B., Wang, Z., Wang, T., and Jiang, G. (2013). Evaluation of different extraction procedures for determination of organic Mercury species in petroleum by high performance liquid chromatography coupled with cold vapor atomic fluorescence spectrometry. *Talanta*, 106, 60-65.

Zabihi, M., Asl, A. H., and Ahmadpour, A. H. M. A. D. (2010). Studies on adsorption of mercury from aqueous solution on activated carbons prepared from walnut shell. *Journal of Hazardous Materials*, 174(1), 251-256.

Zhai, H., Su, Z., Chen, Z., Liu, Z., Yuan, K., and Huang, L. (2015). Molecularly imprinted coated graphene oxide solid-phase extraction monolithic capillary column for selective extraction and sensitive determination of phloxine B in coffee bean. *Analytica Chimica Acta*, 865, 16-21.

Zhao, J., Han, B., Zhang, Y., and Wang, D. (2007). Synthesis of Zn (II) ion-imprinted solid-phase extraction material and its analytical application. *Analytica Chimica Acta*, 603(1), 87-92.

Zheng, Y., Jensen, A. D., Windelin, C., and Jensen, F. (2012). Review of technologies for mercury removal from flue gas from cement production processes. *Progress in Energy and Combustion Science,* 38(5), 599-629.