NOVEL TREATMENT AND VALUE-ADDED UTILIZATION OF OILY SLUDGE USING IONIC LIQUID AND PYROLYSIS

by

Yuan Tian

B.E., Anhui University of Science and Technology, 2010 M.E., Beijing Institute of Technology, 2013

THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN NATURAL RESOURCES AND ENVIRONMENTAL STUDIES

UNIVERSITY OF NORTHERN BRITISH COLUMBIA

October 2019

© Yuan Tian, 2019

ABSTRACT

The effective treatment of oily sludge has been a challenging problem faced by the petroleum industry worldwide. It is a semi-solid mixture of hydrocarbons, water, metallic ions, and suspended fine solids. The recalcitrant nature of oily sludge makes the treatment a difficult and costly task. The objective of this dissertation research was to develop environmentally friendly and economically competitive techniques for oily sludge treatment. Three different approaches were developed: ionic liquid (IL)-enhanced solvent extraction, co-pyrolysis with wood waste, and value-added utilization of oily sludge as sorbent to remove lead (Pb^{2+}) and cadmium (Cd^{2+}) from solution. Firstly, as compared to conventional solvent extraction, the ILenhanced solvent extraction not only improved oil recovery efficiency but also greatly reduced solvent and energy consumption as well as shortening the treatment duration even at low IL concentration. Secondly, co-pyrolysis of oily waste and hog fuel was conducted in a fixed bed reactor. Three experimental parameters (pyrolysis temperature, reaction time, and hog fuel addition) were explored to optimize both oil recovery and metal ion immobilization. The latter was tested through sequential extraction techniques with high temperature pyrolysis leading to metal ions fixed within the residues. The addition of hog fuel had a significant synergistic effect on the distribution of metal ions in the various extraction fractions resulting in lower risk index (RI) values. Thirdly, the oily sludge-derived char (OS500) obtained at 500 °C could effectively remove Pb^{2+} from solution with the maximum sorption capacity of 373.2 mg/g (based on a Langmuir model). Sorption of Pb²⁺ by the OS500 was mainly attributed to its precipitation with carbonate (CO_3^{2-}) originating in OS500. The maximum sorption capacity for Cd²⁺, using a Langmuir model, was 23.19 mg/g. Complexation and metal ion exchange dominated Cd²⁺ sorption on OS500. The Pb²⁺ sorption capacity dramatically decreased as the pyrolysis temperature increased from 500 to 900 °C due to the decomposition of minerals which could release CO_3^{2-} at high temperature. The activated OS500 showed a higher sorption capacity (90.06 mg/g) for Cd²⁺ than OS500 (23.95 mg/g) because conversion of barite (BaSO₄) to witherite (BaCO₃) after chemical activation favored the precipitation of Cd-carbonate.

CO-AUTHORSHIP

For all the chapters in this dissertation, I was the principal investigator including design of studies, acquisition of data, and analysis of data. I wrote the manuscripts and was responsible for incorporating comments and feedbacks in the revised manuscripts. Dr. Jianbing Li supervised the experiments and contributed to experimental design, data analysis, and revision of the manuscripts. He is included in authorship on all resulting publications. Dr. Bill McGill and Dr. Todd Whitcombe contributed to the design and implementation of experiments and helped review and improve the manuscripts, so they were included in some of my publications. Dr. Ron Thring and Dr. Xiuyi Yan provided useful suggestions in co-pyrolysis experiment and contributed some comments on the manuscripts, so they were included in related publications.

Publication and authorships from this dissertation (Published or prepared for submission):

Tian, Y., McGill, W.B., Whitcombe, T.W., Li, J., 2019. Ionic liquid-enhanced solvent extraction for oil recovery from oily sludge. Energy Fuels 33, 3429–3438. DOI: 10.1021/acs.energyfuels.9b00224. (Chapter 3)

Tian, Y., Li, J., Yan, X., Whitcombe, T., Thring, R., 2019. Co-pyrolysis of metal contaminated oily waste for oil recovery and heavy metal immobilization. J. Hazard. Mater. 373, 1–10. DOI: 10.1016/j.jhazmat.2019.03.061. (Chapter 4)

Tian, Y., Li, J., Whitcombe, T., McGill, W.B. Thring, R., 2019. Application of oily sludgederived char for lead and cadmium removal from aqueous solution. Submitted to Chem. Eng. J. on Aug 27, 2019. (Chapter 5)

Tian, Y., Li, J., McGill, W.B., Whitcombe, T., 2019. Sorption of lead and cadmium on oily sludge-derived chars prepared at different pyrolysis temperatures and chemical activation. Prepared for submission to J. Hazard. Mater. (Chapter 6)

ABSTRACTii
CO-AUTHORSHIP iv
TABLE OF CONTENTSv
LIST OF TABLES
LIST OF FIGURESx
GLOSSARY xiii
ACKNOWLEDGEMENT xvi
Chapter 1 GENERAL INTRODUCTION1
1.1. Background
1.2. Statement of the problem
1.3. Objectives of the study
1.4. Organization of the dissertation
Chapter 2 LITERATURE REVIEW
2.1. Sources of oily sludge7
2.2. Characteristics of oily sludge
2.3. Toxicity of oily sludge
2.4. Techniques for treating oily sludge
2.5. Ionic liquid-enhanced solvent extraction
2.5.1. Solvent extraction
2.5.1.1. Selection of solvent
2.5.1.2. Parameters affecting extraction performance
2.5.2. Ionic liquid
2.6. Pyrolysis
2.6.1. Pyrolysis in oily sludge treatment
2.6.2. Effects of parameters on liquid production
2.6.3. Effects of parameters on gas production
2.6.4. Effects of parameters on solid production
2.6.5. Co-pyrolysis
2.7. Summary of literature review

Chapter 3 IONIC LIQUID-ENHANCED SOLVENT EXTRACTION FOR OIL

TABLE OF CONTENTS

Abstract	
3.1. Introduction	
3.2. Materials and methods	49
3.2.1. Materials and reagents	49
3.2.2. Single factor experiments	50
3.2.3. Optimization of solvent extraction and IL-enhanced solvent extraction	53
3.2.4. Laboratory analysis	55
3.2.4.1. Hydrocarbon analysis using gas chromatograph	55
3.2.4.2. Characterization of recovered oil and residual sand/clay	56
3.3. Results and discussion	57
3.3.1. Single factor experiments	57
3.3.2. Multifactor orthogonal experiments	60
3.3.2.1. Solvent extraction alone	60
2.3.2.2. IL-enhanced solvent extraction	64
2.3.3. Characteristics of the recovered oil and residual sand/clay	67
3.4. Summary	75
Chapter 4 CO-PYROLYSIS OF METAL CONTAMINATED OILY WASTE FOR	₹ OIL
RECOVERY AND HEAVY METAL IMMOBILIZATION	76
Abstract	76
4.1. Introduction	77
4.2. Materials and methods	
4.2.1. Materials	
4.2.2. Experimental set up	
4.2.3. Experimental design	
4.2.4. Chemical analysis and heavy metal species characterization	
4.2.5. Determination of potential ecological risk index (RI)	
4.3. Results and discussion	89
4.3.1. Response surface model and statistical analysis	
4.3.2. TPH recovery rate	
4.3.3. Properties of solid residues	
4.3.4. Heavy metal speciation characteristics	
4.3.5. Potential ecological risk assessment	103
4.4. Summary	106

Chapter 5 APPLICATION OF OILY SLUDGE-DERIVED CHAR FOR LE	AD AND
CADMIUM REMOVAL FROM AQUEOUS SOLUTION	107
Abstract	
5.1. Introduction	
5.2. Materials and methods	110
5.2.1. Materials and reagents	110
5.2.2. Char preparation	111
5.2.3. Char characterization	112
5.2.4. Batch sorption studies	
5.2.5. Post-sorption analysis	
5.3. Results and discussion	118
5.3.1. Characteristics of char	118
5.3.2. Sorption kinetics	122
5.3.3. Sorption isotherms	126
5.3.4. Post-sorption characteristics and sorption mechanisms	
5.3.4.1. XRD and FTIR results	
5.3.4.2. Sequential extraction results	
5.4. Summary	
Chapter 6 SORPTION OF LEAD AND CADMIUM ON OILY SLUDGE-D	ERIVED
CHAR PREPARED AT DIFFERENT PYROLYSIS TEMPERATURES AND	D CHEMICAL
Abstract	142
Abstract	
6.1. Introduction	
6.2. Materials and methods	
6.2.1. Materials and reagents	
6.2.2. Chars preparation and characterization	
6.2.4 Definition of the second s	
6.2.4. Post-sorption analysis	
6.3. Results and discussion	
6.3.1. Characteristics of chars	
6.3.2. XRD and FTIR results	155
6.3.3. Sequential extraction results	
6.4. Summary	

Chapter 7 CONCLUSION AND RECOMMENDATIONS	170
7.1. Synthesis and conclusion	170
7.2. Limitations and future research	174
References	177
APPENDIX A	208
APPENDIX B	214
APPENDIX C	219
APPENDIX D	223

LIST OF TABLES

Table 2.1. Heavy metal content in oily sludge generated from various refineries
Table 2.2. Summary of technologies for the oily sludge treatment 16
Table 2.3. Summary of ionic liquids used in bitumen recovery from oil sands
Table 3.1. Characteristics of the oily sludge 50
Table 3.2. Single-factor experimental conditions 51
Table 3.3. Orthogonal array L9 (3 ⁴) experimental design and factor levels 54
Table 3.4. Results of the orthogonal experiments for solvent extraction alone
Table 3.5. Results of the orthogonal experiments for IL-enhanced solvent extraction 65
Table 3.6. Properties of extracted oil and residual sand/clay after extraction in different
systems
Table 4.1. Soil texture and synthetic oily waste properties
Table 4.2. Coded (xi) and un-coded (Xi) Box-Behnken design matrix with the experimental
results
Table 4.3. ANOVA of the regression model for TPH recovery
Table 4.4. ANOVA of the regression model for RI in solid residue
Table 4.5. Total C, H, N, and pH in the feedstock and the solid residue after pyrolysis 97
Table 5.1. Properties of oily sludge
Table 5.2. Physicochemical properties of OS500 ^a 120
Table 5.3. The fitting results of Pb^{2+} and Cd^{2+} sorption on OS500 using the pseudo first
order kinetic (PF-order), pseudo second order kinetic (PS-order), Elovich, and
intraparticle diffusion (IPD) models
Table 5.4. Langmuir (L), Freundlich (F), Sips (S), Redlich-Peterson (RP), Temkin (T), and
Dubinin-Radushkevich (DR) isotherm parameters of Pb^{2+} and Cd^{2+} sorption on
OS500
Table 5.5. Summary of the literature data on sorption of Pb^{2+} and Cd^{2+} to different biochars
or other sorbents
Table 5.6. The release of K^+ , Ca^{2+} , Mg^{2+} , and Ba^{2+} during Pb^{2+} and Cd^{2+} sorption by OS500

Table 6.1. Preliminary sorption results of chars
Table 6.2. Physicochemical properties of chars ^a 151
Table 6.3. The release of K^+ , Ca^{2+} , Mg^{2+} , and Ba^{2+} during Pb^{2+} and Cd^{2+} sorption by OSDCs
Table 6.4. Quantitative analysis of sorption mechanisms of Pb ²⁺ /Cd ²⁺ onto OSDCs
Table A1. Mass balance calculation of the F2, F3, and F4 fractions of TPH for orthogonal
experiments of solvent extraction alone
Table A2. Mass balance calculation of the F2, F3, and F4 fractions of TPH for orthogonal
experiments of IL-enhanced solvent extraction process
Table A3. ANOVA for TPH, F2, F3, and F4 recovery in solvent extraction alone
Table A4. ANOVA for TPH recovery in IL-enhanced solvent extraction process
Table B1. Concentrations of extractable fractions of heavy metals in the oily waste (SRC)
and its solid residues
Table C1. Sequential extraction results of OS500-B 219
Table C2. Sequential extraction results of OS500-Pb and OS500-Cd
Table C3. Recovery of sequential extraction results of OS500-Pb and OS500-Cd
Table D1. Sequential extraction results of OSDCs before Pb ²⁺ /Cd ²⁺ sorption
Table D2. Sequential extraction results of Pb-loaded/Cd-loaded OSDCs 224
Table D3. Recovery of sequential extraction results of Pb-loaded/Cd-loaded OSDCs 225
Table D4. Pearson correlation coefficient matrix between OSDCs properties and Pb ²⁺ /Cd ²⁺
sorption mechanism

LIST OF FIGURES

Figure 3.1. The phases formed by mixing, (a) oily sludge with [Emim][BF ₄] and	
cyclohexane in the proportion of 1:3:2 (by weight), and (b) oily sludge with	
cyclohexane in the proportion of 1:2 (by weight)5	2
Figure 3.2. Influence of different operational parameters on TPH recovery: (a) So/Sl ratio	
(shaking speed: 200 rpm, extraction duration: 30 min, IL/Sl ratio: 1:1 mL/g), (b)	
shaking speed (So/SI ratio: 2:1 mL/g, extraction duration: 30 min, IL/SI ratio: 1:1	
mL/g), and (c) extraction duration (So/SI ratio: 2:1 mL/g, shaking speed: 200 rpm,	
IL/SI ratio: 1:1 mL/g). Significant ($P < 0.05$) differences are shown by different	
letters: lowercase letter for the solvent extraction, and uppercase letter for the IL-	
enhanced solvent extraction	8
Figure 3.3. Influence of IL/sludge (IL/Sl) ratio on TPH recovery (So/Sl ratio: 2:1 mL/g,	
shaking speed: 200 rpm, extraction duration: 30 min). Different lowercase letters (a,t	5)
indicates significant ($P < 0.05$) differences	ó
Figure 3.4. Effect of independent factors on (a) TPH recovery, (b) F2 recovery, (c) F3	
recovery, and (d) F4 recovery of the solvent extraction alone process	3
Figure 3.5. Effect of independent factors on TPH recovery of the IL-enhanced solvent	
extraction process	5
Figure 3.6. GC chromatogram of petroleum hydrocarbons in (a) recovered oil using solvent	
extraction alone, (b) recovered oil from top oil/solvent layer using IL-enhanced	
solvent extraction, and (c) recovered oil from oil/solvent-IL interface using IL-	
enhanced solvent extraction	8
Figure 3.7. Distribution of PHCs fractions in crude oil, recovered oil (RO) using solvent	
extraction alone, recovered oil in top oil/solvent layer using IL-enhanced solvent	
extraction, and recovered oil in oil/solvent-IL interface using IL-enhanced solvent	
extraction	<i>i</i> 9
Figure 3.8. FTIR spectra of the (a) oily sludge, (b) recovered oil, and (c) residual sand/clay	
for solvent extraction alone	0
Figure 3.9. FTIR spectra of the (a) recovered oil from top oil/solvent layer, (b) recovered oil	1
from oil/solvent-IL interface, (c) residual sand/clay, and (d) [Emim][BF ₄] in IL-	
enhanced solvent extraction. Residual sand/clay was treated with water and washed 3	3
times7	2
Figure 4.1. Schematic diagram of fixed-bed pyrolysis reactor (1 - N ₂ gas cylinder, 2 - flow	
meter, 3 - thermal couple, 4 - quartz tube, 5 - sample ark, 6 - tube furnace, 7 -	
temperature controller, 8 - ice-water bath, 9 - Tedlar gas bag)	1
Figure 4.2. Gas chromatogram of (a) oil from untreated oily waste and (b) recovered oil after	er
pyrolysis treatment (run #11))3
Figure 4.3. The statistical evaluation of the effect of single factor on TPH recovery rate. (a)	
pyrolysis temperature (reaction time: 75 min. hog fuel ratio: 10%). (b) reaction time	
(pyrolysis temperature: 500 °C, hog fuel ratio: 10%), and (c) hog fuel addition	
(pyrolysis temperature: 500 °C, reaction time: 75 min)	94

Figure	4.4. Contour plot of TPH recovery (%) as function of pyrolysis temperature and reaction time at hog fuel addition = 10%
Figure	4.5. Response surface graph of TPH recovery as function of (a) reaction time and hog fuel addition at pyrolysis temperature = 500 °C , and (b) pyrolysis temperature and hog fuel addition at reaction time = 75 min
Figure	4.6. Fraction distribution of metals in oily waste before and after pyrolysis treatment.
Figure	4.7. Response surface graph of risk index (RI) as function of (a) pyrolysis temperature and reaction time (at hog fuel addition = 10%), (b) pyrolysis temperature and hog fuel addition (at reaction time = 75 min), and (c) reaction time and hog fuel addition (at pyrolysis temperature = 500 °C)
Figure	5.1. (a) Nitrogen adsorption/desorption isotherms and (b) pore size distribution of the OS500
Figure	5.2. The influence of contact time on (a) Pb^{2+} and (b) Cd^{2+} sorption onto OS500 and the fit of the data by pseudo first order, pseudo second order, and Elovich equation (0.1g char in 30 mL solution (0.01 M NaNO ₃), initial $Pb^{2+}(Cd^{2+})$ concentration 1600 (1000) mg/L; room temperature 24 °C; initial solution pH 5)
Figure	5.3. Isotherms of (a) Pb ²⁺ and (b) Cd ²⁺ sorption onto OS500 (0.1g char in 30 mL solution (0.01 M NaNO ₃); contact time 128 h; room temperature 24 °C; initial solution pH 5)
Figure	 5.4. XRD patterns of OS500 before (OS500-B) and after Pb²⁺/Cd²⁺ sorption (OS500-Pb and OS500-Cd). Minerals with peaks labeled: M, Muscovite 2M2, K_{0.77}Al_{1.93}(Al_{0.5}Si_{3.5})O₁₀(OH)₂; B, Barite, BaSO₄; Q, Quartz, SiO₂; C, Calcite, CaCO₃; D, Dolomite, CaMg(CO₃)₂; Ce, Cerussite, PbCO₃; H, hydrocerrusite, Pb₃(CO₃)₂(OH)₂.
Figure	5.5. Comparisons between solution pH before and after (a) Pb ²⁺ sorption and (b) Cd ²⁺ sorption in equilibrium studies
Figure	5.6. FTIR spectra of OS500 before (OS500-B) and after Pb ²⁺ /Cd ²⁺ sorption (OS500-Pb and OS500-Cd). 137
Figure	5.7. Sequential extraction results for (a) OS500-Pb, and (b) OS500-Cd (WS: water soluble fraction, EX: exchangeable fraction, CB: fraction bound to carbonate, OX: fraction bound to Fe-Mn oxides, OM: fraction bound to organic matter, RS: residual fraction)
Figure	6.1. (a) Nitrogen adsorption/desorption isotherms and (b) pore size distribution of the OSDCs prepared at different pyrolysis temperatures
Figure	6.2. (a) Nitrogen adsorption/desorption isotherms and (b) pore size distribution of the non-activated OSDC and activated OSDC obtained at 500 °C
Figure	6.3. XRD patterns of (a) OS300, (b) OS500, (c) OS700, (d) OS900, and (e) OS500N100-8M before and after Pb ²⁺ /Cd ²⁺ sorption
Figure	6.4. FTIR spectra of (a) OS300, (b) OS500, (c) OS700, (d) OS900, and (e) OS500N100-8M before and after Pb^{2+}/Cd^{2+} sorption
Figure	6.5. Sequentially extracted (a) Pb^{2+} and (b) Cd^{2+} amounts in the OSDCs after Pb^{2+} or Cd^{2+} sorption. Fractions of (c) Pb^{2+} and (d) Cd^{2+} in each step of sequential extraction

(WS: water soluble fraction, EX: exchangeable fraction, CB: fraction bound to
carbonate, OX: fraction bound to Fe-Mn oxides, OM: fraction bound to organic
matter, RS: residual fraction)
Figure B1. FT-IR spectra of the feedstock and solid residues after pyrolysis (SRC: solid
residue sample from control experiment without pyrolysis treatment; SROx: solid
residue from oily waste pyrolysis alone at X (°C) temperature and reaction time = 75
min; SROHx: solid residue from co-pyrolysis of oily waste and hog fuel at X (°C)
temperature and reaction time = 75 min and hog fuel addition = 20%
Figure C1. Determination of pH_{PZC} for OS500. Thick straight line represents $pH_{initial} =$
pH _{final} line
Figure C2. Intraparticle diffusion plot for the sorption of (a) Pb^{2+} and (b) Cd^{2+} on OS500
(0.1g char in 30 mL solution (0.01 M NaNO ₃), initial Pb ²⁺ (or Cd ²⁺) concentration
1600 (1000) mg/L; room temperature 24 °C; initial solution pH 5) 221
Figure C3. Isotherms of (1) Pb^{2+} and (2) Cd^{2+} sorption onto OS500 (0.1g char in 30 mL
solution (0.01 M NaNO ₃); contact time 128 h; room temperature 24 °C; initial
solution pH 5)
Figure D1. XRD patterns of OSDCs before Pb ²⁺ /Cd ²⁺ sorption (OSDC-B). Minerals with
peaks labeled: M, Muscovite 2M2, K _{0.77} Al _{1.93} (Al _{0.5} Si _{3.5})O ₁₀ (OH) ₂ ; B, Barite, BaSO ₄ ;
Q, Quartz, SiO ₂ ; C, Calcite, CaCO ₃ ; D, Dolomite, CaMg(CO ₃) ₂ ; O, Calcium oxide,
CaO; Cl, Celsian, BaAl ₂ Si ₂ O ₈ ; Bo, Barium oxide hydrate, BaO ₂ (H ₂ O) ₈ ; F,
Ferritungstite, (W, Fe)(O,OH) ₃ ; W, Witherite, BaCO ₃
Figure D2. FTIR spectra of OSDC before Pb ²⁺ /Cd ²⁺ sorption (OSDC-B)

GLOSSARY

AAEMs	Alkali and alkaline earth metallic species
AC	Activated carbon
ANOVA	Analysis of variance
API	American Petroleum Institute
ASTM	American Society for Testing and Materials
ATR	Attenuated total reflection
BET	Brunauer-Emmett-Teller
BJH	Barrett-Joyner-Halenda
BP	British Petroleum
BTEX	Benzene, toluene, ethylbenzene, and xylenes
CCME	Council of Ministers of the Environment
CEC	Effective cation exchange capacity
D _P	Average pore diameter
DCM	Dichloromethane
DR	Dubinin-Radushkevich
DTG	Differential thermogravimetric analysis
F	Freundlich
FFU	Flocculation/flotation unit
FSOS500	Ferric-activated char
FTIR	Fourier transform infrared spectroscopy
GC-FID	Gas chromatography with a flame ionization detector
HCs	Hydrocarbons
HHV	High heating value
IARC	International Agency for Research on Cancer
ICP-OES	Inductively coupled plasma optical emission spectrometry
ILs	Ionic liquids
IL/S1	Ionic liquid/sludge ratio
IPD	Intraparticle diffusion model
IUPAC	International union of pure and applied chemistry
L	Langmuir
MCL	Maximum contaminant level

NSO	Nitrogen sulfur oxygen
O/W	Oil-in-water
OSDC	Oily sludge-derived char
OS _X	Oily sludge-derived char produced from pyrolysis at X (°C) temperature
OS _X -B	Oily sludge-derived char produced from pyrolysis at X (°C) temperature before sorption
OS _X -Cd	Oily sludge-derived char produced from pyrolysis at X (°C) temperature after cadmium (Cd ²⁺) sorption
OS _X -Pb	Oily sludge-derived char produced from pyrolysis at X (°C) temperature after lead (Pb^{2+}) sorption
OS500N24-2M	Activated char obtained from hydrothermal treatment of OS500 with 2M NaOH solution at 24 °C
OS500N100-2M	Activated char obtained from hydrothermal treatment of OS500 with 2M NaOH solution at 100 °C
OS500N100-8M	Activated char obtained from hydrothermal treatment of OS500 with 8M NaOH solution at 100 °C
OS500N900	Activated char obtained from chemical activation of OS500 with NaOH at 900 °C
OSHA	Occupational Safety and Health Administration
PAHs	Polycyclic aromatic hydrocarbons
PF-order	Pseudo first order
pH _{PZC}	The point of zero charge
PHCs	Petroleum hydrocarbons
PS-order	Pseudo second order
PV	Total pore volume
Qt	Total extracted Pb^{2+}/Cd^{2+} in sequential extraction (mg/g)
Qp	The amount of Pb^{2+}/Cd^{2+} sorbed through precipitation (mg/g)
Qcf	The amount of Pb ²⁺ /Cd ²⁺ sorbed through complexation with free carboxyl/hydroxyl functional groups (mg/g)
Q _{cm}	The amount of Pb^{2+}/Cd^{2+} substituted with metal ions to form complexes (mg/g)
RI	Potential ecological risk index
RP	Redlich-Peterson

RSM	Response surface methodology
S _{BET}	The Brunauer-Emmett-Teller (BET) surface area
S	Sips
S/N	Signal to noise
So/Sl ratio	Solvent/sludge ratio
SRC	Original oily waste
SRO _X	Solid residue after pyrolysis at X (°C) temperature
SROH _X	Solid residue from the co-pyrolysis at X (°C) temperature
Т	Temkin
TGA	Thermogravimetric analysis
TOC	Total organic carbon content
ТРН	Total petroleum hydrocarbon
TSA	Total surface acidity
TSB	Total surface basicity
UHQ	Ultra high purity
USEPA	US Environmental Protection Agency
VOCs	Volatile organic compounds
W/O	Water-in-oil
XRD	X-ray diffraction

ACKNOWLEDGEMENT

First of all, I would like to express my gratitude and appreciation for my supervisor Dr. Jianbing Li whose guidance, support and encouragement have been invaluable throughout this study. Without his help and advice, I would not have been able to complete this research. Further, I would like to thank my supervisory committee members: Dr. Liang Chen, Dr. Bill McGill, Dr. Ron Thring, and Dr. Todd Whitcombe for their insightful comments, guidance, and discussions.

Special thanks to Dr. Joselito Arocena, for sharing his expertise. I would also like to thank Dr. Xiuyi Yan from China University of Petroleum. She continuously provided encouragement and was always willing to help me with my research. I would like to express my thanks to Dr. Art Fredeen, Dr. Neil Hanlon, Dr. Ken Otter, and Dr. Ellen Petticrew as my course supervisors in my first year of PhD. They encouraged me to take a broader view of my research and this later helped me to identify my research questions.

This research was financially supported by the Natural Sciences and Engineering Research Council of Canada and Fisheries and Oceans Canada's Multi-Partner Oil Spill Research Initiative (MPRI). Additional support from the UNBC Graduate Teaching Assistantship, Graduate Conference Travel Award, Research Project Awards, and PhD Dissertation Completion Award were much appreciated.

Many thanks to Dr. Hossein Kazemian, Charles Bradshaw, and Erwin Rehl for their support and professional advice with sample analysis at UNBC Northern Analytical Laboratory Service. I would like to thank Conan Ma working at UNBC Chemstore for his support with sample delivery and lab materials supply. I would also like to thank Dr. Umesh Pashotam for his patience and helpful instructions as the supervisor of my teaching assistant position at UNBC. I would like to extend my thanks to several UNBC faculty and staff: Jenia Blair, Dr. Liz Dunn, Dr. Daniel Erasmus, John Orlowsky, Dr. Mike Rutherford, Doug Thompson, and Dr. Youqin Wang who lend me their lab equipment and supplies, provided me assistance in sample preparation, or helped me in other ways.

My gratitude also extends to the graduate students at UNBC for sharing their knowledge, skills, and thoughts; they are Talaat Bakri, Dr. Guangji Hu, Huan Liu, Marzieh Mortezapour, Jingjing Shi, and Zeyi Tong. I would also like to extend my gratitude to all my friends in China and Canada for always being supportive, inspiring, and understanding. The friendship from my friends has helped me to gather my strength to pass through many hard times during my PhD study.

I would like to dedicate this work to my families for their unconditional supports and love. Special thanks go to my mother, who is a strong woman and my role model, and my grandfather, who has taught me to be brave and not afraid of any challenges in my life.

Chapter 1

GENERAL INTRODUCTION

1.1. Background

A considerable amount of oily sludge is generated by the activities involved in petroleum industry such as drilling, production, transport, processing and distribution. It is estimated that more than 11,000 tons of oily sludge is generated in refineries daily (da Silva et al., 2012). Oily sludge can accumulate in a refinery at various points, such as pump, desalter, tank, and pipeline (Kuriakose and Manjooran, 2001).

The properties of oily sludges vary depending on the source producing them, the nature of the crude oil, the refinery processing scheme, and the equipment and reagents used in wastewater treatment (Elektorowicz and Habibi, 2005; Mazlova and Meshcheryakov, 1999). Generally, an oily sludge is a complex water-in-oil (W/O) or oil-in-water (O/W) emulsion, typically consisting of 10-56 wt% oil, 30-85 wt% water, and 13-46 wt% solids (API, 2010; Mazlova and Meshcheryakov, 1999). The stability of the emulsion depends on a film formed at the oil-water interface that acts as a barrier to prevent droplet coalescence (Sullivan and Kilpatrick, 2002). A variety of compounds including natural emulsifiers such as asphaltenes and resins, carboxylic organic acids and fine inorganic particles play important roles in enhancing emulsion stabilization (Kilpatrick, 2012). Oily sludge is classified as a hazardous waste since it contains toxic compounds such as benzene, toluene, ethylbenzene, and xylenes (BTEX), polycyclic aromatic hydrocarbons (PAHs), and some heavy metals (e.g., cadmium, lead, and mercury) (USEPA, 2012). The improper disposal of oily sludge can lead to environmental pollution and pose serious threats to public health and the environment (Hejazi et al., 2003; Kuang et al., 2011; Robertson et al., 2007). Most of the oily sludge is

conventionally disposed by landfill or incineration (van Oudenhoven et al., 1995). However, the use of a landfill is associated with various disadvantages, such as the need for large space, low degradation efficiency, a long treatment period, and the risk of harmful compounds leaching into the environment (da Silva et al., 2012; Renou et al., 2008). Moreover, more restrictive disposal regulations (e.g., Ontario Environmental Protection Act Regulation 347) have been enacted over the past few decades limiting the use of land disposal for hazardous waste (da Silva et al., 2012; Revised Regulations of Ontario, 1990). Incineration can greatly reduce the volume of waste but the costs of processing oily sludge by incineration are usually very high due to the need for flue gas treatment (Ball et al., 2012; van Oudenhoven et al., 1995). Over the last decade or so, various treatment methods, such as ultrasonic treatment, electrokinetics. solvent extraction, pyrolysis, oxidation, land-farming, bio-slurry, and solidification/stabilization, have been explored as methods to deal with oily sludge (Ferrarese et al., 2008; Hu et al., 2015, 2017; Jasmine and Mukherji, 2019; Karamalidis and Voudrias, 2007; Marin et al., 2005; Yang et al., 2005; Zhang et al., 2012). Most of these technologies do not achieve a reasonable compromise between satisfying environmental regulations and treatment costs. Some of these technologies, such as bioslurry, are effective in removing petroleum hydrocarbons (PHCs) but are very expensive. Others, such as land-farming, have a relatively low cost but fail to meet the requirements for current or future regulations. Therefore, the development of new technologies for treating oily sludge with high efficiency and low costs is needed.

1.2. Statement of the problem

Recycling is the most desirable strategy for handing oily sludge since it enables the petroleum industry to re-use valuable oil by reprocessing, reformulating or recovering energy

through burning (Elektorowicz and Habibi, 2005). Recycling of oily sludge can minimize the disposal of wastes outside an industrial zone, reduce overall contamination, and decrease the use of natural nonrenewable resources (Elektorowicz and Habibi, 2005). Solvent extraction is a commonly used approach to recycling hydrocarbons from oily sludge. In this technology, solvent is mixed with an oily sludge to ensure complete miscibility allowing semi-volatile and non-volatile organic compounds to be removed from soil/water matrices effectively. Solvent extraction can recover most useable PHCs from oily sludge, but this method needs a large amount of organic solvent to achieve a promising oil recovery rate. The major concern of applying solvent extraction to oily sludge is the toxicity of the organic solvents used to both the process operators and the environment. Moreover, the volatile and flammable nature of organic solvents makes them a potential explosion hazard (Schmid et al., 1998). There is a growing interest in environmentally friendly solvents with high efficiency in the past few years. Ionic liquids (ILs) are purely ionic materials with melting temperature below 100 °C and have been considered as "green, eco-friendly solvents" because of their unique properties (Rogers and Seddon, 2003). ILs have a very low vapor pressure, outstanding thermal stability, and are non-flammable (Guzmán-Lucero et al., 2010). As a consequence of their unique properties, researchers working in the petroleum industry have been examining potential applications for ILs in the process of refining, recovery, or upgrade of oil (José-Alberto and Jorge, 2011). Studies on the use of ILs in environmental remediation are still scarce, especially oil recovery from oily sludge.

Pyrolysis is a thermo-chemical decomposition process of a material in a closed oxygen-free reactor system with elevated temperatures (usually 400–600 °C). The application of pyrolysis technology to oily sludge is attractive because pyrolysis can effectively recover the oil from

waste (Schmidt and Kaminsky, 2001) while also immobilizing heavy metal ions (Devi and Saroha, 2014). Experiment on the co-pyrolysis of oily sludge with wood waste has also shown that the overall yield of oil was greater than the yield obtained by the pyrolysis of the oily sludge and the wood waste separately indicating a synergistic effect (Hu et al., 2017). Some of the oil properties, such as high heating value (HHV) and carbon content, have been found to be improved by co-pyrolysis (Q. Cao et al., 2009). In addition to the potential advantages of increasing oil yield and improving oil quality, co-pyrolysis with other waste material could even enhance the heavy metal immobilization in solid residues (Debela et al., 2012; Jin et al., 2017). To study the fate of heavy metals during the thermal treatment of waste, several articles have focused on the total heavy metal content and leaching behavior of residues after treatment (Jin et al., 2014; Thurnau, 1996). Their results can hardly be used for examining the mobility and eco-toxicity of heavy metals, which depend on their specific chemical forms or binding patterns (He et al., 2010).

Growing interest has been shown in the application of oily sludge-derived char (OSDC) to the removal of pollutants from wastewater in recent years. For example, Mohammadi and Mirghaffari (2015) produced activated carbon (AC) from oily sludge through a chemical method and they found a surface area of 327.96 m²/g. To further improve the adsorption capability of an AC derived from oily sludge, Wang et al. (2017b) added a solvent de-oiling step before activation. The surface area of the AC prepared with the de-oiling step reached 3292 m²/g. As a result, oily sludge could be a potential material for producing effective adsorbent. However, there is a lack of information on the roles of different sorption mechanisms for OSDC. Also limited information is available on how the preparation condition (i.e., pyrolysis temperature and chemical activation) and resulting OSDC properties translate into the heavy metal sorption capacities.

1.3. Objectives of the study

The main objective of this research is to develop novel technologies for oily sludge management with added economic and environmental benefits. Based on literature review in Chapter 2, the specific objectives include:

- Evaluating the effect of IL (i.e., 1-ethyl-3-methyl-imidazolium tetrafluoroborate ([Emim][BF4])) on oil recovery from oily sludge by comparing to solvent extraction without IL addition. Several experimental factors including solvent/sludge ratio, shaking speed, extraction duration, and IL/sludge ratio were studied for their effects on oil recovery. The optimal conditions for oil recovery in the two processes (i.e., solvent extraction and IL enhanced solvent extraction) were also investigated.
- Investigating the pyrolysis of oily waste containing heavy metals for both oil recovery and heavy metal immobilization. Hog fuel (i.e. wood waste) from lumber production was used as an additive, aiming to explore the reduced bioavailability and toxicity of heavy metals in the pyrolysis char. The metal ion chemical speciation in the solid char residue was examined to evaluate the ecological risk posed by oily waste treatment. The effects of three selected experimental variables (pyrolysis temperature, reaction time, and wood waste addition) on the process performance were studied using a response surface methodology (RSM).
- Evaluating the application potential of OSDC as a cost-effective sorbent for the removal of Pb²⁺ and Cd²⁺ in aqueous solution. The mechanism of Pb²⁺ and Cd²⁺ sorption by OSDC was investigated using batch sorption studies, Fourier transform

infrared spectroscopy (FTIR), and X-ray diffraction (XRD). The contribution of different mechanisms to the overall sorption of Pb^{2+} and Cd^{2+} by OSDC was also quantified using a modified sequential extraction test.

• Examining how the preparation condition (i.e., pyrolysis temperature and chemical activation) of OSDC affected the heavy metal sorption capacities. To relate the heavy metal removal performance of OSDCs to their properties, the adsorption of nitrogen, pH drift method, Boehm titration, and element analysis were used to characterize the surface features. The sorption mechanisms of heavy metal ions on activated and non-activated OSDC were investigated by qualitative methods (i.e., FTIR and XRD) and quantitative method (i.e., sequential extraction).

1.4. Organization of the dissertation

The dissertation is structured as follows: in chapter 2, literatures were reviewed and summarized; in chapters 3–6, three different approaches to treat oily sludge was developed, including IL-enhanced solvent extraction (chapter 3), co-pyrolysis with wood waste (chapter 4), and value-added utilization of oily sludge as sorbent to remove Pb²⁺ and Cd²⁺ from solution (chapters 5 and 6); in chapter 7, the conclusion of this research and recommendations for future research were provided.

Chapter 2

LITERATURE REVIEW

2.1. Sources of oily sludge

Oily sludge is one of the most significant solid wastes generated in petroleum industry. The petroleum industry is usually divided into three major components: upstream, midstream, and downstream. The upstream includes the exploration and production of crude oil. The midstream includes transportation and storage of crude oil, while the downstream includes refining and processing of crude oil. According to a study conducted by the American Petroleum Institute (API), in 1995, US onshore and coastal oil-field exploration and production operations generated approximately 278,180 tons of oily sludge from tank bottoms (ICF Consulting, 2000). In the upstream operation, oily sludge might also originate from oil debris, dehydration waste, used oils, etc (Hu et al., 2013; ICF Consulting, 2000).

During the refining process, impurities such as sulfur, nitrogen, and metal ions are separated from petroleum. These impurities along with the residual hydrocarbons, mineral particles, water, and chemicals form oily sludge (Kriipsalu et al., 2008). The demand for refined petroleum products has been increasing worldwide due to rapid industrialization. According to British Petroleum's (BP) annual report, the refining throughput worldwide in 2018 was 13,188,076 m³/day, representing an 11% increase in throughput compared to 2008 (11,889,030 m³/day) (BP, 2019). In general, a higher refining throughput could bring about greater oily sludge production (Hu et al., 2013). The total amount of oily sludge produced by the European refineries in 1993 was 856,274 tons, which corresponded to 0.16 wt% of refinery throughput (van Oudenhoven et al., 1995). Even based on optimistic estimates and assuming oily sludge

production is only 0.1 wt% of refinery throughput, more than 11,000 tons of oily sludge is produced daily worldwide (da Silva et al., 2012).

Within refineries, the major sources of oily sludge include slop oil emulsion solid, separator sludge, flocculation/flotation unit (FFU) sludge, and tank bottom sludge (Shie et al., 2000). Depending upon the sources of the crude oil and the point in the processing where the oily sludge is generated, it can vary significantly in its oil, water, and solid content. For example, the oily sludge (i.e., separator sludge and FFU sludge) from wastewater treatment tends to contain a higher percentage of water (API, 2010). In contrast, tank bottom sludge contains a higher percentage of the solids (API, 2010). Other factors such as the type of crude oil, the refinery processing scheme, and the chemicals and equipment used in the wastewater treatment can also affect the composition of oily sludge (Mazlova and Meshcheryakov, 1999). As a consequence of all the factors affecting its production, oily sludges can range across a range of compositions, typically oil 10–56%, water 30–85%, and solids 13–46% by weight. (API, 2010; Mazlova and Meshcheryakov, 1999).

2.2. Characteristics of oily sludge

The physical properties of an oily sludge, such as water solubility, boiling point, and vapor pressure, are significantly affected by the oil, water, and solids content (API, 2010). For instance, as the oil content of oily sludge decreases, the overall boiling point decrease, whereas the volatility increase. Moreover, properties such as polarity and molecular weight of hydrocarbons can be used to predict the other related properties in oily sludge (API, 2010). The aromatic constituents in oily sludge have a higher boiling point, higher water solubility, and lower vapor pressure than the aliphatic constituents (Gustafson et al., 1997). The hydrocarbons with higher molecular weight have a higher boiling point, lower water solubility,

and lower vapor pressure as compared to those with lower molecular weight (Gustafson et al., 1997).

The chemical composition of oily sludge is complex and depends on the type of petroleum and its source. The oil phase of oily sludge ranges from 52–67% aliphatics, 15–31% aromatics, 7-8% nitrogen sulfur oxygen (NSO) containing compounds, and 10-12% asphaltenes (Mishra et al., 2001; Mrayyan and Battikhi, 2005; Tahhan and Abu-Ateih, 2009). According to Kriipsalu et al. (2008), the most abundant compounds among the aliphatic and aromatic groups are alkenes, cyclic alkenes, benzene, toluene, ethylbenzene, and xylenes. Small amounts of phenols and polycyclic aromatic hydrocarbons (PAHs) such as naphthalene, fluorene, phenanthrene, and chrysene can be also found in oily sludge (Kriipsalu et al., 2008). Generally, oily sludge is identified as either a water-in-oil (W/O) or an oil-in-water (O/W) emulsion (Elektorowicz et al., 2006; Long et al., 2013). An emulsion is the mixture of two immiscible liquids in which one of the liquids is stably suspended in the other (Kilpatrick, 2012). The fine particles and natural emulsifiers such as asphaltenes and resins accumulate and form a film at the oil-water interface, acting as a barrier to prevent droplet coalescence (Ali and Algam, 2000). Asphaltenes are condensed polyaromatic hydrocarbons that contain heteroatoms such as N, S, and O polar groups (Sullivan and Kilpatrick, 2002). Resins are organic molecules consisting of a hydrophobic end (alkyl chains) and a hydrophilic end (polar functional groups) (Sullivan and Kilpatrick, 2002). These amphiphilic substances (i.e., asphaltenes and resins) play important roles in stabilizing emulsion. In addition, long-chain carboxylic acids and fine inorganic particles also contribute to the stability of emulsions of oily sludge. The emulsion stabilization mechanisms associated with these three types of components were reviewed by Kilpatrick (2012).

Heavy metals such as copper, lead, zinc, nickel, chromium, etc. are also present in oily sludge in ionic form. It was reported that some metals (i.e., zinc, calcium, and magnesium) in crude oil usually exist in combination with naphthenic acid as soaps, while other metals (i.e., vanadium, copper, and nickel) exist in the form of oil-soluble complexes such as metalloporphyrins (Ali and Abbas, 2006). The heavy metal ion content in oily sludge varies most likely due to the diversity of crude oil and differences in the methods for oil-water separation and oil storage (Kriipsalu et al., 2008). High concentrations of heavy metal ions in oily sludge have been reported in some studies, i.e., 500 mg/kg copper (Cu), 565 mg/kg lead (Pb), 2100 mg/kg zinc (Zn), 1300 mg/kg nickel (Ni), 480 mg/kg chromium (Cr), 120 mg/kg mercury (Hg), 2400 mg/kg vanadium (V), 3900 mg/kg calcium (Ca), 622 mg/kg magnesium (Mg) (Table 2.1).

Type of oily	Copper	Lead	Zinc	Nickel	Chromium	Mercury	Vanadium	Calcium	Magnesium	Reference
sludge	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	
Tank bottom	214	565	769	125	119	a	_	_	542	(da Rocha et al.,
										2010)
Tank bottom	2-26	34-	74–	0–19	4–18	2-6	_	_	_	(Alfutaisi et al
	-	148	759		-	-				2007)
Tank bottom	55	49	91	16	14	_	6	3900	622	(Jasmine and
Tunk oottom	55	17	71	10	11		0	5700	022	(Jushinie and Mukherij 2015)
Tank bottom	1/	20	02	12	7	25		1056	06	(Ship at al
Talik Douolli	14	20	92	12	/	33	—	1030	90	
	5 00	270	(00	400	100		2400			2000)
Open storage	500	270	690	480	480	_	2400	—	—	(Admon et al.,
impoundments										2001)
FFU	34–	29–	520-	120-	12–110	19–120	66–380	—	—	(Kriipsalu et al.,
	370	400	2100	1300						2008)
Refinery oily	0.03	_	0.60	_	0.04	_	_	_	_	(Mishra et al.,
sludge										2001)
Refinery oily	32-	0.001-	7-80	17-25	27-80	_	_	_	19-24	(Bhattacharyya
sludge	120	0.12	1 00	17 20	27 00				17 21	and Shekdar
siddge	120	0.12								2002
Definers aller	12 02	4 0	(5 01	1 0	1 2		0.26	210	105 120	2003)
Refinery only	13-93	4–9	03-84	4–8	1-3	_	9–20	310-	105-150	(Maziova and
sludge								360		Meshcheryakov,
										1999)

Table 2.1. Heavy metal content in oily sludge generated from various refineries

^a The data was not obtained.

2.3. Toxicity of oily sludge

Oily sludge was classified as hazardous waste because of the presence of toxic components such as benzene, toluene, ethylbenzene, and xylenes (BTEX), and PAH (USEPA, 2012). The improper disposal of oily sludge may pose serious threats to public health and the environment. The volatilization of oily sludge can cause volatile organic compounds (VOCs) in the atmosphere, leading to human health risk to the onsite workers and surrounding communities. Among these risks, the aromatic VOCs, including benzene, toluene, ethylbenzene, and isomers of xylene (BTEX) are considered a primary health concern (Hejazi et al., 2003). Exposure to BTEX can cause a variety of health problems such as cancer, liver and kidney damage, and impairment of the central nervous system (Hejazi et al., 2003). The US Occupational Safety and Health Administration (OSHA) has established 8 h work exposure limits for BTEX: 1ppm (3.19 mg/m^3) for benzene, 200ppm (753.6 mg/m³) for toluene, 100ppm (434 mg/m³) for ethylbenzene, and 100ppm (434 mg/m³) for xylene (NIOSH, 2018). The Ministry of Environment in British Columbia (BCMOE) has established the following threshold limits for disposal of oily waste in landfill: 25 mg/kg for benzene, 150 mg/kg for toluene, 250 mg/kg for ethylbenzene, and 250 mg/kg for xylene (BCMOE, 2016). When BTEX values are above these limits, the oily waste must be pretreated before landfill.

The petroleum hydrocarbons (PHCs) and heavy metals from oily sludge may migrate through the soil and contaminate the terrestrial environment. PHCs contamination could reduce water retention capacity (i.e., wettability) of soils, leading to desiccation of surface soils on slops and to severe erosional problems (McGill et al., 1981). The hydrophobic films formed near the soil surface due to the accumulation of degradation products may reduce the water availability while limiting water and gas exchange between the soil and the atmosphere (Robertson et al., 2007). High concentration of PHCs may create nutrient-deficient conditions, inhibit seed germination, reduce plant yields, slow plant growth, and directly kill plants (McGill et al., 1981). It has been noted that microbial activity is stimulated by the addition of PHCs to soil, which was probably due to the adaptation and growth of the microbial petroleum-decomposing population (McGill et al., 1981). The presence of PHCs increased the total microbial number in soil; however, the population diversity is lower in PHC-contaminated soil compared to unpolluted soil (McGill et al., 1981).

The petroleum hydrocarbons (PHCs) and heavy metal ions may leach into the groundwater that is linked with other aquatic system. The fate of PHCs once they are released into aquatic environment depends on the hydrologic conditions (e.g., tides and winds) of the receiving water, the soil and water temperature, and the composition of PHCs (Hall et al., 1978). The light volatile compounds are lost through volatilization (Wake, 2005). The dissolved/dispersed hydrocarbon in water was due to the presence of the compounds with water solubility such as aromatics (González et al., 2006). Some PHCs can be degraded by chemical and biotic pathways, while others may incorporate into sediments and beach (Hall et al., 1978). The effects of PHCs on marine organisms are broad and sometimes persistent, including growth inhibition, respiratory distress, reduced reproduction, and bio-magnification of hydrocarbon compounds through the food web (Wake, 2005).

Aromatic hydrocarbons are generally more toxic than aliphatics. Therefore, the quantity and composition of aromatic hydrocarbons are of special concern in the evaluation of toxicity of PHC mixtures. Polycyclic aromatic hydrocarbons (PAHs) are chemical compounds containing two or more benzene rings in a linear, cluster, or angular arrangement. PAHs with four or more benzene rings are often mutagenic and/or carcinogenic (Pacheco and Santos, 1997). The International Agency for Research on Cancer (IARC) classifies some PAHs as known, possibly, or probably human carcinogens (IARC WGECRH, 2010). Among these are benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, indone(1,2,3-cd)pyrene, and dibenzo(a,h)anthracene (IARC WGECRH, 2010). Humans and other ecological receptors can absorb PAHs through inhalation, ingestion, or direct dermal contact (K.-H. Kim et al., 2013). Health effects from exposure to PAHs include eye and skin irritation, nausea and vomiting, inflammation, decreased immune efficiency, cataracts, kidney and liver damage, skin, lung, bladder, and gastrointestinal cancers, and DNA damage (K.-H. Kim et al., 2013). The Canadian Council of Ministers of the Environment (CCME) set the soil quality guideline value for benzo(a)pyrene, the most carcinogenic PAH, at 0.6 mg/kg or 5.3 mg/kg, based on incremental lifetime cancer risks (ILCR) of 10⁻⁶ or 10⁻⁵, respectively (CCME, 2008a). According to the US EPA, the maximum contaminant level (MCL) for benzo(a)pyrene in drinking water is 0.0002 mg/L (USEPA, 2015).

Heavy metal ions from oily sludge pose a risk to public health because of their toxicity, persistence, high solubility, mobility, and biological accumulation. Some heavy metals (e.g., copper, cobalt, iron, manganese, and zinc) are essential for living organisms but excessive levels of essential metals are harmful. The non-essential metals (e.g., cadmium, lead, and mercury) undergo bio-magnification and have the potential to cause serious health effects, such as liver and kidney damage, brain and nerve damage, and cancers (Wu et al., 2016). The US EPA established strict MCL goals for heavy metal ions in drinking water: 1.3 mg/L for Cu, 0.015 mg/L for Pb, 0.1 mg/L for Cr, and 0.002 mg/L for Hg (USEPA, 2015). The coexistence of PHCs and heavy metals in oily sludge contaminated soil could have complex impacts on its microbial community. Some studies have demonstrated that heavy metal ions can retard the

rate of oil biodegradation in the environment due to the presence of toxic metal ions inhibiting the activity of the organic-degrading microorganisms (AL-Saleh and Obuekwe, 2005; Said and Lewis, 1991). However, the stimulating effects of heavy metal ions on microbial processes have also been documented (Chen et al., 1997; Shen et al., 2005). For example, Shen et al. (2005) reported the interaction between Zn and phenanthrene enhanced urease activity over an incubation time of 21 days.

2.4. Techniques for treating oily sludge

A plausible solution in oily sludge management should consider the implementation of the 3Rs (Reduce, Reuse, and Recycle) policies and strategies (Demirbas, 2011):

a) Reduce: action that reduces the amount of oily sludge generated;

b) **Re-use:** technology that focuses on the re-use of oily sludge without treatments that modify its physicochemical properties; and

c) **Recycle**: technology that allows a profit to be generated from oily sludge by altering its physicochemical properties (da Silva et al., 2012).

The selection of the oily sludge treatment will always be site specific and rely on factors such as the amount and type of oily sludge available, the cost of treatment, time, and legal and environmental considerations. Comprehensive reviews of physical, chemical, and biological processes specifically for oily sludge treatment are available in the literature (da Silva et al., 2012; Hu et al., 2013). A summary of oily sludge treatment methods is shown in Table 2.2.

Technology	Description	Advantages	Disadvantages
Physical methods			
Separation	Solids/liquids separation by floatation or centrifugation	Easy to operate, low space requirements	Viscosity reducing pre- treatment requirement, noise problem for centrifugation
Landfill	The isolation of oily sludge from air and water is achieved through the use of thick layers of impermeable clay and synthetic liner	Relatively low cost, large treatment capacity	Slow process, requiring a large space, leachates may need proper treatment
Electrokinetic (EK)	The application of a low level direct current electric potential through electrodes, which are placed into the contaminated soil, ionic contaminations are transported to the oppositely charged electrode by electromigration, soluble contaminants may be removed by electroosmotic flow	Cost-effective, has the potential to remove co- existing heavy metal and organic pollutants from soils	Low removal efficiency for non-polar organic pollutants, long remediation time
Solvent extraction	Sufficient solvent is mixed with the oily sludge to ensure complete miscibility, semi-volatile and non-volatile organic compounds can be effectively removed from soil/water matrices	Simple, fast, effective, energy recovery	Large volume of solvent consumed, high cost, depending upon solvent may not be environmentally sound
Chemical methods			
Incineration	High temperature oxidation which converts oily sludge into gaseous products and ash	Waste reduction, complete removal of	The generation of off-gases containing PAH and BTEX, auxiliary fuel is required

Table 2.2. Summary of technologies for the oily sludge treatment

Technology	Description	Advantages	Disadvantages
		PHCs, heat value can be reused	
Oxidation	PHCs are degraded through chemical (e.g., Fenton's reagent and ozone) or other advanced oxidation reactions (e.g., photocatalytic degradation)	Relative insensitive to external disturbances (e.g., temperature), short treatment duration	High cost, a large volume of chemical oxidant is needed
Stabilization/ Solidification (S/S)	S/S involves the addition of binders to achieve: (a) stabilization of oily sludge by converting contaminants into a less toxic and/or less soluble form, and (b) solidification of the oily sludge into a durable matrix with high structural integrity	Rapid treatment, able to immobilize heavy metals	Risk associated with long term stabilization, an increase in the volume of waste
Pyrolysis	Thermal desorption of organic materials into a solid (char) and volatile matter (liquid and gases) in an inert environment	Fast, energy recovery, waste reduction, and less secondary pollution, able to immobilize heavy metals	High energy consuming, high capital, maintenance, and operational costs
Biological methods			
Land-farming	Oily sludge is scattered and mixed into the thin soil layer (≤ 1.5 m) in a controlled manner allowing the microbiota in the ground to act as a degrading agent	Low cost, simple operation, low energy consumption, large treatment capacity	Slow process, not efficient in degrading the heavy components of petroleum, VOCs emission problem, risk of underground water pollution
Biopile	The piling of oily sludge contaminated soil into piles, aerobic microbial activity is situmlated by aeration and the addition of minerals, nutrients, and moisture	Faster and more effective than land-farming, VOCs emissions are controlled	Higher cost and smaller treatment capacity than land- farming

Technology	Description	Advantages	Disadvantages
Bio-slurry	Bio-slurry dissolves oily sludge into an aqueous phase, and microbially degrading the PHCs, it allows the addition of nutrients, oxygen, microorganisms, and surfactants	Fastest biodegradation approach, VOCs emission is controlled	High cost, the fine solids after bio-slurry treatment still need dewatering and disposal
Phytoremediation	Phytoremediation uses plants and their associated microorganisms to remove pollutants from the environment or to make them harmless, plants take up, accumulate, stabilize, and/or degrade pollutants	Low cost, aesthetically pleasing, minimum environmental disturbance	Slow process, climate may limit plant growth, disposal of the plants used is required, contaminants may enter the food chain

(Source: da Silva et al., 2012; Hu et al., 2013; Khan et al., 2004)

Physical separation is often used as a pretreatment technique prior to other techniques, such as landfilling and incineration (van Oudenhoven et al., 1995). In the past few decades, landfill has been one of the most commonly used methods for the disposal of oily sludge (van Oudenhoven et al., 1995). The disposal in landfills needs much space and it is still possible for the harmful compounds, especially PAHs and heavy metals, to leach out of the treated soil and contaminating the surrounding ecological system (Renou et al., 2008). Moreover, the use of landfills is being gradually prohibited or restricted because of more restrictive disposal regulations (da Silva et al., 2012; Elektorowicz and Habibi, 2005). According to the Hazardous Waste Regulation issued by BCMOE, oily sludge containing more than 10 % oil (by weight) cannot be accepted at any landfills in British Columbia (BCMOE, 2016). Consequently, the use of landfill is only considered when other techniques, such as re-using or recycling, are not readily available.

Another common method of disposing of oily sludge is incineration. Although incineration can greatly reduce the volume of waste, it has certain limitations such as the need for auxiliary fuel, the emission of hazardous off-gases (PAH, BTEX, dioxins, and furans), and high cost (da Silva et al., 2012). To meet air pollution regulations, the off-gases must be cleaned before being discharged into the atmosphere. Capital equipment costs for an incinerator that processes between 3 and 10 tons h^{-1} range from US\$ 3.5–5 million (Ball et al., 2012). The operational costs associated with remediating petroleum-contaminated solids by incineration can range from US\$140 to US\$700 per tonne (Ball et al., 2012; van Oudenhoven et al., 1995).

Biological treatment by land-farming or by using a biopile may have large treatment capacity and low operational cost, but they are often ineffective in removing high molecular weight hydrocarbons (Khan et al., 2004). Additionally, the microbial degradation process in land-farming and biopile can be very time-consuming (from 6 months to 2 years) (Khan et al., 2004). In terms of a bio-slurry treatment, the biodegradation process occurs in a confined and highly controlled system. The conditions such as temperature, moisture, pH, oxygen, nutrients, supplementation of microorganisms, and addition of surfactant are controlled, which results in an increase in the rate of biodegradation (Ball et al., 2012). The treatment times for bio-slurry can range from less than 1 month to more than 6 months (Khan et al., 2004). The major obstacle to applying this technology to field-scale oily sludge treatment is the high cost. For example, Castaldi (2003) reported the cost of operating a bio-slurry process for oily sludge was US\$625 per ton. In comparison, an estimate for land-farm bioremediation of hydrocarbon-contaminated soil (based on 2700 m³ of material) was reported to be US\$10.3 per ton (Line et al., 1996).

In summary, some treatments such as incineration are effective in totally removing PHCs from oily sludge but have the highest costs. Other treatments such as land-farming have lower costs but their degradation process can be very time-consuming and/or they fail to meet the requirements for the reduction of large molecular weight species and metal ions in the oily sludge. As the basic theme of United Nations Conference on Environment and Development (UNCED) in 1992 stated, "Sustainable development" is commonly understood as development that "meets the needs of the present without compromising the ability of future generations to meet their own needs". A sustainable technique for oily sludge management needs to be both environmentally effective and economically affordable (Morrissey and Browne, 2004). Most of the available techniques do not satisfy a sustainable development approach. There is a demand for the development of new techniques for recycling and treating oily sludge with added environmental and economic benefits.
2.5. Ionic liquid-enhanced solvent extraction

2.5.1. Solvent extraction

2.5.1.1. Selection of solvent

Solvent extraction is a simple process achieved by mixing an oily sludge and a solvent at proportions which ensure adequate miscibility of the oil in the solvent (Al-Zahrani and Putra, 2013). The main advantages of solvent extraction are low energy requirement, high efficiency of oil recovery, short treatment duration, and the possibility of solvent reuse (Hu et al., 2013). In solvent extraction process, the solvent molecules tend to diffuse into the oil phase since the viscosity of the solvent is much lower than that of the oil (X. Li et al., 2012). The soluble materials in the oily sludge readily mix into the solvent until they reach an equilibration between the two media. However, the insoluble fractions tend to stay on the surface of the sand grains, forming a porous network structure (Funk, 1979). Additionally, some lighter fractions can be attached to the surface of insoluble asphaltenens, which resulted in the increase of the amount of soluble materials in the network at equilibrium (X. Li et al., 2012).

From the thermodynamic point of view, solvent extraction of oily sludge can be seen as the mixing/dissolving of solvent and solute (i.e., oil components). The solubility parameter is an important physical property which characterizes the overall capability of a solvent to dissolve a solute. In 1950, Hildebrand and Scott first introduced the solubility parameter and theoretically described the relationship between solubility, heat of evaporation, and the enthalpy (heat) of mixing (Hildebrand and Scott, 1950). The solubility parameter is defined as the square root of the cohesive energy density:

$$\delta = \left(\frac{\Delta H_v - RI}{V}\right)^{1/2} \tag{2.1}$$

where δ is the Hildebrand solubility parameter, ΔH_v is the heat of evaporation, *R* is the gas constant, *T* is the absolute temperature, *V* is the molar volume of the solute. According to the Hildebrand solution theory (eq. 2.2), if solvent is miscible with solute, which means enthalpy of mixing is small and their solubility parameters would tend toward equality ($\delta_1 = \delta_2$).

$$\Delta H = V_{\rm m} \varphi_1 \varphi_2 (\delta_1 - \delta_2)^2 \tag{2.2}$$

where ΔH is the enthalpy of mixing, $V_{\rm m}$ is the molar volume of the solution, φ_1 and φ_2 are the volume fractions of the solvent and solute, respectively, and δ_1 and δ_2 are the solubility parameters of the solvent and solute, respectively.

In the middle 1960s, Hansen proposed the splitting of the Hildebrand solubility parameter into three components derived from different types of cohesive energy (i.e., dispersion, polarity, and hydrogen bonding) (Hansen, 2007):

$$\delta = \left(\delta_{\rm d}^2 + \delta_{\rm p}^2 + \delta_{\rm h}^2\right)^{1/2} \tag{2.3}$$

where δ_d is the dispersion force parameter, δ_p is the polar force parameter, and δ_h is the hydrogen-bonding force parameter. Based on the theory of Hanson solubility, good solvents always possess parameter distributions (i.e., dispersion force, polar force, and hydrogen-bonding force) in a specific range depending upon the solute (Hansen, 2007). Wang et al. (2014) reported good solvents for the dissolution of bitumen generally have relatively high values for δ_d and δ_h and a low value for δ_p .

Therefore, in the solvent extraction of oil from oily sludge, the dissolving capacity of solvent is a combination of the Hildebrand solubility parameter (δ), and the parameter distribution of the acting force parameter (δ_d , δ_p , and δ_h). According to Wang et al. (2014), a solvent with a solubility parameter close to that of asphaltene and a parameter distribution close to that of toluene is desirable for the bitumen recovery from oil sands.

2.5.1.2. Parameters affecting extraction performance

Extraction performance is also affected by operational factors such as temperature, solventto-sludge ratio, extraction duration, and stirring rate. The increase of temperature can decrease the viscosity of the oil and increase its solubility in a solvent, thereby increasing the oil recovery. However, high temperature means a large energy consumption and the loss of PHCs and solvent.

An increase in the solvent-to-sludge ratio will enhance the interaction between the oil and solvents, as well as increase the concentrations gradient between liquid-solid phases, which may result in a higher oil recovery. Additionally, the quality of recovered oil can be improved with increasing solvent-to-sludge ratio, which is evidenced by the reduction in ash, carbon residue, and asphaltene content in recovered oil when more solvent is used (Zubaidy and Abouelnasr, 2010). The aspheltene content in the extracted oil generally has a positive relationship with the concentration of oil in the solvent phase, which is likely due to the mechanism that it is the extracted oil and not the solvent that extracts the asphaltene from oily sludge (Wang et al., 2014; Zubaidy and Abouelnasr, 2010). With increasing solvent-to-sludge ratio, the concentration of oil in the solvent phase decreased (if the increase of the solvent mass exceeded the increase of extracted oil), which contributed to a lower asphaltene content (Wang et al., 2014). There is also a possibility that an increasing solvent-to-sludge ratio can decrease the oil recovery (Wang et al., 2014; Wu and Dabros, 2012). At high solvent-to-sludge ratio, some asphaltenes self-associate and form larger aggregations, leading to a lower oil recovery (Wu and Dabros, 2012).

The optimal extraction duration is affected by temperature, solvent-to-sludge ratio, and the stirring rate. As the extraction duration increases, an extraction equilibrium is reached and any

further increases in time are unlikely to significantly improve oil recovery. Finding the optimal extraction time is important in order to save costs for an extraction process. The oil recovery from oily sludge can be promoted by increasing the stirring rate. The diffusion of the dissolved materials into the solvent phase can be facilitated by stirring or agitation. In addition, external shear forces break the porous network structure into smaller particles (X. Li et al., 2012). These particles tend to be suspended in the solvent phase thus increasing the interfacial area between bitumen and solvent thereby leading to a higher rate of mass transfer.

2.5.2. Ionic liquid

The utilization of solvent is essential to solvent extraction. However, it also limits the extension of this technology to field-scale oily sludge treatment. The cost of recovering solvent from the spent or extracted sand/clay is prohibitive, especially for high-boiling-point solvents. Moreover, organic solvent exposure is associated with various health hazards, such as reproductive damage, liver and kidney damage, cancer, and toxicity to the nervous system (NIOSH, 1977). Ionic liquids (ILs) are organic salts that are composed of organic cations with organic or inorganic anions and exist in liquid state at or close to room temperature. ILs possess high thermal stabilities and negligible vapor pressure making them favorable in the applications of petroleum industry (José-Alberto and Jorge, 2011). More importantly, ILs can be customized by choosing the appropriate combination of anion and cation for specific applications (Bera and Belhaj, 2016).

Various studies have been reported on the application of ILs to reduce the precipitation of asphaltenes and other organic compounds while enhancing the stability of crude oils (Boukherissa et al., 2009; Hu and Guo, 2005; Subramanian et al., 2015). Hu and Guo (2005) studied the effect of the structures of ILs on the inhibition of asphaltnene precipitation in CO₂-

injected reservoir oils. It was found that inhibition abilities of ILs *p*-alkylpiridinium chloride ([C_npy][Cl]) decreases with the increase of alkyl chain length from n=4 to n=12 (Hu and Guo, 2005). The ILs with high anionic charge density and low cation charge density were effective in inhibiting asphaltene precipitation (Hu and Guo, 2005). According to the mechanism they proposed, the local non-neutrality of the charge density promotes the acid-base interaction between ILs and the asphaltene, thus breaking intramolecular associations within the asphaltenes (Hu and Guo, 2005). Boukherissa et al. (2009) evaluated imidazolium ILs consisting of either a boronic acid or a propenyl group with bromide anions as dispersants for petroleum asphaltenes. They observed that the viscosity of the oil was reduced from 16 Pa·s to 3 Pa·s as the IL/asphaltenes ratio increased from 0 to 2 (2 wt% asphaltene at nheptane/tolune = 2) (Boukherissa et al., 2009). The presence of boronic acid favored the interaction between the Lewis-acid moiety of the ILs and the basic regions of the asphaltene molecules, which consequently reduced the viscosity (Boukherissa et al., 2009). Subramanian et al. (2015) found small amounts of ILs (between 1ppm and 10 ppm), dissolved in toluene, reduced the viscosity of crude oil up to 35 % (with reference to the oil containing toluene). They attributed this effect to the intermolecular interactions, such as π - π , aliphatic, and acidbase interactions between the functionalized molecules and the asphaltene molecules (Subramanian et al., 2015).

Some ILs have similar surface activity and micelle formation capacity as surfactants and are thus considered to be good candidates for enhanced oil recovery process (Bera and Belhaj, 2016). Guzmán-Lucero et al. (2010) evaluated 10 ILs as de-emulsification agents to break water-in-oil (W/O) emulsions. All of the ILs tested showed good demulsifying activities in water-in-medium-crude-oil emulsions. The demulsification efficiency were greatly affected by

the structure of ILs. It was observed that the ILs with longer alkyl chain or more hydrophobic anion provided higher separation efficiency of W/O emulsions (Silva et al., 2013). Lemos et al. (2010) studied the effect of 1-octyl-3-methylimidazolium tetrafluoroborate ([Omim][BF4]) and 1-octyl-3-methylimidazolium hexafluorphosfate ([Omim][PF6]) on the demulsification of a W/O emulsion. They pointed out that the greater anion size of [Omim][PF6] hindered the aggregation of this IL in the medium, which resulted in a greater demulsification efficiency (Lemos et al., 2010). In addition, the use of microwave irradiation can dramatically increase efficiency to the demulsification of W/O emulsion by ILs. For example, very high demulsification efficiency (beyond 95%) was obtained in 30 min by the joint use of trioctylmethylammonium chloride (TOACI) and microwave irradiation (Guzmán-Lucero et al., 2010).

Apart from the oil-water separation, ILs are also used in the extraction of bitumen from oil sands. Painter et al. (2010a) evaluated the extra heavy oil production from Utah tar sands using ILs. Tar sands were mixed with three hydrophilic ILs, [Bmmim][BF4], [Bmim][CF₃SO₃], and [Emim][Ac] (Table 2.3), and toluene to give a rise to a three-phase system. The tested ILs and toluene were effective in breaking up large particles of tar sands and giving more than a 90% yield of bitumen (Painter et al., 2010a). The cleanest separation between the phases was given by [Bmmim][BF4] while extractions using [Bmim][CF₃SO₃], and [Emim][Ac] resulted in some incorporation of IL into the bitumen phase (Painter et al., 2010a). Williams et al. (2010) reported the use of the IL [Bmmim][BF4] allowed for a cleaner separation compared to solvent extraction alone. The clay bands were clearly displayed in the infrared spectrum of the toluene extract of low-grade oil sands (Williams et al., 2010). Such phenomenon was attributed to the solids in the weathered oil sands possessing a strong hydrophobicity, resulting in an adhesive

force between the bitumen and fines (Liu et al., 2005). However, there were no mineral fines in the extracts utilizing IL, while some clay fines remained suspended into the middle IL phase (Williams et al., 2010). This might be because the electrostatic interaction between the IL and the mineral fines are much more favorable than those between bitumen and fines (Williams et al., 2010).

Nevertheless, ionic liquids with high viscosity, like [Bmmim][BF4], could strongly adhere to the inner wall of pipelines and blocked the equipment increasing the difficulty of its industrial application. In this regard, some authors applied ILs with low viscosity (e.g., [Emim][BF₄]) to enhance solvent extraction (Li et al., 2011; Sui et al., 2016; Tourvieille et al., 2017). Li et al. (2011) reported the maximum bitumen recovery was 86% at the acetone-to-nheptane ratio of 2:6 (v/v) in solvent extraction alone. With IL [Emim][BF4] enhancement (1.3 mL/g of IL/oil sand ratio), an additional improvement of 10% of bitumen recovery was observed (Li et al., 2011). Since 92 % (by weight) bitumen recovery was obtained even when the IL was reused 10 times, the solvent extraction technology using composite solvent enhanced by IL was encouraged to be extended from bench scale to the oil sand industry by Li et al. (2011). Sui et al. (2016) examined the effect of operational parameters (i.e., IL-to-oil sands ratio, agitation time, and conditioning time) on bitumen recovery from oil sands using IL enhanced solvent extraction. It was found that bitumen recovery increased as IL-to-oil sands ratio and agitation time increased, whereas the conditioning time had a negligible effect on bitumen recovery. Tourvieille et al. (2017) assessed the impact of variables (i.e., temperature, contact time, solvent-to-oil sands ratio, IL-to-oil sands ratio, water-to-IL ratio, solvent, and IL types) on bitumen recovery and bitumen quality. It was observed that the IL-to-solids ratio (0.75-2 g/g) and type of IL had no significant effect (P > 0.05) on bitumen recovery (Tourvieille et al., 2017). However, types of IL used does play a significant role in aluminum (Al) content in recovered bitumen. [Amim][DCA] leads to an increase of Al content in bitumen, whereas [EtNH₃][NO₃] was significant in decreasing Al content in bitumen (Tourvieille et al., 2017). [Amim][DCA] was less capable in retaining inorganic material because of its longer hydrocarbon tail and increased π - π interactions (Tourvieille et al., 2017). Conversely, the shorter hydrocarbon tail and higher viscosity for the [EtNH₃][NO₃] may be responsible for its efficiency in capturing fines from bitumen (Tourvieille et al., 2017). Table 2.3 provides the structures and physical properties of some of the ionic liquids employed in various studies of oil recovery from tar sands.

Ionic liquid	Structure	Viscosity (mPa·s) at 25 °C	Density (g/cm ³) at 25 °C	Performance	References
1-butyl-2,3-dimethyl- imidazolium tetrafluoroborate ([Bmmim][BF ₄])	$\begin{array}{c} \begin{array}{c} \begin{array}{c} \bullet \\ N \end{array} \\ \hline \\ N \end{array} \\ \hline \\ CH_3 \end{array} \\ F \end{array} \\ \begin{array}{c} F \\ F \end{array} \\ F \\ \hline \\ CH_3 \end{array} \\ F \\ \hline \\ CH_3 \end{array}$	456 (Bou Malham and Turmine, 2008)	1.19 (Bou Malham and Turmine, 2008)	>90% bitumen recovery, high viscosity, clean separation (no IL and fines in the bitumen)	(Li et al., 2011; Painter et al., 2010a)
1-butyl-3-methyl-imidazolium trifluoromethanesulfonate ([Bmim][CF ₃ SO ₃])	$ \begin{array}{c} \stackrel{+}{{\underset{N}{}{\underset{F}{}{\underset{F}{}{\underset{O}{}{\underset{O}{}{\underset{F}{}{\underset{O}{}{\underset{O}{}{\underset{O}{}{\underset{O}{}{\underset{O}{}{\underset{O}{}{\underset{O}{}{\underset{O}{}{\underset{O}{}{\underset{O}{}{\underset{O}{}{\underset{O}{}{\underset{O}{}{\underset{O}{}{\underset{O}{}{\underset{O}{}{\underset{O}{}{\underset{O}{}{\underset{O}{}{\underset{O}{}{\underset{O}{}{\underset{O}{}{\underset{O}{}{\underset{O}{}{\underset{O}{}{\underset{O}{}{\underset{O}{}{\underset{O}{}{\underset{O}{}{\underset{O}{}{\underset{O}{}{\underset{O}{}{\underset{O}{}{\underset{O}{}{\underset{O}{}{\underset{O}{}{\underset{O}{}{\underset{O}{}{\underset{O}{}{\underset{O}{}{\underset{O}{}{\underset{O}{}{\underset{O}{}{\underset{O}{}{\underset{O}{}{\underset{O}{}{\underset{O}{}{\underset{O}{}{\underset{O}{}{\underset{O}{}{\underset{O}{}{\underset{O}{}{\underset{O}{}{\underset{O}{}{\underset{O}{}{\underset{O}{}{\underset{O}{}{\underset{O}{}{\underset{O}{}{\underset{O}{}{\underset{O}{}{\underset{O}{}{\underset{O}{O$	75.3 (Ge et al., 2008)	1.30 (Ge et al., 2008)	>90% bitumen recovery, less clean (small amounts of IL was found in the bitumen)	(Painter et al., 2010a)
1-ethyl-3-methyl-imidazolium acetate ([Emim][Ac])	⁺ CH ₃ O O CH ₃	141.1 (Nazet et al., 2015)	1.09 (Nazet et al., 2015)	>90% bitumen recovery, less clean (small amounts of IL was found in the bitumen)	(Painter et al., 2010a)
1-ethyl-3-methyl-imidazolium tetrafluoroborate ([Emim][BF ₄])	$ \begin{array}{c} $	66.5 (Huddleston et al., 2001)	1.25 (Seddon et al., 2002)	Up to 95% bitumen recovery, relatively low viscosity, clean separation (no IL and fines in the bitumen)	(Li et al., 2011; Sui et al., 2016)

Table 2.3. Summary of ionic liquids used in bitumen recovery from oil sands

Ionic liquid	Structure	Viscosity (mPa·s) at 25 °C	Density (g/cm ³) at 25 °C	Performance	References
ethylammonium nitrate ([EtNH ₃][NO ₃])	H_3C $NH_3^+ O = N_{+}^+ O^-$	32.0 (Greaves et al., 2006)	1.22 (Greaves et al., 2006)	IL type had no significant effect on bitumen recovery, low aluminum content in the bitumen	(Tourvieille et al., 2017)
1-Allyl-3-methylimidazolium dicyanamide ([Amim][DCA])	⁺ CH ₃ N≡−N CH ₂ N	14.0 (Tourvieille et al., 2017)	_	IL type had no significant effect on bitumen recovery, high aluminum content in the bitumen	(Tourvieille et al., 2017)

2.6. Pyrolysis

2.6.1. Pyrolysis in oily sludge treatment

Pyrolysis is a thermal disposal method which converts organic materials into a carbon-rich solid (char) and volatile matter (liquid and gases) in an inert environment. It has the unique characteristic of being able to break down large molecules into smaller ones ("cracking"). In pyrolysis, the emission of hazardous materials (e.g., NO_X, SO₂, and heavy metals) may be decreased relative to straight incineration (Li et al., 1999). Moreover, the reduced air flow rate and lower temperature make emission controls easier for pyrolysis than for incineration (Li et al., 1999). The most important advantage of pyrolysis is that it can generate solid, liquid, and gaseous fractions all of which can be used as fuels in subsequent applications or to drive the pyrolysis process while the liquid fuels are easily stored and transported (Martínez et al., 2014). The solid product of pyrolysis (i.e., char) has the potential ability to enhance soil quality and/or immobilize metal ions due to its unique properties (e.g., retention of water and nutrients, porous structure, and cation exchange capacity) (Mullen et al., 2010; Uchimiya et al., 2010).

Pyrolysis is a promising strategic approach to the sustainable management of oily sludge having the ability to not only minimize the solid waste, but also to yield valuable products. Schmidt and Kaminsky (2001) reported that about 70–84 % of the oil can be separated from oily sludge during the pyrolysis in fluidized bed reactors at temperatures from 460–650 °C. Shie et al. (2000) studied the kinetic and thermal conversion behavior of oily sludge pyrolysis at various heating rates (i.e., 5.2, 12.8, and 21.8 °C/min) by thermogravimetric analysis (TGA). The TGA curves were represented by the two- and three-reaction models relatively well (Shie et al., 2000). As the heating rate increased, the peak value of reaction rate increased, and the TGA curve shifted to higher temperatures (i.e., the weight loss occurred at higher temperatures)

(Shie et al., 2000). According to the differential thermogravimetric analysis (DTG) curve of oily sludge, the major mass loss of the oily sludge was observed in a temperature range of 100–550 °C with peak mass losses at temperatures of 110–150 and 150–550 °C probably due to the decomposition of light PHCs and complex PHCs, respectively (Hu et al., 2017). At temperatures above 550 °C, the decomposition of inorganic compounds (such as CaCO₃, MgCO₃, etc.) might take place (Liu et al., 2009; Wang et al., 2007).

Chang et al. (2000) investigated the major products obtained from the pyrolysis of oily sludge at 600 °C. It was observed that the mass fraction of solid residues, liquids, and gases in the final product was 13.10 wt%, 69.93 wt%, and 3.57 wt%, respectively (Chang et al., 2000). The liquid product consisted of 66.58 wt% light gas oil with a boiling range between 204–338 °C, indicating the distillation characteristics of liquid product was close to that of diesel oil (Chang et al., 2000). Their results also indicated that the major gaseous products excluding N₂, were CO₂ (50.88 wt%), hydrocarbons (HCs) (25.23 wt%), H₂O (17.78 wt%), and CO (6.11 wt%) while the HCs gases mainly consisted of low molecular weight organic species, especially C_{1-2} (51.61 wt%). The research by Liu et al. (2009) has shown that around 80% of total organic carbon content (TOC) in oily sludge can be converted into HCs by a pyrolysis process, with significant HCs yields occurring in the temperature range of 327–450 °C. They found that a higher heating rate resulted in a higher peak value of HCs evolution rate and a higher temperature for its occurrence.

2.6.2. Effects of parameters on liquid production

Qin et al. (2015) found oil yield increased initially with pyrolysis temperature with a maximum oil yield (59.2 wt% of feed oily sludge) occurring at 500 °C, which was consistent with other studies (Hu et al., 2017; Shen and Zhang, 2003). The decrease in oil yield above

500 °C may be attributed to the secondary decomposition reactions which break the oil into lighter, gaseous hydrocarbons (Qin et al., 2015). Liu et al. (2008) studied the effects of temperature on the composition of oil produced from pyrolysis of oily sludge in a fixed bed reactor. It was found that as the temperature increased from 350 to 550 °C, the light oil content increased from 49.8 to 69.2 wt%, whereas the heavy oil content decreased from 31.2 to 10.8 wt%. This result is in agreement with another pyrolysis study carried out in a fluidized bed reactor (Shen and Zhang, 2003). According to Liu et al. (2008), the alkene and aromatic content in the oil product increased with rising temperature. The decarboxylation reaction accompanied by cracking might be responsible for the rise in the alkene compounds (Jindarom et al., 2007b). The formation of aromatic compounds at high temperatures was mainly attributed to Diels-Alder reactions (Park et al., 2008; Zhang et al., 2011).

Shen and Zhang (2003) found oil yield decreased from a maximum of 30 to 21 wt% with increasing gas residence time from 1.5 to 3.5 s due to the occurrence of secondary cracking reactions. Their results also indicated that the proportion of lighter compounds increased when the gas residence time increased. Similarly, Wang et al. (2007) found the operation of holding at 400 °C for 20 min decreased the amount of heavy oil product and increased the amount of gasoline and diesel oil. Thangalazhy-Gopakumar et al. (2015) reported high heating rates supplied more thermal energy to overcome the temperature gradient inside the oily sludge leading to an increase in the gas and liquid fractions. Wang et al. (2007) also found that more oil was produced as the heating rate increased from 5 to 20 °C/min. They attributed this effect to the preferable formation of free radicals at high heating rates.

Shie et al. (2004) found chemical additives (i.e., sodium and potassium compounds) enhanced the reaction rate when the temperatures were in 377–437 °C probably due to the

dispersion of the inorganic additives throughout the mixture and their catalytic properties. Ma et al. (2014) evaluated quartz sand as a solid heat carrier in the pyrolysis process of oily sludge and they found oil yield increased from 16.63 wt% at the sludge/sand ratio of 1:0 to the maximum yield of 28.87 wt% at sludge/sand ratio of 1:2. They suggested this could be due to the higher heat transfer coefficient of quartz sand (i.e., 1.03 W/m·K) than that of the gas medium (i.e., 0.25 W/m·K) (Cheng et al., 2016a; Ma et al., 2014). Studies on the addition of oily sludge ash in the pyrolysis of oily sludge have been carried out with TGA (Shie et al., 2004) and stirred tank reactor (Cheng et al., 2016a, 2016b). It was reported that the addition of oily sludge ash not only decreased the carbon residue of the oil product but also increased the light oil/heavy oil ratio. These improvements might be due to the high contents of Fe and Ca in the oily sludge ash (Shie et al., 2004). Results from other studies also indicated that additives of metal oxides (Al₂O₃, Fe₂O₃, and CaO), metal salts (Fe₂(SO₄)₃H₂O and AlCl₃) and zeolite catalysts (ZSM-5, Y-zeolite) affect the reaction efficiency, yield and quality of oil product (Pánek et al., 2014; Shie et al., 2004; Wang et al., 2017a).

2.6.3. Effects of parameters on gas production

Generally, an increase in pyrolysis temperature increases gas yield, as reported by Liu et al., (2008), Qin et al., (2015) Shen and Zhang, (2003), and Wang et al., (2007). According to Qin et al. (2015), the increase of the gaseous products at 400–500 °C was mainly due to the vaporization of oil, while the increase of the gaseous products at 500–600 °C was attributed to the secondary cracking or thermal decomposition of the oils. Liu et al. (2008) found the content of HCs and H₂ increased as the temperature increased from 350 to 550 °C resulting from the further cracking of organic compounds at higher temperatures. In contrast, the concentrations of CO and CO₂ decreased with temperature increasing from 350 to 550 °C. This might be

because the decomposition of carbonyl and carboxyl functional groups occurred at lower temperatures (<450 °C) (Liu et al., 2008). In contrast, Qin et al. (2015) showed an increase in CO concentration when the temperature was above 550 °C. This might result from the reaction shown in eq. (2.4) occurring at high temperatures (Qin et al., 2015). Moreover, high temperatures (>550 °C) may also be responsible for the reduction of C_mH_n (C_2H_4 , C_2H_6 , and C_3H_8) (Qin et al., 2015; Wang et al., 2007). Typical reactions are shown in eq. (2.5) and (2.6) (Leung et al., 2002).

$$C + H_2O \rightarrow CO + H_2 \quad \Delta H_{298K} = 132 \text{ KJ/mol}$$
 (2.4)

$$C_2H_6 \rightarrow C_2H_6 + H_2 \tag{2.5}$$

$$C_2H_4 \to CH_4 + H_2 \tag{2.6}$$

Shen and Zhang (2003) observed that an increase in the gas residence time from 1.5s to 3.5 s led to an increase in the gas fraction due to secondary cracking reactions. Wang et al. (2007) studied the changes of C_{1-6} hydrocarbons content utilizing an interval holding at 400 °C for 20 min. They found the concentration of C_{1-3} hydrocarbons had increased while the concentration of C_{4-6} hydrocarbons significantly decreased regardless of the final pyrolysis temperature of either 500 or 700 °C.

Wang et al. (2007) found the gas yield increased slightly from 15.3 to 17.8 wt% when increasing the heating rate from 2.5 to 10 °C/min. Inguanzo et al. (2002) investigated the effect of heating rates on the characteristics of the gas product. When the heating rate was 5 °C/min, a maximum heating value of gas (i.e., 25 MJ/m³) was obtained at 455 °C with the maximum release of C₂H₄ and C₂H₆. However, the maximum heating value of gas (i.e., 20 MJ/m³) at the heating rate of 60 °C/min appeared at 600 °C.

Wang et al. (2007) studied the effect of adding catalyst (i.e., FCC (a fluid catalytic cracking catalyst), NaOH, and Cu(NO₃)₂·3H₂O) on the gas yield and composition. They found pyrolysis of oily sludge with these three additives resulted in a higher production of gas and an increase in the light hydrocarbons (i.e., C_{1-3}) content, suggesting the additives were favorable to induce the formation of free radicals. Ma et al. (2014) found gas yield increased from 2.89 wt% at the sludge/sand ratio of 1:0 to 28.25 wt% at the sludge/sand ratio of 1:3 due to the high heat transfer coefficient in sand. Cheng et al. (2016a) found the addition of oily sludge ash increased the H₂ content from 26.62 wt% (no addition) to 34.05 wt%. The increase of H₂ content could be attributed to the catalytic effect of CaO contained in the oily sludge ash (Cheng et al., 2016b). It was reported that the active site of CaO can promote the breakage of the C–H bond and intensify the dehydrogenation during pyrolysis (Yongbin et al., 2004).

2.6.4. Effects of parameters on solid production

The yield of solid from pyrolysis has been found to decrease with increasing pyrolysis temperature (Liu et al., 2008; Qin et al., 2015; Shen and Zhang, 2003). This might be attributed to the de-volatilization of the hydrocarbons and partial gasification of the carbonaceous residues in the char at high temperatures (Zhang et al., 2011). Shen and Zhang (2003) observed that an increase in the gas residue time led to a decrease in solid yields. Other authors studying the influence of the temperature and gas residue time have found similar trends for the yield of solids (Fonts et al., 2008). However, the heating rate was reported to have an insignificant influence on the solid yield from the pyrolysis of oily sludge (Punnaruttanakun et al., 2003; Wang et al., 2007).

The HHV of chars given in the existing literature varied between 7.02–34.4 MJ/kg due to the different origins of the oily sludge and pyrolysis conditions (Liu et al., 2008; Qin et al.,

2015; Thangalazhy-Gopakumar et al., 2015). Differenting from the chars generated from biomass, the sludge chars generally have a higher ash content (Karayildirim et al., 2006; Zhang et al., 2015). This might be because most of the inorganic content such as silicon, aluminum, and iron remained in the char while the organic content was reduced during pyrolysis of oily sludge (Zhang et al., 2015). An HHV near to 7 MJ/kg and high ash content make them unattractive for use in incineration. For this reason, some authors advocate the use of oily sludge-derived char (OSDC) for adsorbent production. For example, Mohammadi and Mirghaffari (2015) produced char from oily sludge by pyrolysis and found the Brunauer-Emmett-Teller (BET) surface area of the char was relatively low (i.e., $3.63 \text{ m}^2/\text{g}$). To improve the surface area, they used potassium hydroxide (KOH) as an activator to produce activated char with a much higher surface area (i.e., $327.97 \text{ m}^2/\text{g}$). It was observed that the maximum sorption amount for Cd²⁺ by the activated char (i.e., 19.23 mg/g) was higher than that of nonactivated char (i.e., 1.49 mg/g). Wang et al. (2017b) produced high quality activated char from oily sludge by adding a solvent de-oiling step before activation, with the resulting surface area reaching 3292 m²/g. After the de-oiling treatment, the methylene blue adsorption capacity significantly increased from 267 mg/g to 969 mg/g.

Many efforts have been made to investigate the production of sewage sludge-derived biochars and their sorption mechanisms (Smith et al., 2009). Jindarom et al. (2007a) developed a potential adsorbent for dye removal by pyrolysis of sewage sludge at 750 °C under a CO₂ atmosphere. The maximum adsorption capacities of acid yellow 49, basic blue 41, and reactive red 198 dyes were reported to be 116 mg/g, 588 mg/g, and 25 mg/g, respectively and the electrostatic interactions and dispersive interactions were deemed the dominant mechanisms for dye adsorption. Seredych and Bandosz (2006) found the sewage sludge-derived biochar

obtained at 650 °C had the Cu²⁺ removal capacity of 63.48 mg/g, which is higher than that of the biochar obtained at 900 °C (34.01 mg/g). They found the major sorption mechanism of Cu²⁺ on biochar obtained at 650 °C was via a cation exchange reaction, leading to the release of Mg²⁺, Ca²⁺, and Zn²⁺ during sorption process. However, high temperature pyrolysis at 950 °C resulted in biochar with a high degree of mineralization and therefore Cu²⁺ was mainly sorbed via surface complexation and precipitation such as the formation of copper hydroxide. Lu et al. (2012) found the biochar derived from pyrolysis of sewage sludge at 550 °C effectively removed Pb²⁺ from acidic solution (pH 5) with the capacity of 30.88 mg/g. Their results also showed that the Pb²⁺ sorption involved the coordination with organic carboxyl and hydroxyl functional groups (accounting for 38.2%) and the precipitation or complexation on mineral surface (accounting for 61.8%).

Pyrolysis temperature plays a significant role in changing biochar properties and its removal efficiency for contaminants. For example, T. Chen et al. (2014) studied the influence of pyrolysis temperature (500–900 °C) on properties and heavy metal adsorption ability of sewage sludge biochar and found the best result was obtained for biochar pyrolyzed at 800 °C, with the Cd²⁺ removal capacity of more than 15 mg/g. It was found that with the increasing temperature, the ash content and microstructure development of biochar was promoted but the concentrations of surface functional groups remained low. Generally, the biochar produced from sewage sludge pyrolysis at low temperature was acidic whereas at high temperature it was of a basic nature (Hossain et al., 2011; Zhang et al., 2015). Some authors have attributed this behavior to the reduction of acidic surface groups during pyrolysis (Gascó et al., 2005). It was found that aromatic ratios of H/C and O/C decreased with increasing pyrolysis temperature, suggesting the reduction of surface functional groups on the biochars (T. Chen et al., 2014;

Zhang et al., 2015). As a result, biochar samples obtained at higher temperatures were less polar and had greater aromaticity compared to those prepared at lower temperatures. Ahmad et al. (2012) reported better adsorbent properties of biochar produced at higher temperature as a consequence of the higher aromaticity and lower polarity.

During pyrolysis, the carbon content structurally rearranges and condenses to biochar with a higher density. Further activation can promote pore development leading to a biochar which is less dense and more porous (Lima et al., 2009). Activated char can be produced by either physical activation or chemical activation or a combination of both. Jindarom et al. (2007a) found the CO_2 activation enhanced the formation of micropores in sewage sludge char. The surface area was increased to 60.7 m²/g for CO₂ activated char (at 750 °C), which is 1.8 times that of non-activated char (at 750 °C). This may be attributed to the fact that CO₂ gasification could remove carbon atoms from the interior of the particle, leading to the expansion of opened micropores or the opening up of closed micropores (Jindarom et al., 2007a). Chemical activation of sewage sludge-derived biochars can be performed using a pyrolysis process emplying a dehydrating reagents such as KOH (Lillo-Ródenas et al., 2008), NaOH (Zou et al., 2013), ZnCl₂ (Zhang et al., 2005), and H₃PO₄ (Ros et al., 2006). All these agents could enlarge the BET surface area of biochars and eventually lead to better sorption capacity (Ros et al., 2006; Zhang et al., 2005). Chemical activation with $ZnCl_2$ promoted the aromatization of the carbon skeleton, while inhibiting tar formation, thus improving the porosity of materials (Gupta and Garg, 2015). The presence of H_3PO_4 during activation can increase the yield of porous biochar by promoting depolymerisation, dehydration, and redistribution of constituent biopolymers (Kumar and Jena, 2016). Zhang et al. (2005) found the BET surface area of H_3PO_4 activated biochar (289 m^2/g) was about two times higher than that of non-activated biochar

(137 m²/g). However, Ros et al. (2006) found chemical activation with H₃PO₄ was ineffective for porosity development of sewage sludge-derived biochar with BET surface areas of 6–17 m²/g. They attributed the difference to the higher activation temperature employed by Zhang et al. (2005). Zou et al. (2013) characterized the activated biochar from sewage sludge by chemical activation with NaOH and found the BET surface area and pore volume of activated char was about 3 times higher than that of non-activated char (121.3 m²/g and 0.102 cm³/g) at the same temperature (600 °C). They also found more oxygen-containing functional groups on the surface of NaOH activated biochar facilitated hydrogen bonding with organic pollutants, and enhanced its adsorption capacity. During the activation process, the oxidation of carbon into carbonate and formation of intercalated compounds, such as Na₂SiO₃, can cause gasification and emission of steam and carbon-dioxide, resulting in the formation of pores (Zou et al., 2013). A scheme for NaOH activation mechanism is presented in eq. (2.4) to (2.10) (Zou et al., 2013):

$$C + H_2O \rightarrow CO + H_2 \tag{2.4}$$

$$CO + H_2O \rightarrow CO_2 + H_2 \tag{2.7}$$

$$2NaOH + CO_2 \rightarrow Na_2CO_3 + H_2O$$
(2.8)

$$Na_2CO_3 \rightarrow Na_2O + CO_2 \text{ or } 2NaOH \rightarrow Na_2O + H_2O$$
 (2.9)

$$Na_2O + SiO_2 \rightarrow Na_2SiO_3$$
 (2.10)

2.6.5. Co-pyrolysis

A great number of studies have been reported on the investigation of the co-pyrolysis of biomass with other materials, such as coal (Yuan et al., 2012), oily sludge (Hu et al., 2017), waste tires (Q. Cao et al., 2009), and plastics (Önal et al., 2014). For example, Brebu et al. (2010) studied the co-pyrolysis of pine cone with synthetic polymers and showed significant

synergies in pyrolysis product yields. It was observed that experimental oil yield (i.e., 52.3 wt%) from the co-pyrolysis was higher than the anticipated theoretical yield (i.e., 47.1 wt%) calculated based on the yields from the pyrolysis of the pine cone and polystyrene alone. Such synergetic effect in co-pyrolysis has also been reported in other studies (G. Chen et al., 2014; Hu et al., 2017; Kar, 2011; Önal et al., 2014; Song et al., 2014). The synergetic effect may be a result of the high H/C and O/C molar ratios in biomass which can generate a large number of hydrogen and hydroxyl radicals. These radicals could promote the cracking reaction of aromatic compounds within the oily sludge (Yuan et al., 2012). Meanwhile, some radicals species such as amyl, hydroxyl, and methoxyl could combine with each other to form organic compounds (e.g., aldehydes, carboxylic acids, and ketones), and thus increase the yield of bottom oil (derived from biomass) (Zuo et al., 2014). Önal et al. (2014) observed that the produced oil from co-pyrolysis with almond shells (polyethylene/almond shell = 1:1 w/w) had higher carbon (26% higher) and hydrocarbon contents (78% higher), lower oxygen content (86% less) and a high heating value (HHV) (38% higher) than those of biomass oil. Q. Cao et al. (2009) found co-pyrolysis of sawdust and waste tires had the advantage of inhibiting the formation of PAH produced by pyrolysis of the tires alone. The improvement of oil quality in aspects of elemental composition, HHV, and content of PAHs reflected a synergistic effect exist during co-pyrolysis of the biomass and tire (Cao et al., 2009).

Debela et al. (2012) investigated the immobilization of heavy metals in contaminated soil by co-pyrolysis with woody biomass and found heat treatment without the addition of biomass can be effective in immobilizing heavy metals such as Pb and Cd. Their results also showed the additional biomass enhanced further declines in Zn and Cd leaching. Kistler et al. (1987) observed the metals (i.e., Cr, Ni, Cu, Zn, Cd, and Pb) in the sewage sludge after pyrolysis at 500 °C was not mobilized by acidic leachates (50 g of char with 2070 mL of pH 3.2 HCl). This may be attributed to the well-buffered neutral to alkaline properties of char (Kistler et al., 1987). Devi and Saroha (2014) studied the transformation behavior of heavy metal ions (i.e., Cr, Cu, Ni, Zn, Pb, and Cd) during the pyrolysis of paper mill effluent treatment plant sludge at different temperatures (200–700 °C). It was observed that the mobile and bioavailable heavy metal ion fractions were transformed into relatively stable fractions after pyrolysis and most of the heavy metal ions were found to exist in the residual form in the biochar pyrolyzed at 700 °C (Devi and Saroha, 2014). Similarly, Islam and Park, (2017) found the hydrothermal treatment (270 °C) significantly decreased the bioavailable fraction of Pb in contaminated soil from 41.33 to 14.66 %, while the Pb content in the non-bio-available fraction increased from 2.90 to 15.76%. They explained Pb immobilization may result from mechanisms such as cation exchange and precipitation.

Shi et al. (2013b) reported that the addition of rice husk during the hydrothermal treatment of sewage sludge exhibited a reduction effect on the leaching toxicity of heavy metals in sludge residues. It was observed that at the rice husk/sludge ratio of 1/1.75, the concentrations of leachable Cr, Ni, Cu, and Cd decreased by 17%, 89%, 95%, and 93% respectively. More importantly, addition of rice husks led to further transformation of the metals within residual fractions. They postulated that a biomass-sewage sludge matrix was formed during hydrothermal treatment with rice husk addition in which the metals were further entrapped by the enlarged structure of rice husk or chelated with some functional groups, resulting in an enhanced immobilization effect on the metals. A similar cumulative effect of biomass addition on lowering the contamination risk of heavy metals in biochar has been reported by other authors (H. Chen et al., 2014; Jin et al., 2017).

2.7. Summary of literature review

Oily sludge is one of the most significant solid waste generated in petroleum industry during the process of drilling, production, transport, storage, and refining (da Silva et al., 2012). Such sludge usually contains various pollutants, such as heavy metals (da Rocha et al., 2010), PAHs (Kriipsalu et al., 2008), and BTEX (Kriipsalu et al., 2008), posing risks to human health and the environment (Kuang et al., 2011; Robertson et al., 2007). The effective treatment of oily sludge has attracted widespread attention due to its hazardous and recalcitrant nature (Hu et al., 2013). A variety of remediation technologies are available for oily sludge treatment (Table 2.2). However, no single technology is universally applicable because properties of oily sludge from different sources vary. Moreover, each method is associated with different advantages and disadvantages. Some treatments are effective in removing PHCs but are very expensive. Other treatments have relatively low cost but require long treatment duration and/or fail to meet the requirements for the reduction of large molecular weight species and metal ions in the oily sludge. Future research should focus on the development of new techniques for recycling and treating oily sludge with high efficiency and low costs.

Solvent extraction is a simple and commonly used approach to recycle petroleum hydrocarbons from oily sludge. Extraction performance depends on solvent type, temperature, solvent-to-sludge ratio, extraction duration, and stirring rate. The utilization of solvent is essential to solvent extraction. However, it also limits the extension of this technology to field-scale oily sludge treatment due to the high cost of solvent recovery and toxicity of the organic solvent. In the past years, growing interest has been shown in the application of ILs to recover bitumen from oil sands (Painter et al., 2010b; Sui et al., 2016; Tourvieille et al., 2017). The literature suggests that ILs are potentially good candidates for the enhancement of the

liberation of oil from solid matrices during solvent extraction. However, limited studies have been reported on the use of ILs in environmental remediation, especially oil recovery from oily sludge.

Pyrolysis is a promising strategic approach to the sustainable management of oily sludge, having the ability to not only minimize the solid waste, but also to yield valuable products (i.e., liquid, gas, and char). A number of operating variables may affect the yield and composition of the liquid and gas product, such as pyrolysis temperature, reaction time, heating rate, and chemical additives (Qin et al., 2015; Shie et al., 2003; Wang et al., 2007). Due to the different origins of the oily sludge and pyrolysis conditions, the HHV of chars can range from 7.02 MJ/kg to 34.4 MJ/kg (Liu et al., 2008; Qin et al., 2015; Thangalazhy-Gopakumar et al., 2015). An HHV near to 7 MJ/kg and high ash content make chars unattractive for use in incineration. Therefore, some authors advocate the use of oily sludge-derived char (OSDC) for adsorbent production (Mohammadi and Mirghaffari, 2015; Wang et al., 2017b). However, there is a lack of information on the roles of different sorption mechanisms for OSDC. Pyrolysis conditions such as temperature and chemical activation play important roles in changing biochar physiochemical properties and its removal efficiency of contaminants (Ahmad et al., 2012; T. Chen et al., 2014; Zhang et al., 2005; Zou et al., 2013). However, very limited research tried to establish the relationship among properties of OSDC, metal sorption behavior, and pyrolysis conditions. Therefore, investigating the exact mechanisms for Pb²⁺ and Cd²⁺ sorption on OSDC prepared at different pyrolysis temperature and activation methods is also necessary. The addition of biomass during pyrolysis of oily sludge resulted in a synergistic effect on oil yield (Hu et al., 2017). Some of the oil properties such as HHV and carbon content were found to be improved by co-pyrolysis (Q. Cao et al., 2009). Some efforts have been made to investigate

the cumulative effect of biomass addition on lowering the contamination risk of heavy metals in sewage sludge residues (H. Chen et al., 2014; Jin et al., 2017; Shi et al., 2013b). However, there has been limited research investigating co-pyrolysis effect of oily sludge and sawdust on heavy metal immobilization.

Chapter 3

IONIC LIQUID-ENHANCED SOLVENT EXTRACTION FOR OIL RECOVERY FROM OILY SLUDGE¹

Abstract

An ionic liquid (IL), 1-ethyl-3-methyl-imidazolium tetrafluoroborate ([Emim][BF4]), was investigated for its effectiveness on enhancing oil recovery from hazardous crude oil tank bottom sludge using solvent. A range of solvent (cyclohexane)/sludge ratio (2–8 mL/g), shaking speed (100–400 rpm), extraction duration (10–120 min), and IL/sludge ratio (0.25–1.0 mL/g), were examined. The addition of IL (i.e., 1 mL/g of IL/sludge ratio) increased total petroleum hydrocarbon (TPH) recovery by 9.4% (from $84.4 \pm 2.4\%$ to $93.8 \pm 2.3\%$ at the solvent/sludge ratio of 8 mL/g). An orthogonal experimental design was subsequently applied to optimize extraction conditions. The use of IL (i.e., 0.1 mL/g of IL/sludge ratio) with solvent yielded higher TPH recovery (above 95%) at shorter extraction duration (10 min), lower solvent/sludge ratio (4:5 mL/g), and lower energy consumption (100 rpm). The recovered oil had similar calorific value but a higher F3 fraction compared with crude oil. The results suggested the IL-enhanced solvent extraction with lower solvent consumption is an effective approach for oily sludge treatment.

Keywords: oily sludge, ionic liquid, solvent extraction, oil recovery, total petroleum hydrocarbon

¹ This work has been published as Tian, Y., McGill, W.B., Whitcombe, T.W., Li, J., 2019. Ionic liquid-enhanced solvent extraction for oil recovery from oily sludge. Energy Fuels 33, 3429–3438. DOI: 10.1021/acs.energyfuels.9b00224.

3.1. Introduction

The petroleum industry produces a large quantity of oily sludge during its oil exploration and processing activities (da Silva et al., 2012; Xu et al., 2009). Such sludge is a complex water/oil emulsion typically including 30-50% oils, 10-20% solids and 30-50% water by weight (Ramaswamy et al., 2007). It also contains some aromatic hydrocarbons (e.g., benzene) and polycyclic aromatic hydrocarbons (PAHs) that are mutagenic and carcinogenic (IARC WGECRH, 2010, 1987). Therefore, oily sludge has been classified as a hazardous waste in many countries. Its improper treatment can pose a serious threat to the environment and humans (Hejazi et al., 2003; Kuang et al., 2011; Robertson et al., 2007). Most conventional methods for dealing with oily sludge are landfills or incineration. Due to stringent regulations in recent years, landfilling is being gradually prohibited or restricted (da Silva et al., 2012; Elektorowicz and Habibi, 2005). Although incineration reduces a large volume of oily sludge, it requires a substantial amount of auxiliary fuel and generates a large volume of off-gases containing PAHs (C.-T. Li et al., 1995). Recycling is an alternative option to handle oily sludge by providing the possibility for reusing valuable oil for reprocessing and recovering energy (Elektorowicz and Habibi, 2005; Hu et al., 2013). Solvent extraction is a commonly used approach to recycle hydrocarbons from oily waste by mixing with a desirable amount of solvent (Hu et al., 2016). Many studies reported that a variety of variables could affect oil recovery in solvent extraction processes (e.g., temperature, pressure, solvent-to-waste ratio, mixing, and the property of solvent) (Fisher et al., 1997; Taiwo and Otolorin, 2009; Zubaidy and Abouelnasr, 2010). The application of solvent extraction to oily sludge treatment is desirable, but challenged by its unsatisfactory extraction efficiency, large volume of solvent consumption, and long extraction duration (Hu et al., 2013; Li et al., 2011).

Ionic liquid (IL) is purely ionic material with a melting temperature below 100 °C. It has been considered as "green and eco-friendly solvent" because of its unique properties (e.g., thermal and chemical stability) (José-Alberto and Jorge, 2011). In the past few years, growing interest has been shown in the application of ionic liquid (IL) to recover bitumen from oil sands (Hogshead et al., 2011; Painter et al., 2010b; Sui et al., 2016; Tourvieille et al., 2017). Painter et al. (2010a) demonstrated that more than 90% (by weight) of bitumen was recovered from oil sands when using an imidazolium-based IL and toluene, while the use of IL could allow for a cleaner separation. Li et al. (2011) investigated the effect of IL on bitumen recovery from oil sands using a composite solvent (acetone and n-heptane), and found that the bitumen recovery was increased by up to 10% (by weight) by adding IL (i.e., 1.3 mL/g of IL/oil sands ratio). A recent study by Sui et al. (2016) found that bitumen recovery from oil sands using IL-enhanced solvent extraction increased with IL-to-oil sands ratio and agitation time. As a result, IL can be potentially effective candidates for enhancing the liberation of oil from solid matrices during solvent extraction. However, few studies have been reported on the use of IL in oily sludge treatment. The objective of this study was then to propose an IL-enhanced solvent extraction method for oil recovery from oily sludge. Several factors including solvent/sludge ratio, shaking speed, extraction duration, and IL/sludge ratio were examined for their impacts on oil recovery. The optimal conditions of oil recovery for two processes (i.e. solvent extraction and IL-enhanced solvent extraction) were also investigated.

3.2. Materials and methods

3.2.1. Materials and reagents

The oily sludge used in this study was obtained from a crude oil tank bottom in an oil refinery plant in western Canada. The appearance of the oily sludge was black and sticky. Table 3.1 lists its characteristics. The total petroleum hydrocarbon (TPH) extraction followed the US EPA 3540C method (USEPA, 1996a). The water content was analyzed based on the ASTM D2974-00 Method A (ASTM, 2000), and the solid content was calculated according to the measured TPH and water contents. Dichloromethane (DCM) and cyclohexane used for sample extraction were of HPLC grade (>97%, VWR International). Previous studies on ILenhanced bitumen extraction from oil sands showed that among various ionic liquids, the use of 1-ethyl-3-methyl-imidazolium tetrafluoroborate ([Emim][BF₄]) and 1-butyl-2,3-dimethylimidazolium tetrafluoroborate ([Bmmim][BF4]) led to high-efficiency IL-free bitumen recovery (Li et al., 2011; Painter et al., 2010b, 2010a; Sui et al., 2016). Moreover, [Emim][BF4] has a much less viscosity (0.06 Pa·s) than that of [Bmmim][BF4] (0.46 Pa·s at 298 K), which allows an easier industrial operation (i.e., no equipment blockage). Therefore, [Emim][BF4] at HPLC-grade (≥98%)) purchased from Sigma-Aldrich was used as the ionic liquid (IL) to be investigated in this study. Silica gel (70–230 mesh, VWR international) activated at 105 °C for 12 h was used to clean up the extraction solution. Anhydrous sodium sulfate (VWR international) dried at 400 °C for 4 h was used to remove moisture in the extract.

Table 3.1. Characteristics of the oily sludge

Parameter	Concentration			
ТРН	58.7 ± 4 % (by mass)			
Water content [*]	22.0 ± 5 % (by mass)			
Solid content	19.3 ± 1 % (by mass)			

*on a wet-weight basis

3.2.2. Single factor experiments

Single factor experiments were designed to evaluate the influence of IL ([Emim][BF₄]) addition on the oil recovery by solvent extraction with cyclohexane. Among various solvents, cyclohexane was reported to have a high bitumen recovery since it has a medium solubility (i.e., 16.8 MPa^{1/2}) which is close to that of asphaltene (i.e., 20.1 MPa^{1/2}) (Wang et al., 2014). Additionally, cyclohexane has a low boiling point (i.e., 80.7 °C) which allows easy solvent recovery, and less toxicity than many other solvents. Our previous study (Hu et al., 2015) also indicated that cyclohexane could achieve a high oil recovery when treating petroleum refinery wastewater treatment pond sludge. Therefore, cyclohexane was selected as the solvent for investigation in this study. A total of four factors were examined, including solvent/sludge (So/SI) ratio, shaking speed, extraction duration, and IL/sludge (IL/SI) ratio. It was reported in our previous study and other authors' work that the extraction performance could be significantly affected by these factors (Hu et al., 2015, 2016; X. Li et al., 2012; Sui et al., 2016). The levels of experimental factors are presented in Table 3.2.

Number	So/Sl ratio	Shaking speed	Extraction	IL/Sl ratio
	(mL/g)	(rpm) duration (min)		(mL/g)
1	2:1, 4:1, 6:1, 8:1	200	30	0
2	2:1, 4:1, 6:1, 8:1	200	30	1:1
3	2:1	100, 200, 300, 400	30	0
4	2:1	100, 200, 300, 400	30	1:1
5	2:1	200	10, 30, 60, 120	0
6	2:1	200	10, 30, 60, 120	1:1
7	2:1	200	30	1:4, 2:4, 3:4, 4:4

 Table 3.2. Single-factor experimental conditions

Solvent extraction using cyclohexane alone was conducted by adding the desired volume of cyclohexane (Table 3.2) to a 15-mL centrifuge tube containing oily sludge (0.5 g). The mixture was then shaken under the designed condition (Table 3.2) by using a Talboy 3500 Orbital shaker, then centrifuged for 8 min at 4704g. The extract cleanup and quantification followed the method of Zhang et al. (2012) and CCME (CCME, 2001). The solvent in the cleaned extract was evaporated in a rotary evaporator. The residue was weighed and designated as recovered TPH (TPH_r). The TPH recovery rate was calculated as follows:

$$R = TPH_r/(C_o \times M_o) \times 100\%$$
(3.1)

where *R* is the TPH recovery rate (%); TPH_r (mg) is the mass of recovered TPH; C_o (mg/g) is the TPH concentrations in the oily sludge sample ($C_o = 5.87 \times 10^5$ mg/kg, as listed in Table 3.1); and M_o (g) is the mass of oily sludge sample.

In terms of solvent extraction with IL addition, preliminary experiments showed that the IL layer stayed between the top oil/solvent layer and the sand/clay layer after mixing oily sludge

with IL and solvent. At the oil/solvent-IL interface, a black film containing suspended oil and some mineral fines was formed as shown in Figure 3.1. Similar phenomenon has also been reported in other studies (Sui et al., 2016; Tourvieille et al., 2017). Given this observation, the recovered TPH in IL-enhanced solvent extraction treatment was calculated as follows:

$$TPH_r = TPH_{rt} + TPH_{ri} \tag{3.2}$$

where TPH_r (mg) is the mass of recovered TPH; TPH_{rt} (mg) is mass of recovered TPH from top oil/solvent layer; and TPH_{ri} (mg) is mass of recovered TPH from oil/solvent-IL interface.



Figure 3.1. The phases formed by mixing, (a) oily sludge with [Emim][BF₄] and cyclohexane in the proportion of 1:3:2 (by weight), and (b) oily sludge with cyclohexane in the proportion of 1:2 (by weight).

In IL-enhanced solvent extraction treatment, a sample of oily sludge, IL, and cyclohexane in proportion (Table 3.2) was placed into a 15-mL centrifuge tube. Extraction, centrifugation, cleanup and evaporation for determining the recovered TPH mass from top oil/solvent layer (TPH_{rt}) were similar as described above. After separation of the top oil/solvent layer from the tube, a small amount of fresh cyclohexane solvent (500 µL) was added and then gently mixed with the oil/solvent-IL interface. The mixture was centrifuged at 4704g for 3 min, and the solvent/oil phase was decanted and saved. The procedure was repeated until the supernatant was colorless. The mass of recovered TPH from oil/solvent-IL interface (TPH_{ri}) was then obtained.

For both the cyclohexane extraction and IL-enhanced cyclohexane extraction, each was performed in triplicate and the results were expressed as mean \pm standard deviation. One way analysis of variance (ANOVA) with Tukey's analysis was used to determine the significant (P < 0.05) differences between levels of treatment.

3.2.3. Optimization of solvent extraction and IL-enhanced solvent extraction

The optimal operational condition for each extraction process, including solvent extraction and IL-enhanced solvent extraction, was examined using a L₉ (3^4) orthogonal experimental design (Table 3.3) (Taguchi et al., 2005). The factors and levels of each factor were chosen depending on the results of single factor experiments. The extraction duration was set as a constant (i.e. 10 min) for IL-enhanced solvent extraction, and all IL treatments were conducted in a 2-mL centrifuge tube. Each experiment was performed in triplicate.

Extraction	Factors	Symbol	Levels			
process			1	2	3	
	So/Sl ratio (mL/g)	А	4:1	8:1	12:1	
Solvent extraction	Shaking speed (rpm)	В	300	400	500	
	Extraction duration (min)	С	30	60	120	
IL-	So/Sl ratio (mL/g)	А	4:5	7:5	10:5	
solvent	IL/Sl ratio (mL/g)	В	1:10	2:10	3:10	
extraction	Shaking speed (rpm)	С	100	200	300	
Experimental No.		Experimental factors and levels				
		А	В	С	E*	
1		1	1	1	1	
2		1	2	2	2	
3		1	3	3	3	
4		2	1	2	3	
5		2	2	3	1	
6		2	3	1	2	
7		3	1	3	2	
8		3	2	1	3	
9		3	3	2	1	

Table 3.3. Orthogonal array L₉ (3⁴) experimental design and factor levels

* Empty column

The TPH recovery rate from each treatment was calculated by eq. (3.1). Additionally, the recovered TPH was transferred into a 10 mL volumetric flask, and then n-hexane was added to bring the final volume to 10 mL. The extract samples were stored at 4 °C for further analysis. In order to calculate the mass balance of TPH for each orthogonal experiment, the TPH mass

in the residual sand/clay after solvent extraction or IL-enhanced solvent extraction was determined. In this study, 10 mL of DCM was added into a 15-mL centrifuge tube containing residual sand/clay at the bottom. The tube was shaken on a Talboy 3500 Orbital shaker at 300 rpm for 30 min and then centrifuged at 4704*g* for 10 min (Schwab et al., 1999). The extraction solution was decanted and kept in a 40 mL glass vial. Another 10 mL clean DCM was added to the same centrifugation tube, and the extraction procedure was repeated for two more times. A total of 30 mL of extraction solution was then collected and used for silica gel cleanup. After evaporation, the TPH extracted from residual sand/clay was brought to 10 mL with n-hexane and stored at 4 °C until analysis.

Signal to noise (S/N) ratio which combines the mean and variance was used to evaluate the experimental data. Since this study aims at maximizing the TPH recovery rate (%), the S/N ratio (dB) was calculated by the following equation:

$$\frac{s}{N} = -10 \log \left\{ \frac{l}{n} \sum_{i=1}^{n} \frac{l}{y_i^2} \right\}$$
(3.3)

where y_i denotes the TPH recovery observed in the *i*th repetition of the experimental run; *n* is the total number of repetitions under the same experimental condition (Hedayatipour et al., 2017; Taguchi et al., 2005; Zolfaghari et al., 2011). In addition to S/N ratio, ANOVA was used to test the significance of independent variables.

3.2.4. Laboratory analysis

3.2.4.1. Hydrocarbon analysis using gas chromatograph

Chromatographic characterization of samples with petroleum hydrocarbons (PHCs) was carried out using an Agilent 6890 Gas Chromatograph with a flame ionization detector (GC-FID). The hydrocarbon mixtures were grouped into four PHC fractions (CCME, 2001): F1 (nC6–nC10), F2 (nC10–nC16), F3 (nC16–nC34), and F4 (nC35–nC50). Decane (nC10), hexadecane (nC16), and tetratriacontane (nC34) were used as the external standards to determine the average response factor and then quantify the PHC fractions. The capillary column used was a ZB-1HT INFERNO column (Phenomenex) with a length of 30 m, an inside diameter of 0.32 mm and a film thickness of 0.25 μ m. Helium was used as the carrier gas at a rate of 2.1 mL/min. TPH extract (1 μ L) was injected into the GC system and a split ratio of 10:1 was performed for each run. Both the injector and detector temperatures were kept at 360 °C during analysis. The initial temperature of the oven was held at 40 °C for 4 min, then increased to 140 °C at 10.0 °C/min, and further increased to 340 °C at 20.0 °C/min and held at 340 °C for 11 min. The total run time was 35 min.

3.2.4.2. Characterization of recovered oil and residual sand/clay

The total carbon (C), nitrogen (N), hydrogen (H), and sulfur (S) of oil were determined using a Costech ECS 4010 elemental analyzer according to ASTM D5291-16 (ASTM, 2016). The calorific values of recovered oil and crude oil (donated by an oil refinery in western Canada) were determined by using a bomb calorimeter (Model: 1341 Plain Jacket Calorimeter, Parr Instrument Company) according to ASTM D2015-85 (ASTM, 1985). The elements (e.g., Fe, Cr, Pb, and Ni) in recovered oil and residual sand/clay were determined by digestion (USEPA 3050B) (USEPA, 1996b) and then quantified by inductively coupled plasma optical emission spectrometry (ICP-OES) (Agilent Technologies 5100) according to ASTM D5185 (ASTM, 2018). The residual sand/clay samples were ground and mixed with KBr to 0.1 wt% and then pressed into pellets. Thin films of recovered oil were prepared by placing a DCM solution containing the oil on a KBr window and allowing DCM to evaporate (Painter et al.,
2010a). The Fourier transform infrared (FTIR) spectra were then obtained using a Nexus 670 Thermo Nicolet Spectrometer.

3.3. Results and discussion

3.3.1. Single factor experiments

As seen from Figure 3.2a-c, the extraction conditions, including solvent/sludge ratio, shaking speed, and extraction duration, had significant (P < 0.05) effects on the performance of solvent extraction alone. The TPH recovery increased from $68.7 \pm 0.8\%$ to $84.4 \pm 2.4\%$ when the solvent/sludge ratio increased from 2:1 to 8:1 mL/g. Such TPH recovery increase could be owing to an increase in the amount of oil dissolved in solvent when increasing solvent/sludge ratio (Elbashir et al., 2002). Other authors using solvent extraction to treat oily sludge (Hu et al., 2015; Zubaidy and Abouelnasr, 2010) and used lubricant oil (Elbashir et al., 2002; Rincón et al., 2005) found that extraction yield remained stable when the solvent/sludge ratio was increased beyond a certain point. However, the stabilization was not observed in this study because even at the highest solvent/sludge ratio (i.e. 8:1), the solvent was not sufficient to dissolve all oil retained by solid matrices. According to Figure 3.2b, the TPH recovery went up gradually from $68.3 \pm 3.9\%$ at 100 rpm to $75.5 \pm 1.5\%$ at 400 rpm. This might be because the oil initially adsorbed on the sand/clay particles was stripped and then driven into the solvent phase by increasing stirring strength (X. Li et al., 2012). As shown in Figure 3.2c, the TPH recovery also experienced an upward trend with the extension of extraction duration (70.5 \pm 1.3% and 76.1 \pm 2.1% at 10 min and 120 min, respectively). With longer extraction time, the interaction between oil and solvent was enhanced, thereby increasing the amount of recovered TPH.



Figure 3.2. Influence of different operational parameters on TPH recovery: (a) So/SI ratio (shaking speed: 200 rpm, extraction duration: 30 min, IL/SI ratio: 1:1 mL/g), (b) shaking speed (So/SI ratio: 2:1 mL/g, extraction duration: 30 min, IL/SI ratio: 1:1 mL/g), and (c) extraction duration (So/SI ratio: 2:1 mL/g, shaking speed: 200 rpm, IL/SI ratio: 1:1 mL/g). Significant (P < 0.05) differences are shown by different letters: lowercase letter for the solvent extraction, and uppercase letter for the IL-enhanced solvent extraction.

However, no significant differences (P > 0.05) among the variables (solvent/sludge ratio, shaking time, and extraction duration) were observed on TPH recovery when IL was used. The TPH recovery was in the range from $88.7 \pm 2.8\%$ to $93.8 \pm 2.3\%$, indicating that an extra

recovery of 7.1–21.5% was achieved as compared to that of solvent extraction alone. The TPH recovery was substantially facilitated with the addition of IL probably due to two factors. First, the adhesion forces between oil and silica were about an order of magnitude smaller in an IL medium than in an aqueous solution, which may be attributed to the fact that IL can form layered ion/charge structures on mineral surfaces (Hogshead et al., 2011). Second, the separation was driven by the solubility characteristics of hydrophilic IL. The IL used in this study was immiscible with hydrocarbons, and thus an intermediate phase separating minerals from the hydrocarbon layer could be formed by IL (Painter et al., 2010a).

Considering the high cost of IL, a set of experiments with small IL/sludge ratios were conducted. The observed TPH recovery is shown in Figure 3.3. The TPH recovery increased from $68.7 \pm 0.8\%$ to $90.6 \pm 1.3\%$ as the IL/sludge ratio increased from 0 to 0.25 mL/g. However, a further increase in IL/sludge ratio didn't lead to significant enhancement of TPH recovery. It was reported that even a low concentration of IL could reduce the viscosity of crude oil by up to 35%, thus greatly facilitating solvent extraction efficiency (Subramanian et al., 2015). Sakthivel et al. (2014) also found that only a low IL/sludge ratio was required for a complete dissolution of oily sludge in solvents. The results suggest that the desirable IL/sludge ratio sufficient to recover most oil from oily sludge could be very low, but requires further investigation. In this regard, further optimization on oil recovery was carried out using IL/sludge ratios in the range from 0.1 to 0.3 mL/g.



Figure 3.3. Influence of IL/sludge (IL/Sl) ratio on TPH recovery (So/Sl ratio: 2:1 mL/g, shaking speed: 200 rpm, extraction duration: 30 min). Different lowercase letters (a,b) indicates significant (P < 0.05) differences.

3.3.2. Multifactor orthogonal experiments

Mass balance calculation of the F2, F3, and F4 fractions of TPH for orthogonal experiments in solvent extraction alone and IL-enhanced solvent extraction are presented in Tables A1 and A2 in the Appendix A, respectively. A good agreement between the TPH_o (TPH in original oily sludge) and TPH_s (the sum of TPH in recovered oil and TPH in residual sand/clay) indicated that the mass loss of TPH in each treatment was small and could be ignored in this study.

3.3.2.1. Solvent extraction alone

Table 3.4 shows the results of orthogonal experiments using solvent extraction alone. The TPH recovery was between $80.66 \pm 2.42\%$ and $95.49 \pm 4.52\%$. The highest TPH recovery ($95.49 \pm 4.52\%$ in experiment # 9) was observed under the following conditions: 12:1 mL/g of

solvent/sludge ratio, 60 min of extraction duration, and shaking speed of 500 rpm. It is noted that the F4 recovery rate for experiment # 7 and 9 was slightly over 100 %. This is because the F4 recovery rate was calculated using the average of mass of F4 fraction in the original oily sludge sample and recovered oil sample (F4_o and F4_t, as seen in Table A1 in the Appendix A) without the consideration of variance.

Exp.	So/Sl ratio (mL/a)	Shaking speed	Extraction	Recovery rate (%)					
INU.	(IIIL/g)	(ipiii)	duration (mm)	TPH	F2	F3	F4		
1	4:1	300	30	80.66	90.01	78.09	65.21		
2	4:1	400	60	84.37	95.41	79.06	74.78		
3	4:1	500	120	82.87	86.44	80.82	81.05		
4	8:1	300	60	88.65	96.46	83.53	86.99		
5	8:1	400	120	89.23	93.65	84.72	94.39		
6	8:1	500	30	86.60	87.92	83.74	93.85		
7	12:1	300	120	93.88	94.43	91.33	102.05		
8	12:1	400	30	89.98	91.95	86.65	97.28		
9	12:1	500	60	95.49	99.62	90.61	102.86		

Table 3.4. Results of the orthogonal experiments for solvent extraction alone

Figure 3.4a shows the main effects of three factors on the TPH recovery from solvent extraction alone. It can be found that the S/N ratio increased rapidly with the increasing solvent/sludge ratio (from 4:1 to 12:1 mL/g), peaking at 39.36 dB. The trend was in accordance with the results for single factor experiments, suggesting that solvent/sludge ratio played a significant role in extracting oil from oily sludge. Further increase of solvent/sludge ratio could be beneficial to TPH recovery to some extent. However, the high solvent/sludge ratio means a high cost of operation, thus 12:1 mL/g of solvent/sludge ratio was chosen as the optimal condition in this study. According to the ANOVA analysis shown in Table A3 in the Appendix A, there is no significant effect (*F*-value = 0.11) on TPH recovery by increasing the shaking speed from 300 rpm to 500 rpm, indicating 300 rpm induced adequate turbulence for mixing the oil and solvent in extraction. Moreover, the S/N ratio was maximized at 60 min of extraction duration then followed by a moderate drop from 60 min to 120 min. By contrast, there was a steady rise in TPH recovery from 60 min to 120 min in single factor experiment (Figure 3.2c). This may be explained by the interaction effect between extraction duration with other factors, especially with solvent/sludge ratio. Table A3 in the Appendix A shows the most significant factor affecting TPH recovery was solvent/sludge ratio (F-value = 30.21) followed by extraction duration (F-value = 4.28). The optimum condition for TPH recovery from oily sludge using solvent extraction alone would be 12:1 mL/g of solvent/sludge ratio, 60 min of extraction duration, and shaking speed of 500 rpm.



Figure 3.4. Effect of independent factors on (a) TPH recovery, (b) F2 recovery, (c) F3 recovery, and (d) F4 recovery of the solvent extraction alone process.

As seen from Figure 3.4b–d and Table A3 in the Appendix A, the F4 recovery was significantly affected by all variables, whereas the solvent/sludge ratio and extraction duration were two significant factors impacting F3 recovery. However, no significant factor was observed for F2 recovery. As compared with long-chain or aromatic hydrocarbons, short-chain hydrocarbons can be more easily desorbed from sand/clay due to their lower intermolecular forces (Feng and Aldrich, 2000). As a result, a high F2 recovery (i.e. $90.01 \pm 2.27\%$) was obtained when the variables were at level 1 and very few, if any, contribution could be seen in F2 recovery by increasing the variables from level 1 to level 3. As seen in Figure 3.4b, the F2 recovery slightly increased with an increase in shaking speed up to 400 rpm, after which it

decreased with shaking speed. Similar changes with the extension of extraction duration occurred. Taking into consideration the fact that the average F2 recovery at 400 rpm of shaking speed (i.e., level 2) and 60 min of extraction duration (i.e., level 2) was as high as 93.67 \pm 1.73% and 97.16 \pm 2.19%, respectively, the re-adsorption of dissolved F2 onto the solid particles surfaces could be responsible for the decline of F2 recovery with further increase in shaking speed (above 400 rpm) or extraction duration (above 60 min) (Feng and Aldrich, 2000).

2.3.2.2. IL-enhanced solvent extraction

The TPH recovery from oily sludge using IL-enhanced solvent extraction was between $91.08 \pm 5.34\%$ and $98.33 \pm 3.57\%$ and the average TPH recovery was $95.80 \pm 4.62\%$ (Table 3.5). As shown in Figure 3.5, the S/N ratio for TPH recovery fluctuated between 39.16 dB and 39.84 dB. It is interesting to note that in IL-enhanced solvent extraction process, all variables including solvent/sludge ratio, IL/sludge ratio, and shaking speed had an insignificant influence on the TPH recovery (Table A4 in the Appendix A). The above results indicated that with the addition of IL, most TPH could be extracted from oily sludge under very mild conditions (e.g., 10 min extraction duration and 100 rpm of shaking speed). This might be due to the IL addition reducing the viscosity of oily sludge, leading to the enhancement of oil liberation from solid matrices during solvent extraction. By considering the operational cost and time, the optimum condition for TPH recovery using IL-enhanced solvent extraction was chosen in this study as 4:5 mL/g of solvent/sludge ratio, 1:10 mL/g of IL/sludge ratio, and 100 rpm of shaking speed.

Exp. No	So/Sl ratio	IL/S1 ratio	Shaking speed	TPH Recovery rate (%)				
110.	(mL/g)	(mL/g)	(rpm)	Total	Top oil/solvent layer	Oil/solvent- IL interface		
1	4:5	1:10	100	96.92	67.59	29.33		
2	4:5	2:10	200	98.33	72.95	25.39		
3	4:5	3:10	300	91.08	70.72	20.35		
4	7:5	1:10	200	97.52	75.21	22.31		
5	7:5	2:10	300	94.85	79.02	15.84		
6	7:5	3:10	100	95.73	70.32	25.41		
7	10:5	1:10	300	97.24	80.00	17.25		
8	10:5	2:10	100	97.63	75.63	22.00		
9	10:5	3:10	200	92.91	71.06	21.84		

Table 3.5. Results of the orthogonal experiments for IL-enhanced solvent extraction



Figure 3.5. Effect of independent factors on TPH recovery of the IL-enhanced solvent extraction process.

In general, a higher quantity of TPH was collected from the top oil/solvent layer when compared with that from oil/solvent-IL interface (Table 3.5). Although the differences in TPH recovery were not statistically significant, the influence of solvent/sludge ratio and shaking speed on TPH recovery from the oil/solvent-IL interface was highly significant (P < 0.01), which can be observed from Table A4 in the Appendix A. As seen from Figure 3.5, the increase of solvent/sludge ratio reduced the S/N ratio from 27.76 to 25.82 dB for TPH recovery from the oil/solvent-IL interface. Correspondingly, the S/N ratio for TPH recovery from the top oil/solvent layer increased from 36.91 to 37.54 dB with the increase of solvent/sludge ratio. Furthermore, increasing the shaking speed from 100 rpm to 300 rpm decreased the S/N ratio from 27.98 to 24.71 dB for TPH recovery from the oil/solvent-IL interface. These results implied that even though the break of incrustation and desorption of oil from solid matrices were high at the low levels (i.e. level 1) of all the three experimental variables, the dissolution of oil into the solvent was not fully complete, leaving the undissolved oil (containing 29.33%) TPH) in the oil/solvent-IL interface. However, higher solvent/sludge ratio and stronger shearing force could enhance the dissolution of suspended oil into the solvent.

Table 3.5 shows that a high TPH recovery (> 95%) could be achieved even when the IL/sludge ratio was as low as 0.1 mL/g. However, the high cost of IL can still be a barrier to the application of IL-enhanced solvent extraction. For example, the cost of 1 kg of [Emim][BF4] can range from \$340 to \$1300 USD depending on its purity. As a result, the reuse of IL is of great importance. Plechkova and Seddon (2008) estimated that more than 10–20 times of IL reuse would make the IL-enhanced solvent extraction less expensive than solvent extraction alone. Even though the effectiveness of recycled [Emim][BF4] was not tested in this study, the works of other authors concerning the recycle of IL showed promising results (Li et al., 2011;

Painter et al., 2010b). For example, no decrease in bitumen yield was observed when the IL was reused five times (Painter et al., 2010b). Li et al. (2011) reused IL 10 times in extraction with bitumen recovery ranging from 92 to 99%. The cost of IL-enhanced solvent extraction should be compared with that of solvent extraction on the basis of extraction performance, operation cost, materials cost, and solvent/IL reuse. For this reason, further research about the reuse of IL and solvent need to be conducted in order to provide valuable information for the application of IL-enhanced solvent extraction for oily sludge treatment.

2.3.3. Characteristics of the recovered oil and residual sand/clay

The recovered oil samples obtained under the optimum conditions of each extraction process were further analyzed. Figure 3.6 shows the gas chromatography (GC) chromatogram of samples from these treatments. No significant differences in composition among samples were observed since the same solvent (i.e., cyclohexane) was used in both extraction processes. Compared to F4 fraction in recovered oil from solvent extraction alone (Figure 3.6a), the F4 fraction in recovered oil from the top oil/solvent layer (Figure 3.6b) decreased and it compensated for an increase of F4 fraction in oil/solvent-IL interface (Figure 3.6c). It is worth noting that PHCs distribution in recovered oil using solvent extraction alone and recovered oil (a combination of top oil/solvent layer and oil/solvent-IL interface) using IL-enhanced solvent extraction were similar, indicating that IL addition did not promote alteration of the long-chain and heavy PHCs.



Figure 3.6. GC chromatogram of petroleum hydrocarbons in (a) recovered oil using solvent extraction alone, (b) recovered oil from top oil/solvent layer using IL-enhanced solvent extraction, and (c) recovered oil from oil/solvent-IL interface using IL-enhanced solvent extraction.

As shown in Figure 3.7, the average F2, F3, and F4 fractions in the recovered oil using solvent extraction alone were 37.5%, 48.1%, and 14.4%, respectively. The F2 and F3 fraction in the oil recovered from top oil/solvent layer using IL-enhanced solvent extraction was higher (i.e., 4.8% and 2.4%), whereas the F4 fraction was lower (i.e., 7.2%) than that using solvent extraction alone. Approximately 92.7% of TPH distributed in F2 and F3 fractions in top oil/solvent layer, compared to 97.4% for the crude oil. However, the highest percentage of F4 fraction (i.e., 26.1%) was found in recovered oil from oil/solvent-IL interface using IL-enhanced extraction, indicating that a certain amount of heavy PHCs was gathered in oil/solvent-IL interface instead of dissolving in solvent. GC analysis of the recovered oil also

showed that it contained less F2 fraction but more F3 fraction than crude oil, which is good petrochemical industry feedstock.



Figure 3.7. Distribution of PHCs fractions in crude oil, recovered oil (RO) using solvent extraction alone, recovered oil in top oil/solvent layer using IL-enhanced solvent extraction, and recovered oil in oil/solvent-IL interface using IL-enhanced solvent extraction.

The infrared spectra of the oily sludge, the residual sand/clay and the oil extracts obtained by solvent extraction alone are shown in Figure 3.8. The functional groups in the recovered oil included C–H stretching of the saturate (2922 and 2852 cm⁻¹), C–H deformation of the saturate (1462 cm⁻¹), C–H symmetric deformation of the saturate (1376 cm⁻¹), and aromatic C–H bending (724 cm⁻¹). These peaks were also present in the residual sand/clay (Figure 3.8c), indicating organics remained in residual solids after extraction. Previous studies reported clay bands (500 cm⁻¹ and 3800 cm⁻¹) were displayed in the spectrum of the solvent extract of oil sands, indicating some fine solid in the recovered bitumen (Li et al., 2011; Painter et al., 2010a; Sui et al., 2016). However, the recovered oil from solvent extraction of oily sludge was free of fines since no clay bands was observed from Figure 3.8b. This might be because the solids in the oil sands with strong hydrophobicity tend to enter the solvent phase (Yang et al., 2012). The broadband between 3700 and 3000 cm⁻¹ corresponded to the stretching vibrations of hydrogen bonded O–H in the water, alcohols, phenols, and carboxylic acids. The peak near 1644 cm⁻¹ was assigned to vibration of the carboxylic acid group present in the oily sludge. The bands at 1110 cm⁻¹ and 1021 cm⁻¹ could be attributed to Si–O stretching from montmorillonite (Wang et al., 2012). Bands due to carbonates, observed near 889 cm⁻¹ absorbed very strongly in the infrared of residual sand/clay.



Figure 3.8. FTIR spectra of the (a) oily sludge, (b) recovered oil, and (c) residual sand/clay for solvent extraction alone.

The infrared spectra of the IL ([Emim][BF₄]), residual sand/clay treated with water washing at room temperature, and recovered oil (in top oil/solvent layer and oil/solvent-IL interface) by IL-enhanced solvent extraction are shown in Figure 3.9. As mentioned before, some of the clay fines were suspended in the middle IL phase after extraction (Figure 3.1). However, the recovered oil from IL-enhanced solvent extraction was free of mineral fines as seen from the absence of mineral bands (near 1100 cm⁻¹ and 890 cm⁻¹) in Figure 9a and b. Williams et al. (2010) proposed that the much more favorable electrostatic interactions between the IL and mineral fines than those between bitumen and mineral fines may contribute to the absence of mineral fines in the extract. The IL ([Emim][BF4]) was completely immiscible with hydrocarbons, which is evidenced by the absence of peaks in the range of 750–1200 cm⁻¹ because of [Emim][BF4] in the spectra of the extracts (Figure 3.9a,b). As a result, the recovered oil from IL-enhanced solvent extraction is free of fine solids or residual IL. In this study, roomtemperature water was used to separate the entrained IL from residual sand/clay. It can be found from Figure 3.9c that no IL exists in the residual sand/clay because the peaks for the residual sand/clay did not overlap with that of [Emim][BF₄]. As a result, the IL after extraction can be removed from the residual sand/clay by water washing at room temperature, and this is of significance for IL reuse.



Figure 3.9. FTIR spectra of the (a) recovered oil from top oil/solvent layer, (b) recovered oil from oil/solvent-IL interface, (c) residual sand/clay, and (d) [Emim][BF₄] in IL-enhanced solvent extraction. Residual sand/clay was treated with water and washed 3 times.

The recovered oil from extraction had a calorific value of 43.92–45.68 MJ/kg and was similar to that of crude oil (43.02 MJ/kg), suggesting the recovered oil can be used as fuel (Table 3.6). However, elemental analysis showed that the recovered oil from solvent extraction contained small amounts of Fe, Ca, and Mg (Table 3.6). The addition of IL reduced the metal content in recovered oil in top oil/solvent layer, but increased the metal content in recovered oil in oil/solvent-IL interface (Table 3.6). There is no clear evidence that the addition of IL improved the recovery of large molecular fractions of oily sludge (i.e., asphaltenes) since the concentration of V and Ni (the main source of V and Ni are asphaltene (Jacobs and Filby,

1983)) in recovered oil from solvent extraction alone and IL-enhanced solvent extraction were similar. Although extraction treatments recovered more than 90% TPH from oily sludge, the TPH content in the residual sand/clay (7.9% and 9.5% for solvent extraction alone and IL-enhanced solvent extraction, respectively) was still much higher than the criteria (<0.7% of extractable PHC in the soil at industrial area) regulated by British Columbia Ministry of Environment, Lands and Parks (CCME, 2008b). The concentrations of elements in the residual sand/clay (such as Cr, Ni, and As) are of concern since they are above the regulatory limits in soils set by CCME (i.e., 87 mg/kg for Cr, 89 mg/kg for Ni, and 12 mg/kg for As at industrial area) (CCME, 1999). Therefore, the residual sand/clay after extraction may still require further treatment.

		Recovered	d oil									Residu	ial sai	nd/clay			
System		Calorific value	С	Н	N	S	Fe	Ca	Mg	V	Ni	С	N	TPH	Cr	Ni	As
			%	%	%	%	mg	mg	mg	mg	mg	%	%	%	mg/	mg	mg/
		MJ/kg					/kg	/kg	/kg	/kg	/kg				kg	/kg	kg
Solvent		43.92	83.6	13.1	0.1	1.7	30	8.8	0.6	2.3	<2	17.8	0.2	7.9	122	82	220
extraction																	
IL+solvent	1^{a}	45.68	84.5	12.9	0.1	1.6	18	<8	< 0.5	2.2	<2	16.6	07	0.5	122	00	222
extraction	2 ^b	44.50	83.4	13.2	0.1	1.3	266	21.1	2.3	2.6	<2	10.0	0.7	9.5	155	00	232

Table 3.6. Properties of extracted oil and residual sand/clay after extraction in different systems

^a Recovered oil in top oil/solvent layer. ^b Recovered oil in oil/solvent-IL interface.

3.4. Summary

An IL-enhanced solvent extraction (using cyclohexane and [Emim][BF4]) was investigated in this study to examine its efficiency of oil recovery from oily sludge. Compared to solvent extraction alone (using cyclohexane), IL-enhanced solvent extraction achieved a similar or higher TPH recovery $(96.92 \pm 4.79\%)$ within a much shorter duration (i.e. 10 min) and a much lower solvent/sludge ratio (i.e. 4:5 mL/g) under less energy consumption (i.e. 100 rpm) condition. The proposed process required a remarkably low concentration of IL [Emim][BF₄] (i.e. 1:10 mL/g of IL/sludge ratio). When compared to crude oil, the recovered oil had a higher level of F3 fraction and similar calorific value. This indicates that oil extracts can be utilized as a potential energy source and petrochemical feedstock. After extraction, IL existed as a separate phase that can be recycled for further utilization. There was no evidence of IL and fine solids existing in the recovered oil after IL-enhanced solvent extraction. Residual IL was completely separated from residual sand/clay after water washing, which is of significance for recycling IL. However, further research about the reuse of IL is still needed. In summary, ILenhanced solvent extraction could present an economically competitive approach for the management of hazardous oily solid waste. Further work also needs to be performed to understand the extraction mechanism of the oil in the presence of IL, which will serve to the selection/design of IL for oil recovery purpose.

Chapter 4

CO-PYROLYSIS OF METAL CONTAMINATED OILY WASTE FOR OIL RECOVERY AND HEAVY METAL IMMOBILIZATION²

Abstract

The treatment of metal-contaminated oily waste was investigated by using an approach of co-pyrolysis with hog fuel in a fixed bed reactor. Both oil recovery and heavy metal immobilization were evaluated. Three experimental parameters, including pyrolysis temperature, reaction time, and hog fuel addition in the feedstock, were examined to find their effects on the treatment performance. Metal immobilization in the solid char obtained from co-pyrolysis was examined from its speciation characteristics. A higher oil recovery was observed at a lower pyrolysis temperature, while metal speciation in the char residue showed great variation with temperature, with more non-bioavailable species observed at a higher temperature. This is also evident from the calculated risk index (RI) for eco-toxicity assessment, with RI of 34.6 and 117.1 at 600 °C and 400 °C, respectively. Moreover, the addition of hog fuel into oily waste for co-pyrolysis led to increased metal immobilization, but the overall oil recovery was decreased. A low temperature co-pyrolysis (400 °C) by adding 20% of hog fuel was found as the most effective oily waste disposal strategy in this study with satisfactory oil recovery and an acceptable risk index of 54.1.

Keywords: co-pyrolysis, heavy metal, hog fuel, oil recovery, risk assessment

² This work has been published as Tian, Y., Li, J., Yan, X., Whitcombe, T., Thring, R., 2019. Copyrolysis of metal contaminated oily waste for oil recovery and heavy metal immobilization. J. Hazard. Mater. 373, 1–10. DOI: 10.1016/j.jhazmat.2019.03.061.

4.1. Introduction

Petroleum hydrocarbons (PHCs) and heavy metals are potential persistent environmental toxins (Roy et al., 2005). They could exist at contaminated sites affected by accidental spills and leaks from petroleum, transportation, and mining industries (Samaksaman et al., 2016). The coexistence of PHCs and high levels of heavy metals has been detected in oily sludge, which is one of the most abundant waste produced from petroleum refineries (da Silva et al., 2012). For example, the heavy metal concentration in oily sludge from a refinery was reported as 500, 480 and 480 mg/kg dry weight for copper, chromium and nickel, respectively (Admon et al., 2001). The concentration of zinc (Zn) and lead (Pb) in a raw oily sludge sample was reported to be 769 and 565 mg/kg, respectively (da Rocha et al., 2010). High concentration of heavy metals have also been found in drill cuttings which are mixtures of drilling fluids with small pieces of formation rock (Ball et al., 2012). For example, the results from an North Sea oil based drill cuttings sample indicated a heavy metal concentration of 160, 374, 61, 489, and 2511 mg/kg for chromium (Cr), copper (Cu), nickel (Ni), lead (Pb), and zinc (Zn), respectively (Breuer et al., 2004). It was reported that heavy metals in the environment may threaten plants, animals, and humans due to their long-term persistence and possible bioaccumulation and biomagnification effects (Monroy et al., 2014). The existence of PHCs such as polycyclic aromatic hydrocarbons (PAHs) would also pose adverse environmental effects, but the cooccurrence of PHCs and heavy metals may have more negative impacts. For example, a stronger inhibition on soil microbial activity was observed in the case of co-existence of PAHs with heavy metals than the individual existence of heavy metals or PAHs (Maliszewska-Kordybach and Smreczak, 2003).

The remediation of soils co-contaminated with PHCs and heavy metals is a challenging problem since each pollutant type requires a different remediation approach. Bioremediation as a method to treat PHCs contaminated soils has the advantage of low cost while enhancing the soil quality and functions. However, the long-term degradation process and the inhibition of toxic heavy metals on the activity of microorganisms would limit its utilization, thus leading to the requirement of other alternatives (AL-Saleh and Obuekwe, 2005). Among various approaches, the pyrolysis of contaminated soil has received growing interests. It can effectively recover oil from organic wastes, while immobilizing heavy metals in the solid residue, thus leading to significantly reduced environmental risks due to decreased bioavailability of heavy metal ions. A number of operating variables may affect the pyrolysis treatment, such as pyrolysis temperature, reaction time, and chemical additives (Shie et al., 2003; Wang et al., 2007). It was reported that the co-pyrolysis with other waste materials could even enhance the treatment performance (Debela et al., 2012; Shi et al., 2013b). For example, Debela et al. (2012) found that the pyrolysis of contaminated soil immobilized some heavy metals such as Pb and Cd, while the Cd leaching was further reduced with the addition of 5, 10, and 15% biomass in the soil. Shi et al. (2013b) also reported that the addition of rice husk during the hydrothermal carbonization of sewage sludge resulted in a synergistic effect on reducing the risk of heavy metals (Cr, Ni, Cu, and Cd) in the solid residues. However, many previous studies on the thermal treatment of waste focused on the total heavy metal contents and the leaching behavior of residues after treatment (Jin et al., 2014; Thurnau, 1996). Their results can hardly be used for evaluating the eco-toxicity of treated waste, which depends on the specific chemical forms or binding patterns of metals (He et al., 2010).

As an extension of our previous study on the co-pyrolysis of oily sludge for energy recovery (Hu et al., 2017), this work was conducted to investigate the pyrolysis of oily waste containing heavy metals for both oil recovery and heavy metal immobilization. Hog fuel (i.e. wood waste) from lumber production was used as an additive, aiming to explore the reduced bioavailability and toxicity of heavy metals in the pyrolysis char. The metal chemical speciation in the solid char residue was examined to evaluate the ecological risk posed by oily waste treatment. The effects of three selected experimental variables (pyrolysis temperature, reaction time, and wood waste addition) on the process performance in terms of oil recovery and the ecological risk of solid char residue, were studied using a response surface methodology (RSM). The results would provide valuable information for developing effective technique to address oily waste problem with added economic and environmental benefits.

4.2. Materials and methods

4.2.1. Materials

The clean soil was collected from a forest site located east of Prince George, BC, and it was air-dried at room temperature for 3–4 days and then sieved to 0.84 mm (passed through a # 20 sieve). Crude oil sample was donated by an oil refinery in western Canada. The wood waste (called hog fuel) used for co-pyrolysis was collected from a local saw mill in Prince George, and it was ground to < 1.0 mm before use. To prepare the synthetic oily waste containing heavy metals, 500 g of clean soil was first mixed well with the appropriate amount of dissolved Cu(NO₃)₂, Cr(NO₃)₃, Ni(NO₃)₂, Pb(NO₃)₂, and ZnCl₂ solution to obtain an initial soil concentration of 1000 mg/kg for Cu²⁺, Cr³⁺, Ni²⁺, Pb²⁺, and Zn²⁺, respectively. The air-dried heavy metal contaminated soil was then thoroughly mixed with 20 wt% of crude oil diluted in

dichloromethane (DCM), and the mixture was left in the fume hood to allow for solvent evaporation. Table 4.1 lists the synthetic oily waste properties, including the concentrations of total petroleum hydrocarbon (TPH) and heavy metals. Such synthetic heavy metal contained oily waste was then used for pyrolysis study through the addition of hog fuel with different mixing ratio of 0%, 10%, and 20% (w/w), respectively.

Synthetic oily waste								
Parameter	Concentration (mg/kg)	Soil texture						
ТРН	$17.5 \pm 0.35\%$ (by mass)	Sand	10.8%					
Copper (Cu)	748 ± 3	Silt	73.9%					
Chromium (Cr)	826 ± 3	Clay	15.3%					
Nickel (Ni)	828 ± 4							
Lead (Pb)	789 ± 1							
Zinc (Zn)	865 ± 4							

Table 4.1. Soil texture and synthetic oily waste properties

4.2.2. Experimental set up

Each pyrolysis experiment was carried out in a fixed-bed tube furnace pyrolysis reactor (quartz tube length: 600 mm, Ø: 50 mm; MTI Corp.[®] GSL-1100X) under nitrogen atmospheric pressure (Figure 4.1). The oily waste sample was put into the sample ark which was placed in the tube reactor center. Before experiment, nitrogen gas was blown into the reactor at a rate of 1 L/min for 30 min to create an oxygen-free environment. The nitrogen flow rate was then set to 100 mL/min and maintained throughout the pyrolysis reaction with a heating rate of 20 °C/min. During the reaction period, the pyrolysis temperature was kept at the set value that was determined from a response surface experimental design method. The condensable volatile

matter was collected in the ice-water cooling traps as the recovered oil. The solid char residue was collected after the furnace was cooled down to room temperature.



Figure 4.1. Schematic diagram of fixed-bed pyrolysis reactor $(1 - N_2 \text{ gas cylinder}, 2 - \text{flow meter}, 3 - thermal couple, 4 - quartz tube, 5 - sample ark, 6 - tube furnace, 7 - temperature controller, 8 - ice-water bath, 9 - Tedlar gas bag).$

4.2.3. Experimental design

In this study, three experimental factors were examined for their effects on the co-pyrolysis performance, including pyrolysis temperature, reaction time, and the mixing ratio of hog fuel with oily waste. The selection of these factors was based on previous pyrolysis studies of organic wastes. Pyrolysis temperature not only affects oil yield but also the structure and chemical characteristics of the solid char residue, including its chemical composition, pH, surface area, and functional groups (H. Li et al., 2017; Qin et al., 2015). Reaction time could affect the completeness of pyrolysis process (Xiu et al., 2010), while the addition of waste biomass to pyrolysis process may generate synergistic effect on metal immobilization (Debela

et al., 2012; Shi et al., 2013b). In this study, a pyrolysis temperature range of 400–600 °C was selected based on our previous study on oily sludge co-pyrolysis for energy recovery, and this range was believed to cover the full decomposition temperature of PHCs (Hu et al., 2017). A reaction time range of 30–120 min was selected based on the works of other authors concerning oil production from biomass by liquefaction/pyrolysis and metal immobilization by thermal treatment (Abnisa et al., 2011; Debela et al., 2012; L. Li et al., 2012; Yang et al., 2004). A hog fuel addition range of 0–20% was selected based on the consideration that one purpose of the study was to examine the synergistic effect of biomass addition but too much hog fuel addition would increase the waste volume.

The relationship between the experimental factors and pyrolysis system performance was examined using a response surface methodology (RSM) for experimental design (Bezerra et al., 2008). When several independent factors and their interaction have influence on the experimental outcome, the RSM is an effective tool for the optimization of these factors with a minimum number of experimental runs (Ahmadi et al., 2005). The RSM design must include three to five replicates of central point runs, but replicating the corner-point experimental run is not mandatory (Montgomery, 2017). In this study, a total of 15 experiments with three replicates in the central point (in order to estimate the pure error) were designed by using Box-Behnken design (BBD) method through the Design Expert software (Ver. 10.1). Such design method was also reported in previous studies (Xu et al., 2018). Table 4.2 lists the arrangement of experiments, with each experimental factor varying over three levels, including high level (+1), low level (-1), and central point (coded level 0). The experiments were carried out in a random order to minimize the effects of uncontrolled factors. The co-pyrolysis process was evaluated for its performance (i.e. response) by analyzing the TPH recovery rate (Y_1 , %) and

the potential ecological risk index (RI) of solid char residue (Y_2). A multiple regression analysis was conducted by using Design Expert software (Ver. 10.1):

$$Y = \beta_0 + \sum_{j=1}^k \beta_j x_j + \sum_{j=1}^k \beta_{jj} x_j^2 + \sum_i \sum_{j=2}^k \beta_{ij} x_i x_j + e_i$$
(4.1)

where Y is the response; k is the number of independent variables; x_i and x_j are variables; β_0 is the model intercept term; β_j is the first order (linear) main effect; β_{jj} is the quadratic effect; β_{ij} is the interaction effect; and e_i is the error (Bezerra et al., 2008). Analysis of variance (ANOVA) was used to test the significance of independent variables and their interaction.

	Pyrolysis		Reaction time		Hog fuel	addition	ТРН	RI
	(°C)	ure	(min)		(%)			
No.	(C)						(70)	
	<i>x</i> ₁	<i>X</i> ₁	<i>x</i> ₂	<i>X</i> ₂	<i>x</i> ₃	<i>X</i> ₃	<i>Y</i> ₁	<i>Y</i> ₂
	(coded)	(un- coded)	(coded)	(un- coded)	(coded)	(un- coded)	(observed)	(observed)
1	-1	400	-1	30	0	10	82.2	87.6
2	1	600	0	75	1	20	68.6	22.0
3	-1	400	0	75	1	20	68.7	53.3
4	0	500	-1	30	1	20	58.3	41.5
5	0	500	-1	30	-1	0	83.6	77.2
6	-1	400	1	120	0	10	65.4	84.3
7	1	600	0	75	-1	0	69.5	35.5
8	1	600	1	120	0	10	62.6	31.7
9	0	500	1	120	1	20	56.8	30.8
10	1	600	-1	30	0	10	68.3	33.2
11	-1	400	0	75	-1	0	82.9	120.2
12	0	500	1	120	-1	0	67.1	59.8
13	0	500	0	75	0	10	74.7	42.2
14	0	500	0	75	0	10	72.5	38.7
15	0	500	0	75	0	10	74.9	39.0

Table 4.2. Coded (x_i) and un-coded (X_i) Box-Behnken design matrix with the experimental results

4.2.4. Chemical analysis and heavy metal species characterization

Analysis of petroleum hydrocarbons

A weighed mass (M) of the recovered oil was collected into a 40 mL vial, followed by the addition of 20 mL DCM solvent to the vial. The vial was then placed on a Talboy 3500 orbital shaker for mechanical extraction at 150 rpm for 30 min. After shaking, the extraction solution was transferred for silica gel column cleanup to remove moisture, particulate, and unwanted polar organic compounds (CCME, 2001). A small amount of glass wool was placed into the bottom of the glass column which has a length of 30 cm and an internal diameter of 16 mm. The column was packed with approximately 6.5 cm of 70-230 mesh silica gel (activated at 110 °C for 12 h) and approximately 2.5 cm of 10–60 mesh anhydrous sodium sulfate (dried at 400 °C for 4 h). Before use, the column was rinsed with 20 mL of solvent (1:1 n-hexane/DCM). The extraction solution was carefully transferred into the column and then followed by another 20 mL of solvent (1:1 n-hexane/DCM) to elute the column. A round flask weighed (M_0) was placed under the bottom of the column to collect the cleaned extract. The solvent in the cleaned extract was evaporated by using a Yamato RE400 rotary evaporator. The round flask containing the PHCs after evaporation was weighed (M_T) . The concentration of TPH in the recovered oil can then be calculated. Similarly, TPH concentration in the original oily waste sample can also be obtained.

$$C = \frac{M_T - M_0}{M} \times 10^6 \tag{4.2}$$

where *M* is the mass of recovered oil or the original oily waste sample (g); M_0 is the mass of the round flask (g); M_T is the mass of round flask containing PHCs (g); and *C* is the TPH concentration in recovered oil or in the original oily waste sample (mg/kg).

The TPH recovery rate was calculated as the ratio of TPH mass in the recovered oil to the mass of TPH in the original oily waste sample:

$$R = \frac{C_r \times M_r}{C_s \times M_s} \times 100\% \tag{4.3}$$

where *R* is the TPH recovery rate (%); C_r and C_s (mg/kg) are TPH concentrations in the recovered oil and oily waste sample, respectively; and M_r and M_s (g) are the mass of recovered oil and oily waste sample, respectively.

The PHCs fractions (F2, F3, and F4) in the recovered oil and original crude oil were also measured using GC analysis method on an Agilent 6890 GC-FID as described in Section 3.2.4.1.

Characterization of solid residue

The total carbon (C), nitrogen (N), and hydrogen (H) of the feed stocks (oily waste and hog fuel) and solid residue samples were measured by combustion elemental analysis using a Costch ECS 4010 elemental analyzer. The pH of the samples was measured in a supernatant of aqueous solution (sample/water = 1:50, w/v) with a Mettler Toledo FG2 portable pH meter (Bagreev et al., 2001). The ash content of sample was determined according to methods recommended for forest soil and plant analysis (Kalra and Maynard, 1991). The samples were also ground and mixed with KBr (0.1 wt%) and then pressed into pellets. The Fourier transform infrared (FTIR) spectra were then obtained using a Nexus 670 Thermo Nicolet Spectrometer.

Sequential extraction of heavy metals

It was recognized that the ecological toxicity of heavy metal depends on its chemical speciation, including water soluble fraction, exchangeable fraction, easily reduced fraction, oxidizable fraction, and residual fraction. These five species can be determined using a five-

step sequential extraction procedure. The heavy metal species in the oily waste and the pyrolysis char residue were analyzed using the following modified procedure (Devi and Saroha, 2014; Pöykiö et al., 2006):

Step 1 (*Water soluble fraction*): 0.5g of sample was extracted with 20 mL of acidified deionized water (pH = 4.0) by shaking on a Talboy 3500 orbital shaker at 60 rpm for 16 h at room temperature. The extract was then collected by centrifugation (Thermo Scientific Sorvall Legend X1) at 5000 rpm for 10 min, filtered through a 0.45-µm nylon filter and stored at 4 °C until further analysis. The remaining solid was washed by shaking at 160 rpm for 1 h with 10 mL of deionized water, followed by centrifugation at 5000 rpm for 10 min. The supernatant was discarded.

Step 2 (*Exchangeable fraction*): the residue from step 1 was shaken on a Talboy 3500 orbital shaker at 60 rpm for 16 h at room temperature with 20 mL of 0.11M acetic acid (pH = 2.8). Similar to step 1, the extract was collected by centrifugation and then filtered. The residue was washed, followed by centrifugal separation as in step 1.

Step 3 (*Easily reduced fraction*): 20 mL of 0.11 M hydroxylammonium chloride solution, acidified to pH of 2 with HNO₃, was added to the residue from the 2nd step, and the mixture was shaken at 60 rpm at room temperature for 16 h. The extract was then subject to centrifugal separation and nylon filter filtration, and the resulting residue was washed as in previous steps.

Step 4 (*Oxidizable fraction*): 5 mL of 30% H₂O₂ was carefully added to the residue from step 3. The mixture was digested in a 50-mL centrifuge tube at room temperature for 1 h with occasional manual shaking. The digestion was continued in a sand bath for 1 h at 85 ± 5 °C, and the volume was reduced to < 1 mL by further heating of the uncapped tube. A second 5 mL of H₂O₂ was added to repeat the digestion procedure. 25 mL of 1 M ammonium acetate,

adjusted to pH of 2, was added to the cool moist residue, and the mixture was shaken at 60 rpm for 16 h at room temperature. Similar to the previous steps, the extract was separated and filtered, and the residue was washed.

Step 5 (*Residual fraction*): the residue from step 4 was digested in concentrated HNO₃ and concentrated HCl, following the microwave assisted digestion method (USEPA 3051A) (USEPA, 2007a). The resulting solutions were used to determine the content of heavy metals.

The concentrations of Zn, Cu, Ni, Pb, and Cr in the extract from each step were analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES) (Agilent Technologies 5100). Two independent replicates were performed for each sample.

4.2.5. Determination of potential ecological risk index (RI)

The potential risk posed by heavy metals in pyrolysis char residue was assessed using a potential ecological risk index (*RI*) as follows (Devi and Saroha, 2014; Jin et al., 2016; Zhao et al., 2012):

$$C_f = C_i / C_n \tag{4.4}$$

$$E_r = T_r C_f \tag{4.5}$$

$$RI = \sum E_r \tag{4.6}$$

where C_f is the contamination factor; C_i is the sum of concentration of metal ions extracted in the first four steps of the sequential extraction; C_n is the concentration of metal ions in residual fraction; E_r is the potential ecological index for individual heavy metal ion; T_r is toxicity factor of the individual heavy metal ion; and *RI* is the potential ecological risk index. The T_r values used in this study are 1, 5, 6, 5 and 2 for Zn, Cu, Ni, Pb, and Cr, respectively (Chabukdhara and Nema, 2011; Devi and Saroha, 2014).

4.3. Results and discussion

4.3.1. Response surface model and statistical analysis

The following second-order polynomial equations were established by applying multiple regression analysis of the experiment results:

$$TPH \ recovery \ (\%) = 137.01 - 0.12X_1 - 0.11X_2 - 2.43X_3 + 6.15 \times 10^{-4}X_1X_2 + 3.33 \times 10^{-3}X_2X_3 + 8.33 \times 10^{-3}X_1X_3 - 2.60 \times 10^{-3}X_2^2 - 2.45 \times 10^{-2}X_3^2$$

$$(4.7)$$

$$RI = 610.68 - 1.65X_1 - 0.69X_2 - 9.86X_3 + 9.83 \times 10^{-5}X_1X_2 + 1.33 \times 10^{-2}X_1X_3 + 3.68 \times 10^{-5}X_1X_2 + 1.33 \times 10^{-5}X_1X_3 + 3.68 \times 10^{-5}X_1X_3 + 3.68 \times 10^{-5}X_1X_2 + 1.33 \times 10^{-5}X_1X_3 + 3.68 \times 10^{-5}X_1X_3 +$$

$${}^{3}X_{2}X_{3} + 1.23 \times 10^{-3}X_{1}^{2} + 3.41 \times 10^{-3}X_{2}^{2} + 5.44 \times 10^{-2}X_{3}^{2}$$

$$(4.8)$$

where X₁, X₂, and X₃ are pyrolysis temperature (°C), reaction time (minutes), and hog fuel addition (%); if 400 °C \leq X₁ \leq 600 °C, 30 min \leq X₂ \leq 120 min, and 0 % \leq X₃ \leq 20 %.

Fitness of the model was assessed using ANOVA (Tables 4.3 and 4.4). The model *F*-values (10.659 and 49.498) indicated that these two models could well describe the TPH recovery rate and RI, with *P* values (0.0049 and 0.0002) all less than 0.05. In terms of the model for TPH recovery, the determination coefficient (R^2) reached 0.9343, while all the variables (x_1, x_2 , and x_3) showed significant effects. In terms of the model for ecological risk index (RI), the determination coefficient (R^2) reached 0.9889, while only pyrolysis temperature (x_1) and hog fuel addition ratio (x_3) had significant effects.

Source	Sum of	DF ^a	Mean square	F-value	$\operatorname{Prob} > F$	Significance
	squares					
Model	891.605	8	111.451	10.659	0.0049	**
<i>x</i> ₁	113.572	1	113.572	10.862	0.0165	*
<i>x</i> ₂	205.885	1	205.885	19.691	0.0044	**
<i>x</i> ₃	322.137	1	322.137	30.809	0.0014	**
<i>x</i> ₁ <i>x</i> ₂	30.597	1	30.597	2.926	0.1380	
<i>x</i> ₁ <i>x</i> ₃	44.217	1	44.217	4.229	0.0855	
$x_{2}x_{3}$	56.227	1	56.227	5.378	0.0595	
x_{2}^{2}	102.897	1	102.897	9.841	0.0201	*
x_{3}^{2}	22.311	1	22.311	2.134	0.1944	
Residual	62.735	6	10.456			
Lack of fit	58.945	4	14.736	7.777	0.1172	
Pure error	3.790	2	1.895			
Cor total	954.340	14				
Std. Dev.	3.23		<i>R</i> ²	0.9343		
mean	70.41		Adj R ²	0.8466		
CV	4.59		Pred R^2	0.3472		
PRESS	623.02		Adeq precision	10.5286		

 Table 4.3. ANOVA of the regression model for TPH recovery

^a Degree of freedom; * Significant (P < 0.05); ** Highly significant (P < 0.01).

Source	Sum of squares	DF ^a	Mean square	F-value	$\operatorname{Prob} > F$	Significance
Model	10473.981	9	1163.776	49.498	0.0002	**
<i>x</i> ₁	6223.529	1	6223.529	264.703	< 0.0001	**
<i>x</i> ₂	135.454	1	135.454	5.761	0.0616	
<i>x</i> ₃	2633.774	1	2633.774	112.021	0.0001	**
<i>x</i> ₁ <i>x</i> ₂	0.783	1	0.783	0.033	0.8624	
<i>x</i> ₁ <i>x</i> ₃	714.331	1	714.331	30.382	0.0027	**
<i>x</i> ₂ <i>x</i> ₃	11.051	1	11.051	0.470	0.5235	
<i>x</i> ² ₁	561.804	1	561.804	23.895	0.0045	**
x_{2}^{2}	175.656	1	175.656	7.471	0.0411	*
x_{3}^{2}	109.398	1	109.398	4.653	0.0835	
Residual	117.557	5	23.511			
Lack of fit	109.948	3	36.649	9.633	0.095505	
Pure error	7.609	2	3.805			
Cor total	10591.538	14				
Std. Dev.	4.85		<i>R</i> ²	0.9889		
mean	53.12		Adj R ²	0.9689		
CV	9.13		Pred R^2	0.8323		
PRESS	1776.28		Adeq precision	23.2560		

Table 4.4. ANOVA of the regression model for RI in solid residue

^a Degree of freedom; * Significant (P < 0.05); ** Highly significant (P < 0.01).

4.3.2. TPH recovery rate

The co-pyrolysis of oily waste and wood waste produced an oil mixture with two phases including a black immiscible liquid likely due to the oil derived from wood waste. Other studies

reported similar phase separation, with oils produced from oily sludge/wood waste blends having two phases (an upper phase and a bottom phase) (Abnisa and Wan Daud, 2015; Hu et al., 2017; Samanya et al., 2012). In this study, the bottom black immiscible liquid phase was not observed in the oil produced from the pyrolysis of oily waste alone, indicating that this phase was originated from the wood waste. Moreover, the yield of the bottom phase increased (from visual observation) when the hog fuel mixing ratio in the feedstock increased. Given this finding, the upper phase of oil mixture was considered as the recovered oil from oily waste in this study.

As shown in Figure 4.2, there is no significant difference in the oil composition between the original oily waste and the recovered oil, indicating that the distillation during pyrolysis is the predominant mechanism for oil recovery. Figure 4.3 shows the variation of TPH recovery against each experimental parameter while all other factors were maintained constant at the coded level of 0. It was reported that the highest liquid yield was generally obtained in the range of 500-600 °C (Akhtar and Amin, 2012; Lam et al., 2010; Liu et al., 2008). At temperatures below this range, incomplete pyrolytic decomposition occurs, while higher temperatures could enhance the production of condensable vapor from waste, leading to a higher yield of liquid oil product. However, at pyrolysis temperatures above this range, oil yield could decrease as a result of potential degradation of oils to gases by secondary cracking (Lam et al., 2010). From Figure 4.3(a), a trend can be observed in which TPH recovery decreased with increasing temperature in the experimental range of 400–600 °C. This trend indicates that the desirable pyrolysis temperature could be less than or equal to 400 °C. Such desirable temperature may vary because of different experimental conditions (e.g., heating rate, type of reactor, and nitrogen flow rate). Sinağ et al. (2010) conducted similar experiments to
treat waste machinery oil and obtained the highest oil yield at 400 °C. Piskorz et al. (1986) also reported that the maximum yield of organic liquid occurred at 400 °C. Our results are consistent with these previous studies, suggesting that temperature higher than 400 °C is not always needed for waste pyrolysis.



Figure 4.2. Gas chromatogram of (a) oil from untreated oily waste and (b) recovered oil after pyrolysis treatment (run #11).



Figure 4.3. The statistical evaluation of the effect of single factor on TPH recovery rate, (a) pyrolysis temperature (reaction time: 75 min, hog fuel ratio: 10%), (b) reaction time (pyrolysis temperature: 500 °C, hog fuel ratio: 10%), and (c) hog fuel addition (pyrolysis temperature: 500 °C, reaction time: 75 min).

As shown in Figure 4.3(b), the TPH recovery reached the maximum (75.8%) at a reaction time of 54 min and then decreased beyond 54 min. An appropriate reaction time could improve pyrolysis conversion, but excessive duration would cause decrease in the TPH recovery, owing to the decomposition of some oil and/or the formation of solid residue by oil repolymerization (Xiu et al., 2010; Yang et al., 2004). As seen in Figure 4.3(c), the TPH recovery decreased with increasing hog fuel ratio in the feedstock. Abnisa and Wan Daud (2015) found lower experimental yield of TPH than the calculated yield when studying the fuel recovery from copyrolysis of palm shell and scrap tire. Similar trends were reported in other co-pyrolysis studies (Hu et al., 2017; Krerkkaiwan et al., 2013; Park et al., 2010; Song et al., 2014). Such effect of hog fuel addition during co-pyrolysis of oily waste could be attributed to the role of alkali and alkaline earth metallic species (AAEMs) present in wood waste (Song et al., 2014).

As shown in Figure 4.4, different combination of pyrolysis temperature and reaction time could achieve similar TPH recovery rate, while an increase in reaction time could compensate for the effect due to a decrease in temperature. However, the pyrolysis temperature did not affect the TPH recovery at reaction time > 110 min, indicating that the secondary cracking of oil was independent of the whole temperature range (400–600 °C). As seen in Figure 4.5(a), the reaction time required for maximizing TPH recovery was dependent on the hog fuel ratio in feedstock, with maximum TPH recovery for 0%, 10%, and 20% hog fuel addition occurred at reaction time of 37.2 min, 53.6 min, and 68.1 min, respectively. This result implied that a longer reaction time was required to allow a complete reaction for the co-pyrolysis of oily waste/wood waste mixture as compared to the pyrolysis of oily waste alone. Figure 4.5(b) shows that the higher TPH recovery rate occurred when both the pyrolysis temperature and hog fuel addition were kept to a lower value, which is consistent with the trends observed from Figure 4.3(a) and (c).



Figure 4.4. Contour plot of TPH recovery (%) as function of pyrolysis temperature and reaction time at hog fuel addition = 10%.



Figure 4.5. Response surface graph of TPH recovery as function of (a) reaction time and hog fuel addition at pyrolysis temperature = $500 \,^{\circ}$ C, and (b) pyrolysis temperature and hog fuel addition at reaction time = $75 \,$ min.

4.3.3. Properties of solid residues

Table 4.5 lists the total C, H, N, and pH in the feedstock, the solid residue derived from pyrolysis of oily waste alone, and the residue from the co-pyrolysis of oily waste and hog fuel

mixture. The aromaticity degree of solid residue can be identified by the H/C ratio (Xiao et al., 2016). The H/C ratios of solid residues decreased with increasing pyrolysis temperature, but they were all below 0.18 at different pyrolysis temperatures, indicating a high degree of aromaticity under which the residues are resistant to decomposition (Yuan et al., 2013). The N/C ratio was decreased from 0.034 for solid residue after pyrolysis at 400 °C (SRO400) to 0.022 for solid residue after pyrolysis at 600 °C (SRO600). This would suggest that the loss of nitrogen-related function groups at higher temperature in the absence of hog fuel (T. Chen et al., 2014). It was also observed that the pH value of solid residues increased with pyrolysis temperature. This may be attributed to the formation of alkali carbonates within the pyrolyzed material (T. Chen et al., 2014).

Sample	C (%) ^a	H (%) ^a	N (%) ^a	H/C	N/C	pН	Ash (%) ^a
Hog Fuel	49.17 ± 1.69	6.17 ± 0.01	0.03 ± 0.04	0.125	0.001	ND	1.59 ± 0.09
SRC	16.71 ± 1.80	2.50 ± 0.69	0.13 ± 0.03	0.150	0.008	3.93 ± 0.14	84.0 ± 0.14
SRO400	2.14 ± 0.06	0.39 ± 0.04	0.07 ± 0.01	0.180	0.034	6.07 ± 0.28	97.7 ± 0.01
SRO600	2.02 ± 0.09	0.10 ± 0.09	0.04 ± 0.01	0.050	0.022	7.20 ± 0.10	98.4 ± 0.04
SROH400	9.37 ± 0.97	0.65 ± 0.01	0.10 ± 0.03	0.069	0.010	6.32 ± 0.05	90.3 ± 0.09
SROH600	7.54 ± 0.48	0.30 ± 0.01	0.07 ± 0.01	0.040	0.009	7.14 ± 0.17	92.7 ± 0.16

Table 4.5. Total C, H, N, and pH in the feedstock and the solid residue after pyrolysis

Note: SRC: solid residue sample from control experiment without pyrolysis treatment; SROx: solid residue from pyrolysis of oily waste alone at X (°C) temperature and reaction time = 75 min; SROHx: solid residue from co-pyrolysis of oily waste and hog fuel at X (°C) temperature and reaction time = 75 min and hog fuel addition = 20%; ND: not detected.

^a On a dry basis.

The FTIR spectra of the feedstock and the solid residues after pyrolysis are shown in Figure B1 in Appendix B. The peak occurring at around 3600 cm⁻¹ corresponds to the vibration of OH groups in the mineralized matter (Hossain et al., 2011). The intensity of the broad band

between 3500 and 3300 cm⁻¹ decreased from feedstock to solid residues as a result of the decomposition of organic OH groups at elevated temperatures (Jin et al., 2016). The pyrolysis resulted in a disappearance in C-H stretching at 2905 and 2850 cm⁻¹, indicating that the carbonaceous materials were transformed into CH₄, CO₂ and other gases or to aromatic structures (Lu et al., 2013). Jin et al. (2016) reported that the amide bond stretching (-CO-NH-) at 1633 cm⁻¹ was offset when the pyrolysis temperature increased, suggesting that the amide functional groups were complexed with heavy metals during pyrolysis. However, the FTIR spectra peak at 1633 cm⁻¹ was more likely to be resulted from C=O stretching vibration of ketone, aldehyde, lacton, amide, and carboxyl in this study. The strong peaks of C-O stretching vibration at 1038 cm⁻¹ suggested that various forms of oxygen were directly bonded to the adjacent carbon element during pyrolysis (T. Chen et al., 2014). The peak intensity between 800–600 cm⁻¹ was likely arising from the aromatic and hetero-aromatic compounds (Hossain et al., 2011), which is consistent with the results for H/C ratio shown in Table 4.5. The peaks below 600 cm⁻¹ were assigned to the metal-ligand stretching vibrations in inorganic compounds (Hossain et al., 2011).

4.3.4. Heavy metal speciation characteristics

Metal ions can be categorized into five species (fractions), including a water soluble fraction (F1), exchangeable fraction (F2), reducible fraction (F3), oxidizable fraction (F4), and residual fraction (F5). The bioavailability and mobilization of these metal species follow the order of F1 > F2 > F3 > F4 > F5. The species in (F1 + F2) are very prone to leaching, and thus they are included in the bioavailable category. Species in (F3 + F4) are identified as potential bioavailable species which can undergo degradation and leaching under very rigorous conditions (e.g., highly acidic conditions and an oxidizing atmosphere). Metals in F5 possess

no toxicity because they are intercalated into clay layers or ionic bound to the surface structures of silicates (Huang and Yuan, 2016).

Figure 4.6 shows the ratio of the five species in each metal in the original oily waste and its solid residue after pyrolysis. In the case of original oily waste, the non-bioavailable species (F5) only accounted for less than 12% in each of the five studied metals, implying a relatively high ecological risk associated with these metals in the oily waste. However, pyrolysis treatment significantly reduced the potential risk by transforming weakly bound metal species (F1 and F2) to more strongly bound complexes (F5) in the solid char residue. After pyrolysis treatment, the ratios of (F1 + F2) in Cu, Ni, Pb, and Zn were significantly decreased, while the (F3 + F4) and F5 ratios increased, except for Pb in solid residue after pyrolysis at 600 °C (SRO600). In terms of Cr, the ratios of F1, F2, F3, and F4 decreased while the F5 ratio increased. This indicates that the pyrolysis treatment enhanced the complexation of chromium ions, generating more tightly bound complexes in F5 than (F3 + F4).



Figure 4.6. Fraction distribution of metals in oily waste before and after pyrolysis treatment.

F4

F4

F3+F4

F5

F3+F4

F5

The concentrations of metal species in the bioavailable category (F1 + F2) were found to decrease with pyrolysis temperature. For example, the percentage of the bioavailable (F1 + F2)species in Cu decreased significantly from 67.32% for the original oily waste (SRC) to 32.07% for solid residue after pyrolysis at 400 °C (SRO400) and further to 16.15% for solid residue after pyrolysis at 600 °C (SRO600). Similar decrease trends were also observed for Cr, Ni, Pb, and Zn (Figure 4.6). The (F1 + F2) ratios in Cr, Ni, Pb, and Zn decreased from 1.09%, 8.39%, 16.68%, and 11.83% for SRO400 to 0.13%, 3.65%, 5.10%, and 3.50% for SRO600, respectively. In addition, the F5 ratios in Cu, Cr, Pb, and Zn were increased by 2.5, 2.9, 4.8, and 2.0 times for SRO600, respectively, as compared to those for SRO400. Interestingly, the immobilization of heavy metals was further enhanced by hog fuel addition. With 20% addition of hog fuel, the ratios of (F1 + F2) and (F3 + F4) in Cu showed a decreasing trend in the solid residue from the co-pyrolysis at 400 °C (SROH400) as compared to that for SRO400. The F5 ratio in Cu was increased to 22.75% for SROH400, which is 2.9 times more than that for SRO400. A decreased ratio of bioavailable (F1 + F2) and potential bioavailable (F3 + F4)species in metal was also found for Ni, Pb, and Zn after co-pyrolysis at 400 °C and 600 °C. However, a slight increase of potential bioavailable species (F3 + F4) was detected for Cr after hog fuel addition, but the ratio of bioavailable Cr species still decreased with co-pyrolysis treatment.

It was found that the distribution pattern of chemical species (F1–F5) was different for each heavy metal after pyrolysis. In general, the bioavailable fractions (F1 and F2) of all the metal ions decreased whereas the residual fraction (F5) increased after pyrolysis treatment, during which the metal immobilization effect could be largely enhanced by increasing the pyrolysis

temperature. This might be caused by the precipitation and complexation between heavy metals and the (crystal) lattice of the solid residue phase (Shi et al., 2013a). It might also be due to the fact that pyrolysis contributes alkalinity to solid residue. The higher the temperature, the more alkaline the solid residue (Hossain et al., 2011; Jin et al., 2016). The high pH could then favor the formation of metal hydroxide, leading to the formation of insoluble metal oxides which are less prone to leaching (Li et al., 2001). As a result, the pyrolysis had a positive effect on the immobilization of heavy metals in solid residue.

Moreover, it is worth noting that compared with pyrolysis of oily waste alone, the addition of hog fuel for co-pyrolysis further decreased the toxicity of solid residue by reducing the bioavailability and potential bioavailability of Cu, Ni, Pb, and Zn. Uchimiya et al. (2010) found similar results from the enhanced retention of Ni and Cd in soil by the addition of bio-char (i.e. a carbon-rich, solid product from pyrolysis of biomass). The increase in soil pH by bio-char amendment was believed to be responsible for the enhanced immobilization of Ni and Cd since a pH increase could lead to the formation of metal (hydro) oxides, carbonates, or phosphate precipitates (Uchimiya et al., 2010). X. Cao et al. (2009) stated that the sorptive interaction via the coordination of metal d-electron to π -electron bonds within the bio-char (cation- π interaction) could be a mechanism for heavy metal retention by bio-char. Some other researchers argued that the complexation of heavy metals with the surface functional groups of bio-chars (especially oxygen, phosphorus, sulfur, and nitrogen function groups) may contribute to enhanced heavy metal immobilization (Jin et al., 2017; Shi et al., 2013b). However, the detailed mechanism of heavy metal immobilization through co-pyrolysis with biomass (e.g., wood waste) still needs further investigation.

4.3.5. Potential ecological risk assessment

Table B1 in Appendix B shows the concentrations of extractable fractions of heavy metals in the oily waste (SRC) and its solid residues, which can be used to assess the potential ecological risk assessment. The potential ecological risk index (RI) posed by heavy metals in the original oily waste (SRC) was calculated to be 302.50, implying a potentially considerable ecological risk (e.g., $300 < \text{RI} \le 600$ indicating considerable risk). However, after any pyrolysis treatment shown in Table 4.2, the risk was reduced from "considerable" to "low" (e.g., $RI \leq$ 150 indicating low risk) (Huang and Yuan, 2016; Jin et al., 2017). Figure 4.7 presents the relationships between RI of solid reside and the experimental variables. Among all the experimental variables, pyrolysis temperature displayed the most significant effect on RI. The higher the pyrolysis temperature, the lower the RI obtained. The effect of hog fuel addition on RI was also important. The increasing hog fuel addition ratio in the feedstock caused a gradually decreasing RI value. These observations are in agreement with the results for metal species variation, in which the transformation from bioavailable category (F1+F2) to less soluble metal forms was enhanced when the pyrolysis temperature and hog fuel addition increased.

Additionally, due to the fact that the interaction between pyrolysis temperature and hog fuel addition was significant (*F*-value = 30.382), the RI value varied with pyrolysis temperature depending on hog fuel addition, and vice versa. As can be observed from Figure 4.7 (b), at 20% hog fuel addition, the pyrolysis temperature had a slight effect on RI, while a low RI (< 55) could always be achieved at different pyrolysis temperatures (400–600 °C). However, when the hog fuel addition was zero, RI was decreased from 117.14 to 34.63 as the pyrolysis temperature increased from 400 °C to 600 °C, indicating a much stronger effect of pyrolysis

temperature on RI. The experimental data illustrated that the co-pyrolysis of oily waste with 20% of hog fuel at 400 °C could greatly transform the potentially toxic metal fractions in the waste into the least soluble fraction, while further increase in pyrolysis temperature showed little beneficial effect.

It was found that the influence of reaction time on RI was not significant (*F*-value = 5.761), which can be also observed from Figure 4.7 (a) and (c). Similarly, very little effect on the reduction of metal leaching by increased heating time (from 1 h to 2 h) was reported by Debela et al. (2012). However, L. Li et al. (2012) found that the effect of reaction time differed at different reaction temperature during the hydrothermal gasification of sewage sludge, and it also varied with metals. They found that at 375 °C the bioavailable metal fractions (F1+F2) of Cu and Zn increased with increasing reaction time (from 30 min to 60 min), but no clear change was observed for Cd, Cr, and Pb (L. Li et al., 2012). In contrast, the bioavailable fractions (F1+F2) of Cu and Zn decreased at 400 °C as reaction time increased, while those for Cd, Cr and Pb increased (L. Li et al., 2012). Based on results from this study and those reported in literatures, the effect of reaction time on the distribution and fraction transformation of heavy metals during pyrolysis treatment remains unclear and further investigations are needed.



Figure 4.7. Response surface graph of risk index (RI) as function of (a) pyrolysis temperature and reaction time (at hog fuel addition = 10%), (b) pyrolysis temperature and hog fuel addition (at reaction time = 75 min), and (c) reaction time and hog fuel addition (at pyrolysis temperature = 500 °C).

4.4. Summary

In this study, a co-pyrolysis of oily waste with wood waste was examined for its oil recovery and heavy metal immobilization. A maximum TPH recovery was obtained at a pyrolysis temperature of 400 °C, but further temperature increase could reduce the potential ecological risk of heavy metals. It was also observed that a longer reaction time could favor the pyrolysis conversion, but had little effect on heavy metal immobilization. The addition of hog fuel for co-pyrolysis reduced TPH recovery, but showed a positive effect on heavy metal immobilization in solid residue. At 400 °C, the RI of solid residue decreased from 117.14 to 54.12 when the hog fuel addition ratio in the co-pyrolysis feedstock increased from 0% to 20%. As a result, the co-pyrolysis of oily waste with other biomass waste is an effective approach for both oil recovery and heavy metal immobilization in the obtained solid residue. However, further studies may be required to explore the detailed mechanism of heavy metal immobilization.

Chapter 5

APPLICATION OF OILY SLUDGE-DERIVED CHAR FOR LEAD AND CADMIUM REMOVAL FROM AQUEOUS SOLUTION

Abstract

The objective of this study was to investigate the physicochemical properties of oily sludgederived char produced from pyrolysis at 500 °C (OS500) and its sorption behavior towards lead (Pb^{2+}) and cadmium (Cd^{2+}) in aqueous solution. The sorption kinetics and isotherm of Pb²⁺ and Cd²⁺ sorption on OS500 were determined. The results were fitted with four kinetics (pseudo first order, pseudo second order, Elovich equation, and intraparticle diffusion) and six isotherm (Langmuir, Freundlich, Sips, Redlich-Peterson, Temkin, and Dubinin-Radushkevich) models. The maximum sorption capacity (Q_L) of Pb²⁺ obtained from the Langmuir model was 373.2 mg/g, while Q_L of Cd²⁺ was 23.19 mg/g. The mechanisms of lead and cadmium sorption on OS500 and their quantitative contributions were further studied by Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD) and sequential extraction test. The results indicated the chemical characteristics (e.g., alkaline minerals and effective cation exchange capacity (CEC)) but not microstructure of OS500 controlled its Pb²⁺ and Cd²⁺ sorption. New mineral precipitates (i.e., hydrocerussite (Pb₃(CO₃)₂(OH)₂) and cerussite (PbCO₃)) formed during Pb²⁺ sorption. The Pb²⁺- π interaction and complexation of Cd²⁺ with hydroxyl functional groups were evidenced by FTIR. Mineral precipitation with Pb²⁺ was the predominant mechanism for Pb²⁺ sorption on OS500 (accounted for 93.79%), whereas the complexation dominated Cd²⁺ sorption (accounted for 84.15%). The OS500 shows application potential in removing heavy metal contaminants from solution, especially Pb²⁺.

Keywords: lead, cadmium, sorption mechanism, oily sludge-derived char (OSDC), speciation

5.1. Introduction

It is estimated that more than 60 million tons of oily sludge is generated annually by oil refineries worldwide (Hu et al., 2013). Such sludge contains high concentration of heavy metals (da Rocha et al., 2010) and hazardous organic substances (Mazlova and Meshcheryakov, 1999), such as polycyclic aromatic hydrocarbon (PAHs), phenol, and benzene, posing risks to human health and the environment (Kuang et al., 2011; Robertson et al., 2007). The effective disposal of oily sludge is a difficult and challenging problem because of its hazardous and recalcitrant nature (Hu et al., 2013). Compared to landfilling and incineration, pyrolysis can be a potential promising method for oily sludge management due to its energy recovery (pyrolysis oil and gas), solid waste reduction, and less secondary pollution (Qin et al., 2015). In addition to the oil and gas recovery, solid residue char is generated from pyrolysis. In the past years, growing interest has been shown in the application of oily sludge-derived char (OSDC) to remove heavy metals from wastewater. For example, Mohammadi and Mirghaffari (2015) reported that the cadmium (Cd^{2+}) sorption capacity for the non-activated OSDC was 1.49 mg/g, compared to that for activated OSDC was 19.23 mg/g. Seredych and Bandosz (2006) produced the OSDC at 650 °C and found the maximum copper (Cu²⁺) sorption ability of OSDC (74.28 mg/g) was about five times higher than that of wood-based (15.88 mg/g) activated carbon. As a result, oily sludge could be a potential material for producing effective sorbent.

Previous work showed that biochar (a carbon-rich solid obtained from pyrolysis of biomass) can adsorb heavy metals through a range of mechanisms including (i) physical sorption; (ii) ion exchange (such as K⁺, Na⁺, Ca²⁺, and Mg²⁺); (iii) surface complexation between metal cation and oxygen-containing functional groups (e.g., –OH and –COOH); (iv) precipitations

with minerals (e.g., CO₃²⁻, SO₄²⁻, and PO₄³⁻); (v) electrostatic interactions between metal cations and negatively charged biochar surface; and (vi) coordination of metal cation with π electrons (Lu et al., 2012; Uchimiya et al., 2010). The organic functional groups are the important components determining the sorption of heavy metals on biochar. For example, Uchimiya et al. (2011b) showed the properties attributable to surface functional groups (i.e., volatile matter, oxygen content, and the point of zero charge) controlled the heavy metal retention ability of cottonseed hull chars, while other properties such as fixed carbon and ash content had minor effect on heavy metal retention ability. Tong et al. (2011) reported that the major sorption mechanism of Cu²⁺ onto crop straw-derived biochar was surface complexation between metal and organic functional group. In addition, the inorganic mineral in the biochar contributes to the heavy metal removal through precipitation and ion exchange. For instance, T. Zhang et al. (2017) indicated that the lead (Pb^{2+}) sorption of celery-derived biochar involved about 59.8% to 62.8% ion exchange, 36.6% to 34.9% precipitation, and 2.3% to 3.6% complexation. Wang et al. (2015) found that the major sorption mechanism of Pb^{2+} on peanut shells-derived biochars was precipitation, which accounts for more than 80% of the total sorption. The above results showed that the sorption capacity and mechanism of metals on biochar largely depend on the feedstock.

Different from most biomass, such as plant or manure, oily sludge generally contains abundant minerals, including quartz, montmorillonite, calcite, and barite (Andrade et al., 2009; Singh et al., 2010). The minerals may be enriched after the pyrolysis process and further participate in metal sorption. As such, it is reasonable to hypothesize that the mineral-rich OSDC could remove heavy metals through a complex mechanism, involving surface adsorption, precipitation and ion exchange. However, there is a lack of information on the roles of different sorption mechanisms for OSDC, which is critical for its field application. Investigation and even quantification of metal sorption mechanisms of OSDC will aid the design of future field-scale remediation projects, and estimation of the long-term performance of OSDC in field conditions.

In this study, OSDC was prepared by pyrolysis of oily sludge at 500 °C in N₂ atmosphere. The microstructure and chemical properties of OSDC were characterized. The objectives of this study were (i) evaluating the application potential of OSDC as a low-cost sorbent for removing Pb²⁺ and Cd²⁺ in aqueous solution; (ii) investigating the mechanism of Pb²⁺ and Cd²⁺ sorption by OSDC using batch sorption studies, Fourier transform infrared spectroscopy (FTIR), and X-ray diffraction (XRD); and (iii) quantifying the contribution of different mechanisms to the overall sorption of Pb²⁺ and Cd²⁺ by OSDC using a modified sequential extraction test.

5.2. Materials and methods

5.2.1. Materials and reagents

The oily sludge used in this study was collected from an oil tank truck bottom in western Canada. The sludge was oven dried at 80 °C for 3-4 days and stored in a sealed glass jar at 24 °C. The properties of oily sludge are listed in Table 5.1. The extractable petroleum hydrocarbons (i.e., nC10–nC19 and nC19–nC32) was determined by USEPA Method 8015C (USEPA, 2007b). The metal elements were measured using inductively coupled plasma (ICP) analysis based on the ASTM D5185 (ASTM, 2018). Sodium nitrate (\geq 99%) and cadmium nitrate tetrahydrate (\geq 98%) were purchased from Sigma-Aldrich. Lead nitrate (\geq 99%) was

purchased from Fisher Scientific. Ultra high purity (UHQ) water with a resistivity of 18.2 $M\Omega \cdot cm$ (ELGA Purelab) was used for all procedures.

Parameter		Concentration (mg/kg)		
TT11	nC10–nC19 ^a	137,000		
Hydrocarbons	nC19-nC32 ^b	99,000		
	Al	3,491		
	Ba	15,698		
	Ca	29,755		
	Fe	10,379		
Metals	K	14,747		
	Mg	13,946		
	Na	12,835		
	Р	759		
	Si	7,953		

 Table 5.1.
 Properties of oily sludge

^a Hydrocarbons that elute between nC10 and nC19.

^b Hydrocarbons that elute between nC19 and nC32.

5.2.2. Char preparation

About 30 g of oily sludge was put into the sample ark and pyrolyzed in a fixed-bed tube furnace pyrolysis reactor (quartz tube length: 600 mm, \emptyset : 50 mm; MTI Corp.[®] GSL-1100X) under N₂ atmosphere. The furnace temperature was gradually increased to 500 °C at a rate of 10 °C/min, and then maintained for 30 min with a 100 mL/min nitrogen flow rate. Our previous study on oily sludge co-pyrolysis for energy recovery found the maximum oil yield occurred in the range of 500–550 °C (Hu et al., 2017). In addition, the preliminary sorption results

indicated the solid char produced at 500 °C exhibited good performance in removal of heavy metals from solution. Therefore, the pyrolysis temperature of 500 °C was chosen for this study. The solid product was then cooled to room temperature under nitrogen flow (100 mL/min) and then washed with UHQ water in a Soxhlet apparatus for 48 h. Subsequently, the sample was oven dried at 105 °C for 2-3 days and ground using a ball mill (Retsch MM200). 2 g of the sample and agate ball (12mm diameter) were mixed in a 10 mL milling cup at 25 Hz for 40 seconds. The resulting sample was referred to as OS500.

5.2.3. Char characterization

The OS500 was analyzed by a Costech ECS 4010 elemental analyzer to obtain the elemental concentrations of carbon (C), nitrogen (N), hydrogen (H), and sulfur (S). The elements (K, Na, Ca, Mg, Cd, and Pb) in OS500 were determined by inductively coupled plasma optical emission spectrometry (ICP-OES) (Agilent Technologies 5100) after digestion in a nitric/hydrochloric acid mixture (USEPA, 1996b). Ash content was determined after burning the char to a constant weight in a muffle furnace at 600 °C for 16 h. The pH value of char was measured in UHQ water at the ratio of 1:50 w/v after being shaken for 24h at 200 rpm on Talboy 3500 Orbital shaker (Seredych and Bandosz, 2006).

The point of zero charge (pH_{PZC}) of char was determined by the pH drift method (Uchimiya et al., 2011a). A solution of 5mM CaCl₂ was boiled to remove CO₂ and cooled to room temperature. The pH of CaCl₂ was adjusted to pH 4, 6, 8, 10, and 12 using 0.5 M HCl or 0.5 M NaOH. OS500 (0.06g) was mixed with 20mL of the pH adjusted CaCl₂ solution in 50-mL centrifuge tube. The mixture was shaken for 24 h at 200 rpm and the final pH was measured. The pH_{PZC} is defined as the point where the curve of final pH versus initial pH crosses the

 $pH_{initial} = pH_{final}$ line. The determination of pH_{PZC} for OS500 is shown in Figure C1, Appendix C.

Total surface acidity (TSA) was determined using the modified Boehm titration method (Goertzen et al., 2010). Briefly, 1.2 g char was added to 40mL of 0.05 M NaOH solution. After shaking for 24 h, the char suspension was filtered by a $0.45-\mu$ m nylon filter. The resulting solution (10 mL) was transferred into a 40-mL glass vial, and then 20 mL of 0.05 M HCl solution was added. The N₂ was then bubbled (2–3 bubbles/s) into the vial through a needle submerged in the solution for 2 h to remove CO₂. After degasification, the solution was transferred into a 125 mL-Erlenmeyer flask which had been purged with the N₂ gas and covered with Parafilm, and then back-titrated with 0.05 M NaOH. The degasification was continued during back-titration. Total surface acidity was calculated as the consumption of HCl. Similarly, total surface basicity (TSB) can be determined as the consumption of NaOH. Phenolphthalein was used in acidic samples titrated with NaOH, and methyl orange was used in basic samples titrated with HCl.

The effective cation exchange capacity (CEC) of char was measured using the method of ammonium chloride solution (Schulz and Glaser, 2012). 1 g of char was added to 20 mL 0.5M NH₄Cl. The mixture was rotated end-over-end on a Glass-Col rotator at 37 rpm for 16 h. The extract was collected by centrifugation at 5000 rpm for 10 min. The extraction procedure was repeated and the extracts were combined. A total of 40 mL of extracts was collected and then filtrated through a 0.45- μ m nylon filter. The concentration of exchangeable cations (K⁺, Na⁺, Ca²⁺, Mg²⁺, Ba²⁺, Fe²⁺, Mn²⁺, and Al³⁺) in the filtrate were measured by ICP-OES (Agilent Technologies 5100). The effective CEC was calculated by the sum of exchangeable cations.

The Brunauer-Emmett-Teller (BET) surface area (S_{BET}) and pore structure of char were obtained from N₂ adsorption-desorption isotherms at –196 °C using Quantachrome Autosorb-1 analyzer. Before test, 0.1 g of sample was outgassed at 300 °C for 24h. S_{BET} was calculated based on BET equation. Total pore volume (PV) was determined by the nitrogen adsorption at a relative pressure (P/P₀) of 0.99. Average pore diameter (D_P) and pore size distribution were calculated by the desorption data using Barrett-Joyner-Halenda (BJH) method (Barrett et al., 1951).

5.2.4. Batch sorption studies

 Pb^{2+} and Cd^{2+} were selected as target heavy metals since they are among the most seriously concerned water pollutants due to their high degree of toxicity, non-biodegradability, bioaccumulation, and "known" or "probable" carcinogenicity (IARC WGECRH , 2012, 2006; Tchounwou et al., 2012). The Pb^{2+} (or Cd^{2+}) solution was prepared by dissolving $Pb(NO_3)_2$ (or $Cd(NO_3)_2 \cdot 4H_2O$) in cooled boiled UHQ water. All the tested Pb^{2+} (or Cd^{2+}) solution contained 0.01 M NaNO₃ as the background electrolyte. Before sorption, the pH level was adjusted to 5.0 ± 0.05 using either 0.1 M HNO₃ or NaOH solution. Based on previous results, the sorption of Pb^{2+} (or Cd^{2+}) on biochar increased with solution pH from 2 to 5 and became steady when the initial pH exceeded 5 (Cui et al., 2016; Lu et al., 2012; Tan et al., 2018; Wang et al., 2018). At lower pH, the protonation and competition of H⁺ for sorption sites inhibited the Pb^{2+} (or Cd^{2+}) sorption (Cui et al., 2016; Tan et al., 2018). Therefore, the initial pH of 5 was chosen for sorption studies.

In order to study the kinetics of Pb^{2+} (or Cd^{2+}) sorption onto OS500, 0.1 g of OS500 was placed into a 50-mL centrifuge tubes and mixed with 30 mL of 1600 mg/L Pb^{2+} (or 1000 mg/L Cd^{2+}) solution. The mixture was shaken at 200 rpm and room temperature (24 °C) for different

time (0.125 h, 0.25 h, 0.5 h, 1 h, 2 h, 4 h, 8 h, 16 h, 32 h, 64 h, 128 h, 256 h, and 536 h). After shaking, all mixtures were filtrated through a 0.45- μ m nylon filter and the concentration of Pb²⁺ (or Cd²⁺) in the filtrate was determined by ICP-OES. The final pH values of the filtrate solutions were recorded using a Mettler Toledo FG2 portable pH meter. The sorption isotherms were studied using the same procedures as stated before but the concentration of Pb²⁺ varied from 50 to 9600 mg/L (or Cd²⁺ concentration varied from 31 to 1000 mg/L) and shaking time was 128 h. According to the kinetics sorption results, the sorption amount of Pb²⁺ (or Cd²⁺) on OS500 varied little with time after the contact time exceeded 128 h. Therefore, the shaking time of 128 h was used in sorption isotherm studies.

All the sorption experiments were performed in triplicate, with appropriate blanks without OS500 or without heavy metals. The Pb^{2+} (or Cd^{2+}) sorption capacity of OS500 was calculated as follows:

$$Q_t = \frac{(C_0 - C_t) * V}{W}$$
(5.1)

where Q_t is amount of Pb²⁺ (or Cd²⁺) sorbed per unit mass of char at time t (mg/g); C_0 is the initial concentration of Pb²⁺ (or Cd²⁺) in aqueous solution (mg/L), C_t is the concentration of Pb²⁺ (or Cd²⁺) in solution at time t (mg/L), V is the volume of solution (L), and W is the mass of OS500 (g).

5.2.5. Post-sorption analysis

The equilibrium studies indicated that OS500 reached its maximum sorption capacities of Cd^{2+} at initial Cd^{2+} concentration of 1000 mg/L. The Pb²⁺ sorption ability of OS500 at initial Pb²⁺ concentration of 1600 mg/L was as high as 338.3 ± 7.5 mg/g. Therefore, the OS500 after Pb²⁺ (or Cd²⁺) sorption at initial Pb²⁺ concentration of 1600 mg/L (or initial Cd²⁺ concentration

of 1000 mg/L) was chosen for the post-sorption analysis to identify sorption mechanisms. The OS500 after Pb²⁺ (or Cd²⁺) sorption was quickly washed by 20 mL UHQ water, followed by centrifugation (Thermo Scientific Sorvall Legend X1) at 5000 rpm for 10 min. The supernatant was discarded. The remaining solid was oven dried at 60 °C for 48 h and was then identified as post-sorption OS500 (OS500-Pb or OS500-Cd). The same procedure was applied to control sample without the presence of Pb²⁺ (or Cd²⁺). The resulting sample was identified as OS500 before sorption (OS500-B).

To investigate the sorption mechanisms qualitatively, XRD and FTIR analysis were conducted on OS500-Pb, OS500-Cd, and OS500-B. The FTIR spectra was obtained using Bruker Alpha II spectrometer equipped with an attenuated total reflection (ATR) accessory. 24 scans were taken from 4000 to 370 cm⁻¹ with a resolution of 4 cm⁻¹. XRD analysis was conducted to identify possible crystalline phases. The sample was mounted on a flat sample holder and examined by Rigaku Miniflex 600 diffractometer with Cu-K α at 40 kV and 15 mA. Diffraction patterns were recorded from 3 to 90° (2 θ) at a rate of 10 °C/min and a resolution of 0.02°/step.

The amount of Pb^{2+} (or Cd^{2+}) sorption resulted from the release of cation (K⁺, Ca²⁺, Mg²⁺, and Ba²⁺) was determined by the difference of concentration of cations (K⁺, Ca²⁺, Mg²⁺, and Ba²⁺) in solution before and after sorption. The contribution of different mechanisms for Pb²⁺ (or Cd²⁺) sorption on OS500 was calculated using the following 6-step sequential extraction test (X. Li et al., 1995; Tessier et al., 1979):

Step 1 (*Water soluble fraction, WS*): The solid sample (0.1g OS500 + sorbed Pb²⁺/or Cd²⁺) was added to 20 mL UHQ water. The mixture was shaken at 200 rpm for 24 h at room temperature. The extract was collected by centrifugation at 5000 rpm for 10 min, filtered

through a 0.45-µm nylon filter and stored at 4 °C until further analysis. The remaining solid was washed by shaking at 200 rpm for 15 min with 20 mL of UHQ water, followed by centrifugation at 5000 rpm for 10 min. The supernatant was decanted.

Step 2 (*Exchangeable fraction, EX*): The residue from step 1 was extracted with 8 mL of 0.5 M magnesium chloride (MgCl₂) at pH of 7 by shaking at 200 rpm for 20 min at room temperature. Similar to step 1, the extract was collected by centrifugation and then filtered. The residue was washed, followed by centrifugal separation as in step 1.

Step 3 (*Fraction bound to carbonate, CB*): The residue from step 2 was extracted with 8 mL of 1 M sodium acetate (NaOAc; adjusted to pH 5 with acetic acid, HOAc) by shaking at 200 rpm for 5 h at room temperature. The extract was then subject to centrifugal separation and nylon filter filtration, and the resulting residue was washed as in previous steps.

Step 4 (*Fraction bound to Fe-Mn oxides, OX*): The residue from step 3 was extracted with 20 mL of 0.04 M hydroxylamine hydrochloride (NH₂·OH·HCl) in 25% (v/v) HOAc for 6 h at 96 °C with occasional agitation. The extract solution was diluted to 20 mL with UHQ water and shaken at 200 rpm for 10 min. Similar to the previous steps, the extract was separated and filtered, and the residue was washed.

Step 5 (*Fraction bound to organic matter, OM*): The residue from step 4 was extracted with 3 mL of 0.02 M HNO₃ and 5 mL of 30% H_2O_2 (adjusted to pH 2 with HNO₃). The mixture was heated at 85 °C for 2 h with occasional agitation. A second 3 mL of 30% H_2O_2 (adjusted to pH 2 with HNO₃) was added and the mixture was heated at 85 °C for 3 h with occasional agitation. After cooling, 5 mL of 3.2 M ammonium acetate (NH₄OAc) in 20% (v/v) HNO₃ was added, followed by dilution to a final volume of 20 mL using UHQ water. The sample was

then shaken at 200 rpm for 30 min. The extract was separated, then filtered, and the residue was washed as in previous steps.

Step 6 (*Residual fraction, RS*): The residue from step 5 was digested in concentrated HNO₃ and concentrated HCl, following the US EPA 3050B (USEPA, 1996b). The resulting solutions were used to determine the concentration of Pb^{2+} (or Cd^{2+}).

The concentration of Pb^{2+} (or Cd^{2+}) in the extract from each step were analyzed by ICP-OES (Agilent Technologies 5100). Three independent replicates were performed for each sample.

5.3. Results and discussion

5.3.1. Characteristics of char

The physicochemical properties of OS500 are summarized in Table 5.2. The nitrogen adsorption-desorption isotherms and pore size distribution of OS500 are shown in Figure 5.1. According to international union of pure and applied chemistry (IUPAC), the isotherm of OS500 could be classified as type II (Sing et al., 1985). The type II represents non-porous or macroporous sorbent. The hysteresis loop (type H4) between the adsorption and the desorption isotherm suggests the presence of mesopores (pores in the range 2–50 nm), which is consistent with the measured average pore diameter (3.63 nm, as listed in Table 5.2). The adsorption isotherm increased rapidly at higher P/P₀ could be due to the capillary condensation in the mesopores (Ren et al., 2012). The Type H4 loop is usually associated with aggregates of plant-like particles giving rise to silt-shaped pores (Andrade et al., 2009). As shown in Figure 5.1(b), the pore volume of OS500 was mainly distributed in the mesopore range, with a peak around 3.6 nm. The BET surface area of OS500 was $17.4 \pm 0.6 \text{ m}^2/\text{g}$, which was much smaller than

that (112–642 m²/g) of plant-based biochar such as wheat residue, oak wood, or pine needle (H. Li et al., 2017). This might be because mineral components in oily sludge reduced porosity when pyrolyzed (Cao and Harris, 2010). The high pH of OS500 (10.75 \pm 0.02) could be attributed to the release of alkali salts from the pyrolytic structure at the temperature of 500 °C (Shinogi and Kanri, 2003). OS500 had the high pH_{PZC} of 11.57, which was in agreement with its high ash content since the mineral oxide in ash could increase pH_{PZC} (Godinho et al., 2017). It can be found from Table 5.2 that OS500 contained a large amount of mineral elements such as Ca, Mg, K, and Na, with Ca being the highest at 7.259 \pm 0.270%. The abundant mineral elements can be released and replaced by other cations, thus OS500 had a CEC as high as 86.95 \pm 0.35 cmol/kg.

		OS500
рН		10.75 ± 0.02
pH _{PZC}		11.57
Ash (%) ^b		90.44 ± 0.03
Ultimate analysis	C (%) ^b	6.11 ± 0.04
	H (%) ^b	0.28 ± 0.00
	N (%) ^b	0.08 ± 0.00
Metal content	K (%)	0.372 ± 0.023
	Ca (%)	7.259 ± 0.270
	Na (%)	0.044 ± 0.002
	Mg (%)	1.347 ± 0.071
	Cd (mg/kg)	2.5 ± 0.14
	Pb (mg/kg)	38 ± 2.8
	Cr (mg/kg)	37.2 ± 1.9
	Cu (mg/kg)	66.0 ± 2.8
	Ni (mg/kg)	42.0 ± 2.8
	Zn (mg/kg)	230.5 ± 17.7
CEC (cmol/kg)		86.95 ± 0.35
TSA (mmol/g)		0.07 ± 0.01
TSB (mmol/g)		4.52 ± 0.10
Microstructures	$S_{BET} \left(m^2 / g \right)$	17.4 ± 0.6
	PV (cm^3/g)	0.0643
	D _P (nm)	3.63

 Table 5.2. Physicochemical properties of OS500^a

 a Values are given as mean \pm standard deviation for duplicate measurement. b On a dry basis.



Figure 5.1. (a) Nitrogen adsorption/desorption isotherms and (b) pore size distribution of the OS500.

In addition, OS500 contained heavy metals, such as cadmium $(2.5 \pm 0.1 \text{ mg/kg})$, lead $(38 \pm 2.8 \text{ mg/kg})$, chromium $(37.2 \pm 1.9 \text{ mg/kg})$, copper $(66.0 \pm 2.8 \text{ mg/kg})$, nickel $(42.0 \pm 2.8 \text{ mg/kg})$, and zinc $(230.5 \pm 17.7 \text{ mg/kg})$. As described in our previous study (Tian et al., 2019), the heavy metals $(Cu^{2+}, Cr^{3+}, Ni^{2+}, Pb^{2+})$, and Zn^{2+}) in synthetic oily waste were effectively immobilized after pyrolysis at 400–600 °C. To evaluate the environmental safety of the OS500 when it is used to sorb heavy metals in solution, the mobility and speciation of heavy metals in OS500-B was investigated by the sequential extraction test (the procedures were described in 5.2.5). Table C1 in Appendix C shows the concentrations of extractable fractions of Cd, Pb, Cr, Cu, Ni, and Zn in the OS500. The negligible water soluble and exchangeable fraction of these metals in OS500 indicates OS500 can be used as sorbent in wastewater treatment with no direct risks to plants and humans. In fact, no Cd (or Pb), Cr, Cu, Ni, and Zn was detected in solution after Pb²⁺ (or Cd²⁺) sorption (initial concentration: Pb²⁺ 1600mg/L; or Cd²⁺ 1000 mg/L). Therefore, the effect of Pb and Cd originating from OS500 could be ignored in the sorption studies.

5.3.2. Sorption kinetics

The influence of contact time on the Pb²⁺ or Cd²⁺ sorption by OS500 is shown in Figure 5.2. The initial Pb²⁺ (or Cd²⁺) sorption rate was fast, with approximately 61% (or 65%) of Pb²⁺ (or Cd²⁺) sorption occurring in the first 4 h, followed by a slow approaching to equilibrium. After 128 h, the rate of sorption became very low and the total sorption amount of Pb²⁺ (or Cd²⁺) varied little with time. There was no distinct "endpoint" to the sorption, even at much longer times. 128 h was therefore deemed sufficient to establish equilibrium in this study. The experimental data were further fitted by kinetics models including pseudo first order kinetic model (PF-order, eq. (5.2)), pseudo second order kinetic model (PS-order, eq. (5.3)), Elovich equation (eq. (5.4)), and intraparticle diffusion model (IPD, eq. (5.5)), which can be presented as follows (Chien and Clayton, 1980; Ho and McKay, 1998; Lagergren, 1898; Weber and Morris, 1963):

$$Q_t = Q_e (1 - e^{-k_1 t}) \tag{5.2}$$

$$Q_t = \frac{k_2 Q_e^2 t}{1 + k_2 Q_e^2 t} \tag{5.3}$$

$$Q_t = \frac{1}{\beta} \ln(\alpha \beta t + 1) \tag{5.4}$$

$$Q_t = k_3 t^{0.5} + b \tag{5.5}$$

where Q_t is amount of Pb²⁺ (or Cd²⁺) sorbed at time t (mg/g), Q_e is amount of Pb²⁺ (or Cd²⁺) sorbed at equilibrium (mg/g); k_1 is the pseudo first order rate constant (h⁻¹); k_2 is the pseudo second order rate constant (g/(mg·h)); α is the initial sorption rate (mg/(g·h)); β is the desorption constant, related to activation energies for chemisorption (g/mg); k_3 is the intraparticle diffusion rate constant (mg/(g·h^{0.5})); b is the intercept (mg/g).

The sorption kinetics curves are shown in Figure 5.2 and Figure C2 (Appendix C), and the fitted model parameters are listed in Table 5.3. The correlation coefficients (R^2) of the PS-order model was higher than those of the PF-order model. In addition, the calculated Q_e (339.4 mg/g for Pb²⁺ and 21.29 mg/g for Cd²⁺) using PS-order model well matched the experimental Q_e (355.0 ± 8.5 mg/g for Pb²⁺ and 22.04 ± 2.2 mg/g for Cd²⁺), indicating the PS-order model could preferably describe the Pb²⁺ (or Cd²⁺) sorption. The PF-order kinetic process can be considered as a reversible process with an equilibrium being established between liquid and solid phases while PS-order model assumes that the rate-limiting step is more likely a chemical

sorption involving bonding forces through sharing or exchange of ions/electrons between sorbent and sorbate (Ho and McKay, 1999). The better fitting of the data to the PS-order model suggests the chemical process (e.g., precipitation, ion exchange, and complexation) may be the rate-limiting step in the sorption process of Pb²⁺ and Cd²⁺. The Elovich equation provided the best fit to experimental data since the correlation coefficients (R²) of Elovich equation was higher than other models (Table 5.3). The initial sorption rate (Elovich α) had value of 3866 $mg/(g \cdot h)$ for Pb²⁺ sorption on OS500, which is 2 times greater than that for Cd²⁺. The Elovich equation is often used to describe predominantly chemisorption on highly heterogeneous sorbents. It is based on the assumption that the sorption sites increase exponentially with sorption, which implies a multilayer sorption (Alberti et al., 2012). The Elovich equation fitted the experimental data well, which is consistent with chemical interaction between active sites on the OS500 surface and Pb^{2+} (or Cd^{2+}) in solution. As seen from Figure C2 in Appendix C, the intraparticle diffusion plot exhibited multi-linear nature. The first linear plot corresponds to the film diffusion (transport of Pb^{2+} (or Cd^{2+}) from solution to the exterior surface of OS500) whereas the second linear plot attributes to the intraparticle diffusion. The IDP model was well fitted with the data of Pb^{2+} sorption within 4 h ($R^2 = 0.955$) and Cd^{2+} sorption within 16 h (R^2 =0.887), confirming diffusion was important for Pb^{2+} and Cd^{2+} sorption. Both lines did not pass through the origin and therefore the intraparticle diffusion was not the only control step of sorption process.



Figure 5.2. The influence of contact time on (a) Pb^{2+} and (b) Cd^{2+} sorption onto OS500 and the fit of the data by pseudo first order, pseudo second order, and Elovich equation (0.1g char in 30 mL solution (0.01 M NaNO₃), initial $Pb^{2+}(Cd^{2+})$ concentration 1600 (1000) mg/L; room temperature 24 °C; initial solution pH 5).

		Parameter 1	Parameter 2	\mathbb{R}^2	
Pb ²⁺	PF-order	$k_1 = 0.8811 \text{ h}^{-1}$	$Q_e = 321.9 \text{ mg/g}$	0.775	
	PS-order	$k_2 = 0.00357 \text{ g/(mg \cdot h)}$	$Q_e = 339.4 \text{ mg/g}$	0.869	
	Elovich	$\alpha = 3866 \text{ mg/(g·h)}$	$\beta = 0.02629 \text{ g/mg}$	0.975	
	IPD ^a	$k_3 = 106.8 \text{ mg/(g} \cdot \text{h}^{0.5})$	b = 60.11 mg/g	0.955	
			Experimental $Q_e =$	355.0 mg/g	
Cd^{2+}	PF-order	$k_1 = 1.700 \text{ h}^{-1}$	$Q_e = 20.31 \text{ mg/g}$	0.505	
	PS-order	$k_2 = 0.1161 \text{ g/(mg \cdot h)}$	$Q_e = 21.29 \text{ mg/g}$	0.711	
	Elovich	$\alpha = 1933 \text{ mg/(g·h)}$	$\beta = 0.5130 \text{ g/mg}$	0.964	
	IPD ^b	$k_3 = 2.394 \text{ mg/(g} \cdot \text{h}^{0.5})$	b = 10.10 mg/g	0.887	
			Experimental $Q_e = 22.04 \text{ mg/g}$		

Table 5.3. The fitting results of Pb^{2+} and Cd^{2+} sorption on OS500 using the pseudo first order kinetic (PF-order), pseudo second order kinetic (PS-order), Elovich, and intraparticle diffusion (IPD) models.

^a IPD model was fitted the data of Pb²⁺ sorption within 4 h.

^b IPD model was fitted the data of Cd²⁺ sorption within 16 h.

5.3.3. Sorption isotherms

The sorption isotherm of Pb²⁺ and Cd²⁺ onto the OS500 were simulated using the Langmuir (L), Freundlich (F), Sips (S), Redlich-Peterson (RP), Temkin (T), and Dubinin-Radushkevich (DR) models. The mathematical expression of these models are presented as follows (Dubinin and Radushkevich, 1947; Freundlich, 1906; Langmuir, 1918; Redlich and Peterson, 1959; Sips, 1948; Tempkin and Pyzhev, 1940):

$$Q_e = \frac{Q_L b_L C_e}{1 + b C_e} \text{ Langmuir,}$$
(5.6)

$$Q_e = K_F C_e^{1/n}$$
 Freundlich, (5.7)

$$Q_e = \frac{Q_S K_S C_e^{n_S}}{1 + K_S C_e^{n_S}} \text{ Sips,}$$
(5.8)

$$Q_e = \frac{K_{RP}C_e}{1 + \alpha_{RP}C_e^{\beta_{RP}}} \text{ Redlich-Peterson,}$$
(5.9)

$$Q_e = \frac{RT}{b_T} \ln(K_T C_e) \text{ Temkin,}$$
(5.10)

$$Q_e = Q_{DR} Exp\left[\frac{\left(RT\ln\left(1+\frac{1}{C_e}\right)\right)^2}{-2E^2}\right]$$
Dubinin-Radushkevich, (5.11)

where Q_e is amount of Pb²⁺ (or Cd²⁺) sorbed at equilibrium (mg/g), C_e is the equilibrium concentration of Pb²⁺ (or Cd²⁺) (mg/L), Q_L is maximum sorption capacity based on Langmuir model (mg/g), b_L is the Langmuir isotherm constant (L/mg), K_F is the Freundlich isotherm constant ((mg/g)(L/mg)^{1/n}) related to sorption capacity, n is the Freundlich isotherm constant representing the surface site heterogeneity, Q_S is the maximum sorption capacity based on Sips model (mg/g), K_S is the Sips isotherm constant ((L/mg)ⁿ_s), n_S is the Sips heterogeneity exponent, K_{RP} (L/g), α_{RP} ((L/mg)^{1/ β_{RP}}), and β_{RP} are the Redlich-Peterson isotherm constants, R is the ideal gas constant (8.314 J/mol K), T is the temperature (K), K_T is the Tempkin equilibrium binding constant (L/g), b_T is the Tempkin isotherm constant (kJ/mol), Q_{DR} is maximum sorption capacity based on Dubinin-Radushkevich model (mg/g), and E is the mean free energy (kJ/mol).

The sorption isotherms of Pb^{2+} and Cd^{2+} onto OS500 are presented in Figure 5.3 and Figure C3 (Appendix C), and the fitting parameters are listed in Table 5.4. The equilibrium concentration of Pb^{2+} was below the ICP detection limit (0.09 mg/L for Pb^{2+}) when the initial Pb^{2+} concentrations ranged from 0–400 mg/L, suggesting an irreversible chemisorption behavior. Langmuir isotherm is based on the assumption that monolayer sorption takes place

at specific homogeneous sites, while the Freundlich isotherm assumes sorption occurs on heterogeneous surfaces. The Sips isotherm is a combination of Langmuir and Freundlich models, which incorporate three parameters into an empirical equation. At low sorbate concentrations, it reduces to a Freundlich isotherm; while at high sorbate concentration, it predicts a monolayer sorption capacity characteristic of the Langmuir isotherm. Redlich-Peterson is widely used as a compromise between Langmuir and Freundlich system. It incorporates three parameters where the exponent β_{RP} lies between 0 and 1. It becomes the Henry's equation when $\beta_{RP} = 0$, and becomes the Langmuir isotherm when $\beta_{RP} = 1$. From the correlation coefficient, the sorption of Pb^{2+} was better fitted to Freundlich model ($R^2 = 0.897$) than Langmuir model ($R^2 = 0.839$), while the sorption of Cd^{2+} was better fitted to Langmuir model ($R^2 = 0.977$) than Freundlich model ($R^2 = 0.825$). In general, three parameter isotherms (Sips and Redlich-Peterson) had higher correlation coefficients ($R^2 = 0.898-0.986$) than two parameter isotherms (Langmuir and Freundlich) ($R^2 = 0.825-0.977$). This suggests the heterogeneous surface condition may coexist with monolayer sorption under the experimental conditions. The maximum sorption capacity (Q_L) of Pb²⁺ on OS500 based on Langmuir model was 373.2 mg/g (Table 5.4), which was larger than that of other sorbents, such as plant-based biochar (8.1-113.6 mg/g), manure-based biochar (51.4-230.7 mg/g), and sludge-based char (18.2–82.5 mg/g) (Table 5.5). The maximum sorption capacity (Q_L) of Cd²⁺ on OS500 based on Langmuir model was 23.19 mg/g (Table 5.4), which is comparable to that of other sorbents (7.4–76.3 mg/g) (Table 5.5). The results clearly demonstrated the potential of OS500 to be used as an effective sorbent for Pb^{2+} and Cd^{2+} sorption.

Temkin isotherm contains a factor that takes into account the sorbent-sorbate interactions (Tempkin and Pyzhev, 1940). It assumes the decline of the heat of sorption as a function of
temperature is linear rather than logarithmic (Tempkin and Pyzhev, 1940). A slightly better fit of Temkin isotherm was found for Pb²⁺ sorption (R² = 0.899) compared to that for Cd²⁺ sorption (R² = 0.847), implying that Pb²⁺ sorption process was more likely to be affected by the sorbate/sorbent interaction. Dubinin-Radushkevich isotherm is usually applied to distinguish the physical and chemical sorption of metal ions by mean free energy (*E*) (Saltalı et al., 2007). The *E* values of Pb²⁺ and Cd²⁺ are calculated as 6.551 and 6.733 kJ/mol, respectively, which are lower than 8 kJ/mol, showing the physical sorption (Saltalı et al., 2007). However, in the case of sorption of Pb²⁺ on OS500, a relatively lower R² was found with the Dubinin-Radushkevich model as compared to those of other models (Table 5.4), indicating the application of this model in Pb²⁺ sorption is limited.



Figure 5.3. Isotherms of (a) Pb²⁺ and (b) Cd²⁺ sorption onto OS500 (0.1g char in 30 mL solution (0.01 M NaNO₃); contact time 128 h; room temperature 24 °C; initial solution pH 5).

		Parameter 1	Parameter 2	Parameter 3	R ²
Pb ²⁺	L	$Q_L = 373.2 \text{ mg/g}$	<i>b</i> _{<i>L</i>} = 19.78 L/mg		0.839
	F	$K_F = 273.8 \ (\text{mg/g})(\text{L/mg})^{1/n}$	n = 25.08		0.897
	S	$Q_S = 663.5 \text{ mg/g}$	$K_S = 0.7119 \ (\text{L/mg})^{n_s}$	$n_S = 0.07655$	0.900
	RP	$K_{RP} = 6.249 \times 10^4 \mathrm{L/g}$	$\alpha_{RP} = 221.9 \; (L/mg)^{1/\beta_{RP}}$	$\beta_{RP} = 0.9637$	0.898
	Т	$K_T = 4.325 \times 10^9 \text{L/g}$	$b_T = 0.1980 \text{ kJ/mol}$		0.899
	DR	$Q_{DR} = 373.2 \text{ mg/g}$	E = 6.551 kJ/mol		0.839
			Ç	$Q_{max,exp}^{a} = 373.$	1 mg/g
Cd^{2^+}	L	$Q_L = 23.19 \text{ mg/g}$	$b_L = 21.86 \text{ L/mg}$		0.977
	F	$K_F = 18.35 \ (\text{mg/g})(\text{L/mg})^{1/n}$	<i>n</i> = 23.64		0.825
	S	$Q_{S} = 23.28 \text{ mg/g}$	$K_{S} = 14.88 (L/mg)^{n_{s}}$	$n_S = 0.8450$	0.981
	RP	$K_{RP} = 607.0 \text{ L/g}$	$\alpha_{RP} = 27.49 \; (L/mg)^{1/\beta_{RP}}$	$\beta_{RP} = 0.9905$	0.986
	Т	$K_T = 1.532 \times 10^9 \text{L/g}$	$b_T = 2.832 \text{ kJ/mol}$		0.847
	DR	$Q_{DR} = 23.19 \text{ mg/g}$	E = 6.733 kJ/mol		0.977
				$Q_{max,exp} = 23.2$	4 mg/g

Table 5.4. Langmuir (L), Freundlich (F), Sips (S), Redlich-Peterson (RP), Temkin (T), and Dubinin-Radushkevich (DR) isotherm parameters of Pb²⁺ and Cd²⁺ sorption on OS500.

^a $Q_{max,exp}$ is experimental maximum sorption capacity, mg/g.

		Pyrolysis conditions			Experim	ent condition				
Sorbents	ions	T _p ^a (°C)	$\frac{1}{t_p^b} \qquad (mg/2) \qquad (min)$		Sorbent dosage (g/L)	C ₀ ^d (mg/L)	рН	T ^e (K)	Reference	
Salisbury biochar	Pb ²⁺	600	810	47.6	5	20–1000	5	293	(Shen et al., 2017)	
Wheat Straw pellets biochar	Pb^{2+}	700	NA^{f}	113.6	5	20–1000	5	293	(Shen et al., 2017)	
Rice husk biochar	Pb^{2+}	700	NA	35.0	5	20–1000	5	293	(Shen et al., 2017)	
Soft wood pellets biochar	Pb^{2+}	550	NA	8.1	5	20–1000	5	293	(Shen et al., 2017)	
Magnetic oak bark biochar	Pb^{2+}	450	fast	30.2	3	1–100	5	298	(Mohan et al., 2014)	
Phyllostachys pubscens	Pb^{2+}	700	180	62.1	2	100-800	5	298	(C. Zhang et al., 2017)	
Dairy manure biochar	Pb^{2+}	350	240	88.2	5	0–1037	NA	298	(X. Cao et al., 2009)	
Pig manure biochar	Pb^{2+}	600	NA	230.7	10	207-5175	5	293	(Kołodyńska et al., 2012)	
Anarobically digested animal	Pb^{2+}	600	120	51.4	2	5-600	NA	295	(Inyang et al., 2012)	
Sewage sludge biochar with	Pb^{2+}	600	20	49.7	2	10–160	5	293	(Lin et al., 2012)	
Municipal wastewater sludge	Pb^{2+}	400	120	18.2	2	10–150	5	298	(Zhang et al., 2013)	
Chinese medicine material residues biochar	Pb ²⁺	400	120	82.5	5-7.5	100-1000	5	298	(Wang et al., 2015)	

Table 5.5. Summary of the literature data on sorption of Pb^{2+} and Cd^{2+} to different biochars or other sorbents

	Metal ions	Pyrolysis			Experime	ent condition			
Sorbents		$\frac{\text{condi}}{T_p^a}$	$\frac{tions}{t_p^b}$	Q_{L}^{c} (mg/g)	Sorbent	C_0^{d}	pН	T ^e	Reference
		(°C)	(min)		dosage (g/L)	(mg/L)		(K)	
Miscanthus biochar	Cd^{2+}	500	60	13.2	1	1–50	7	298	(WK. Kim et al., 2013)
Phyllostachys pubescens biochar	Cd^{2+}	700	180	14.7	2	50-600	5	298	(C. Zhang et al., 2017)
Magnetic oak bark biochar	Cd^{2+}	450	fast pyrolysis	7.4	3	1–100	5	298	(Mohan et al., 2014)
Corncob biochar	Cd^{2+}	550	120	33.4	2	20–200	6.8	298	(Luo et al., 2018)
Rape straw biochar	Cd^{2+}	600	60	32.7	1.25	2–200	5.5	298	(B. Li et al., 2017)
Dairy manure biochar	Cd^{2+}	350	240	54.6	5	0–562	NA	298	(Xu et al., 2013)
Pig manure biochar	Cd^{2+}	600	NA	117.0	10	112–2810	5	293	(Kołodyńska et al., 2012)
Sewage sludge biochar	Cd^{2+}	500	60	15.1	10	0.5–252	NA	303	(Gutiérrez-Segura et al., 2012)
Sewage sludge biochar with ZnCl ₂ activation	Cd^{2+}	850	NA	16.7	5	0–100	5.8	298	(Zhai et al., 2004)
Biogas production residue char	Cd^{2+}	600	300	76.3	4	5-500	5.5	295	(Bogusz et al., 2017)

^a T_p is the pyrolysis temperature, °C. ^b t_p is the pyrolysis reaction time, min. ^c Q_L is the maximum sorption capacity fitted by Langmuir model, mg/g. ^d C_0 is the initial concentration of Pb²⁺ (Cd²⁺) solution, mg/L. ^e T is the temperature of sorption experiment, K. ^fNA represents the data was not obtained.

5.3.4. Post-sorption characteristics and sorption mechanisms

5.3.4.1. XRD and FTIR results

Figure 5.4 presents the XRD patterns of OS500-B, OS500-Pb and OS500-Cd. The peak centred at 20 value of 26.640° in OS500-B was assigned to quartz (SiO₂), while that at 25.842° was attributed to barite (BaSO₄). A small peak at 8.854° indicated the presence of muscovite 2M2 ($K_{0.77}Al_{1.93}(Al_{0.5}Si_{3.5})O_{10}(OH)_2$). The peak at 29.400° and 31.007° showed the existence of calcite (CaCO₃) and dolomite (CaMg(CO₃)₂), respectively. The presence of the carbonate minerals is consistent with the alkalinity of the OS500 (Table 5.2). Compared with the OS500-B, XRD evidenced the disappearance of peaks for CaCO₃ (2 θ = 29.400°) in OS500-Pb. The new peaks of hydrocerussite (Pb₃(CO₃)₂(OH)₂) at 27.080° and 34.155° was observed in OS600-Pb. In addition, the characteristic peaks belonging to cerussite (PbCO₃) at 24.792°, 29.057°, 34.611°, 43.469°, and 47.016° were appeared in OS500-Pb. These precipitates formed in OS500-Pb may be attributed to the reactions between Pb²⁺ and the dissolved carbonate from the minerals in OS500. There was no change in XRD patterns before and after Cd²⁺ sorption, providing no evidence of precipitation during Cd²⁺ sorption process.



Figure 5.4. XRD patterns of OS500 before (OS500-B) and after Pb²⁺/Cd²⁺ sorption (OS500-Pb and OS500-Cd). Minerals with peaks labeled: M, Muscovite 2M2, K_{0.77}Al_{1.93}(Al_{0.5}Si_{3.5})O₁₀(OH)₂; B, Barite, BaSO₄; Q, Quartz, SiO₂; C, Calcite, CaCO₃; D, Dolomite, CaMg(CO₃)₂; Ce, Cerussite, PbCO₃; H, hydrocerrusite, Pb₃(CO₃)₂(OH)₂.

Figure 5.5 shows the changes in solution pH during Pb^{2+}/Cd^{2+} sorption by OS500. When the initial Pb^{2+} concentration was 832 mg/L, solution pH increased from about 5 to about 7 due to the alkalinity of OS500. When the initial Pb^{2+} concentration was greater than 3543 mg/L, the solution pH stayed unchanged or became lower. XRD results confirmed that Pb^{2+} can precipitate with the negatively charged ion (i.e., carbonate) released by OS500. Even though Pb^{2+} precipitation might release H⁺ (transformation of H₂O into OH⁻), the carbonate released by OS500 could still increase solution pH due to its strong buffer capacities (Inyang et al., 2012). However, when the initial Pb^{2+} concentration was high, all the available carbonate was consumed and therefore the solution pH decreased. In terms of Cd^{2+} sorption system, such decreasing solution pH was not observed, suggesting the precipitating may not be the dominant sorption mechanism.



Figure 5.5. Comparisons between solution pH before and after (a) Pb^{2+} sorption and (b) Cd^{2+} sorption in equilibrium studies.

The FTIR spectra of OS500-B, OS500-Pb, and OS500-Cd are shown in Figure 5.6. For OS500-B, the weak peak at 3385 cm⁻¹ represented the stretching vibration of O–H groups. The C–O vibration bands at 1417 cm⁻¹ and 694 cm⁻¹ were assigned to CO_3^{2-} groups (T. Zhang et al., 2017). The strong band at 1002 cm⁻¹ may be attributed to either Si–O–Si or Si–O–C groups (Pan et al., 2011), which is associated with the silicon content in oily sludge (Table 5.1). The peaks appearing at 874 cm⁻¹ and 777 cm⁻¹ correspond to the aromatic C–H groups (Uchimiya et al., 2011b). After Pb²⁺ sorption, the peak of CO_3^{2-} at 1417 cm⁻¹ and 694 cm⁻¹ shifted to 1397 cm⁻¹ and 679 cm⁻¹, respectively. Meanwhile, the intensity of the CO_3^{2-} group increased after Pb²⁺ sorption. These results were attributed to the formation of lead carbonates, which is agreed with the observation of XRD analysis. The aromatic C–H stretching vibration, located at 874 cm⁻¹ was found shifting to 837 cm⁻¹ after Pb²⁺ sorption, suggesting the Pb²⁺- π interaction might also be responsible for Pb²⁺ sorption. FTIR analysis evidenced no precipitation formation

during Cd^{2+} sorption since no changes in any peak positions except the peak of O–H groups at 3385 cm⁻¹. The peak at 3385 cm⁻¹ corresponding to O–H groups shifted to 3366 cm⁻¹ in OS500-Cd, indicating a possible complexation of Cd^{2+} with O–H group on the OS500 surface.



Figure 5.6. FTIR spectra of OS500 before (OS500-B) and after Pb²⁺/Cd²⁺ sorption (OS500-Pb and OS500-Cd).

5.3.4.2. Sequential extraction results

The speciation of $Pb^{2+}(Cd^{2+})$ on OS500-Pb (OS500-Cd) are shown in Table C2 (Appendix C) and Figure 5.7. The total recovery of Pb^{2+} (or Cd^{2+}) from sequential extraction can be obtained by dividing the total extracted Pb^{2+} (or Cd^{2+}) in sequential extraction by the total sorbed amount of Pb^{2+} (or Cd^{2+}) and are listed in Table C3 (Appendix C). The recovery for Pb^{2+} and Cd^{2+} were 88.03% and 80.92%, respectively, which were comparable to the recovery of heavy metals using sequential extraction methods in previous studies. A recovery range of

82.4–98.7% was observed for sequential extraction of Cd^{2+} from two Cd-loaded woody biochars (Frišták et al., 2015). The sequential extraction recovery of Pb^{2+} from three biochars after Pb^{2+} sorption was within 78.41–85.52% (Shen et al., 2017).



Figure 5.7. Sequential extraction results for (a) OS500-Pb, and (b) OS500-Cd (WS: water soluble fraction, EX: exchangeable fraction, CB: fraction bound to carbonate, OX: fraction bound to Fe-Mn oxides, OM: fraction bound to organic matter, RS: residual fraction).

The net amount of released cations (K⁺, Ca²⁺, Mg²⁺, and Ba²⁺) during Pb²⁺ and Cd²⁺ sorption by OS500 were calculated and shown in Table 5.6. The sum of net amount of released cations into Pb²⁺ sorption system was 281.45 \pm 1.35 meq/100g, equivalent to 291.58 \pm 1.40 mg Pb²⁺/g, which was accounted for 83.0% of the total sorbed Pb²⁺. Whereas for Cd²⁺ sorption system, the sum of net amount of released cations was only 9.98 \pm 0.36 mg Cd²⁺/g, accounting for 41.7% of the total sorbed Cd²⁺. However, as seen from Figure 5.7, the exchangeable fraction for OS500-Pb and OS500-Cd was low (0.45–15.12%) and their water soluble fraction was negligible (0–0.11%). This means that most of the sorbed Pb²⁺ or Cd²⁺ were non-exchangeable with Mg²⁺. The Pb²⁺ or Cd²⁺ substituted with the cations was mainly attributed to coprecipitation and complexation on mineral surface.

System	The net amo	ount of release	Sum			
	\mathbf{K}^+	Ca ²⁺	Mg^{2+}	Ba ²⁺	(meq/100g)	(mg/g)
Pb ²⁺ sorption	$\begin{array}{c} 0.27 \pm \\ 0.01 \end{array}$	$\begin{array}{c} 229.64 \pm \\ 0.79 \end{array}$	$\begin{array}{c} 48.75 \pm \\ 0.46 \end{array}$	2.78 ± 0.11	281.45 ± 1.35	$\begin{array}{c} 291.58 \pm \\ 1.40 \end{array}$
Cd ²⁺ sorption	$\begin{array}{c} 0.02 \pm \\ 0.02 \end{array}$	$\begin{array}{c} 13.19 \pm \\ 0.54 \end{array}$	$\begin{array}{c} 4.32 \pm \\ 0.11 \end{array}$	$\begin{array}{c} 0.23 \pm \\ 0.02 \end{array}$	$\begin{array}{c} 17.75 \pm \\ 0.65 \end{array}$	$\begin{array}{c} 9.98 \pm \\ 0.36 \end{array}$

Table 5.6. The release of K^+ , Ca^{2+} , Mg^{2+} , and Ba^{2+} during Pb^{2+} and Cd^{2+} sorption by OS500

^a The net amount of released cations were the difference values between the concentration of K^+ , Ca^{2+} , Mg^{2+} , and Ba^{2+} released into Pb^{2+} (or Cd^{2+}) sorption system at 1600 mg/L Pb^{2+} (or 1000 mg/L Cd^{2+}) solution with 0.01M NaNO₃ at pH 5.0 and the corresponding release from OS500 in 0.01M NaNO₃ at pH 5.0.

The Pb^{2+} or Cd^{2+} sorbed on char through physical sorption represent the water soluble fraction, whereas those sorbed through cation exchange with a weak binding strength (no metal exchange reaction) represent the exchangeable fraction (Cao et al., 2019). The fraction bound to carbonate may come from the Pb^{2+} or Cd^{2+} sorbed via cation- π interaction or the formation of precipitates and complex (Morera et al., 2001; Shen et al., 2017). The fractions from step 4, 5, 6 in sequential extraction may result from the formation of stable complexes with organic matter or precipitates that cannot be dissolved in the NaOAc/HOAc solution (Shen et al., 2017). For both OS500-Pb and OS500-Cd, the water soluble fraction was negligible (0-0.11%) and the total fraction from step 4, 5, 6 was low (0.63-1.50%). This result indicated that physical sorption and complexation with organic matter had a limited impact on Pb²⁺ or Cd²⁺ sorption, which is in accordance with the fact that OS500 has a small BET surface area (i.e., 17.4 ± 0.6 m^2/g) and a small amount of acidic surface function group (i.e., $0.07 \pm 0.01 \text{ mmol/g}$) (Table 5.2). The fraction bound to carbonate (98.06%) dominated the existence of Pb²⁺ in OS500-Pb while Cd^{2+} was mainly bound to carbonate (84.15%) and exchangeable fraction (15.12%) (Table C2). Among the amount of Pb^{2+} existed as carbonate fraction (303.42 mg/g, as listed in

Table C2), 290.20 mg/g (= sum of net amount of released cations in Pb²⁺ sorption (291.58 mg/g, as listed in Table 5.6) – the amount of Pb²⁺ existed as exchangeable fraction (1.38 mg/g, as listed in Table C2)) were due to precipitation and the rest (13.22 mg/g) could be attributed to Pb²⁺- π interaction. Therefore, the amount of Pb²⁺ sorption resulting from precipitation was estimated to be 290.20 mg/g, accounted for 93.79% of total sorption of Pb²⁺ on OS500. The contribution of Pb²⁺- π interaction was estimated to be 13.22 mg/g, accounted for 4.27% of total sorption of Pb²⁺ on OS500. Since no precipitation was formed during Cd²⁺ sorption according to XRD and FTIR results, Cd²⁺ sorption primarily involved the surface complexation (accounted for 84.15%, representing carbonate fraction) and cation exchange with a weak binding strength (accounted for 15.12%, representing exchangeable fraction).

5.4. Summary

The oily sludge-derived char from pyrolysis at 500 °C (OS500) sorbed up to 373.2 mg/g of Pb²⁺ from aqueous solution, which is superior to most biochars reported previously. The sorption capacity of Pb²⁺ by OS500 was higher than that of Cd²⁺, which is mainly due to mineral precipitation with Pb²⁺. The kinetics of sorption of Pb²⁺ and Cd²⁺ can be well described by the Elovich equation, indicating the chemical interaction between active sites on the OS500 surface and Pb²⁺ (or Cd²⁺) in solution. The Redlich-Peterson isotherm model best fitted the experimental data with highest correlation coefficients (R²). The OS500 was rich in alkaline minerals and had a high CEC, which contributed to its high sorption capacity. The substitution of Pb²⁺ with alkali or alkaline earth metals led to precipitation in the forms of hydrocerussite (Pb₃(CO₃)₂(OH)₂) and cerussite (PbCO₃) was mainly responsible for Pb²⁺ sorption, with less contribution from Pb²⁺- π interaction. The sorption of Cd²⁺ on OS500 was mainly attributed to complexation and cation exchange. Microstructure of OS500 played a less important role in

the removal of Pb^{2+} and Cd^{2+} since only 0–0.11% of total sorbed Pb^{2+} or Cd^{2+} existed as physically bonded fraction. Overall, converting oily sludge into sorbents can be considered a promising solution to solve disposal problem with the beneficial use of mineral constituents in the sludge. However, the majority of Pb^{2+} (98.06%) and Cd^{2+} (84.15%) was sorbed on OS500 as the carbonate fraction, which may bring challenges for the metal recovery and reuse of OS500. Further study to facilitate the practical application of OS500 is needed in future. Moreover, very limited research tried to establish the relationship among properties of OSDC, metal sorption behavior, and pyrolysis conditions. Therefore, investigating the exact mechanisms for Pb^{2+} and Cd^{2+} sorption on OSDC prepared at different pyrolysis temperature and activation methods is also necessary.

Chapter 6

SORPTION OF LEAD AND CADMIUM ON OILY SLUDGE-DERIVED CHAR PREPARED AT DIFFERENT PYROLYSIS TEMPERATURES AND CHEMICAL ACTIVATION

Abstract

The objective of this study was to investigate the lead (Pb^{2+}) or cadmium (Cd^{2+}) sorption from aqueous solution by oily sludge-derived char (OSDC) prepared at different pyrolysis temperatures and chemical activation. The maximum Pb²⁺ sorption capacity for OSDC at pyrolysis temperature of 500 °C (OS500) was found as 351.48 mg/g, which was greater than that of chars produced at other temperatures. Further investigations of Pb²⁺ sorption onto OSDC by low pyrolysis temperature (\leq 500 °C) indicated that the heavy metal removal was mainly through a precipitation mechanism, which was confirmed by qualitative (i.e., Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD)) and quantitative (i.e., sequential extraction test) characterization of Pb²⁺-loaded chars. With increasing pyrolysis temperature from 500 to 900 °C, the contribution of precipitation to Pb²⁺ sorption decreased from 93.79% to 34.63%, while the contribution of complexation increased from 0% to 44.68%. Sorption results showed that OSDC prepared at pyrolysis temperature of 700 °C (OS700) had the best sorption capacity for Cd^{2+} (92.14 mg/g). The high sorption capacity of OS700 was mainly attributed to the carboxyl/hydroxyl functional groups and complexation with mineral oxides. The complete conversion of barite (BaSO₄) to witherite (BaCO₃) after chemical activation led to the mineral precipitation with Cd^{2+} . The contribution of precipitation to the total Cd^{2+} removal was 0% for OS500, but 76.12% for the activated OS500.

Keywords: heavy metals, oily sludge-derived char (OSDC), pyrolysis temperature, chemical activation, sorption mechanism

6.1. Introduction

One of the consequences of rapid industrialization and urbanization is the widespread contamination of water and soil with heavy metals (Gong et al., 2018). Heavy metals pose a risk to environment and human health due to their toxicity, non-biodegradability, and bioaccumulation in the food chain. Most of the point sources of heavy metal pollutants are industrial wastewater from mining, smelting, battery manufacturing, pesticide application, and others (Inyang et al., 2012). Lead is the most systemic toxicant that affects several organs in the body such as the kidneys, liver, and central nervous system. Cadmium is one of the most toxic heavy metals and can cause serious damage to kidneys. The US Environmental Protection Agency (USEPA) established a maximum permissible limit of 0.015 mg/L for lead and 0.005 mg/L for cadmium in drinking water (USEPA, 2015). Some methods have been used for the removal of heavy metals from wastewater, including chemical precipitation (Djedidi et al., 2009), ion exchange (Cavaco et al., 2007), and membrane filtration (Doke and Yadav, 2014). However, these methods could be associated with high operational cost, disposal of resulting sludge, and/or possible production of secondary toxic compounds (Fu and Wang, 2011).

Sorption has become an attractive alternative for the removal of heavy metals from wastewater due to its simplicity, ease of operation and handling, and regeneration capacity (Saha and Sarkar, 2012). In recent years, growing interest has been shown in the production of low-cost and efficient sludge-based sorbents (Xu et al., 2015). Sewage sludge-derived char, a solid by-product of pyrolysis, was reported to have a high capacity for adsorbing copper (Cu^{2+}) from wastewater due to the complexity of surface chemistry and high specific porosity

(Seredych and Bandosz, 2006). Lu et al. (2012) reported the sewage sludge-derived char effectively removed lead (Pb²⁺) with the capacity of 30.88 mg/g at initial pH 5. It was found that the Pb²⁺ sorption primarily involved the precipitation and complexation on mineral surfaces, which was 57.7–61.8% of the total sorbed Pb^{2+} (Lu et al., 2012). Apart from sewage sludge, industrial oily sludge was also used as material for developing efficient sorbent. For example, Mohammadi and Mirghaffari (2015) produced oily sludge-derived char (OSDC) from pyrolysis of oily sludge with the cadmium (Cd^{2+}) sorption capacity of 1.49 mg/g. To further improve the sorption capability of OSDC, thermochemical treatment was used to prepare the activated OSDC, with cadmium (Cd^{2+}) sorption capacity reaching 19.23 mg/g. My study in Chapter 5 also indicated that OSDC rich in alkaline minerals had higher Pb²⁺ sorption capacity (373.2 mg/g) than most biochars reported previously. However, limited information is available on how pyrolysis temperature could affect the heavy metal sorption by OSDC. In fact, pyrolysis temperature not only affects product distribution but also the structures and chemical characteristics of the biochar, including the chemical composition, pH, surface area, and acidic functional group (Chen et al., 2011). Kloss et al. (2012) observed an accumulation of carbon and increased surface area, but decreased cation exchange capacity (CEC) of biochar with increase in pyrolysis temperature. Ahmad et al. (2012) reported better sorbent properties of biochar produced at higher temperature as a consequence of the higher surface area and lower polarity.

In addition to pyrolysis temperature, a modification of biochar with chemical reagents could also affect the porous structure development as well as the functional group, and consequently change its sorption ability (Liu et al., 2012; Trakal et al., 2014). A few studies were reported to prepare activated OSDC using chemical activation. For example, Guritno et al. (2016) synthesized porous carbon from oily sludge using mesoporous silica template and found the surface area of the produced activated carbon was $250.6 \text{ m}^2/\text{g}$. Wang et al. (2017b) found the potassium hydroxide (KOH)-activated OSDC had a surface area of $1103 \text{ m}^2/\text{g}$. After a solvent de-oiling step before activation, the surface area of activated OSDC increased to $3292 \text{ m}^2/\text{g}$. However, these studies were more focused on microstructure of activated OSDC, and the utilization of activated OSDC in heavy metal removal has not been paid much attention. The objective of this study is then to examine how the preparation condition (i.e., pyrolysis temperature and chemical activation) and resulting OSDC properties translate into the heavy metal sorption capacities. The sorption mechanisms of heavy metal on activated and non-activated OSDC were investigated by qualitative methods (i.e., Fourier transform infrared spectroscopy (FTIR) and X-ray diffraction (XRD)) and quantitative method (i.e., sequential extraction). The results will serve to facilitate the industrial application of the developed OSDC.

6.2. Materials and methods

6.2.1. Materials and reagents

The oily sludge was obtained from the bottom of an oil tank truck in western Canada. The sludge was oven dried at 80 °C for 3-4 days and kept in darkness at 24 °C in a sealed glass jar. The sludge was sticky, and its characteristics are listed in Table 5.1. The test methods for extractable petroleum hydrocarbons (i.e., nC10–nC19 and nC19–nC32) and metal elements in oily sludge can be found in Section 5.2.1. Sodium nitrate (\geq 99%) and cadmium nitrate tetrahydrate (\geq 98%) were purchased from Sigma-Aldrich. Lead nitrate (\geq 99%) were purchased from Fisher Scientific. Sodium hydroxide (\geq 99%) and ferric sulfate (\geq 99%) were purchased

from VWR International. Ultra high purity (UHQ) water with a resistivity of 18.2 M Ω ·cm (ELGA Purelab) was used for all procedures.

6.2.2. Chars preparation and characterization

About 30 g of oily sludge were pyrolyzed at 300, 500, 700, and 900 °C for 30 min under 100 mL/min nitrogen flow rate using a fixed-bed tube furnace (quartz tube length: 600 mm, Ø: 50 mm; MTI Corp.[®] GSL-1100X). The pyrolysis heating rate was 10 °C/min. The solid product was cooled to room temperature, then washed with UHQ water in a Soxhlet apparatus for 48h, dried at 105 °C for 2-3 days, and ground using a ball mill (Retsch MM200). The resulting chars were referred to as OS300, OS500, OS700, and OS900 respectively, according to the pyrolysis temperature.

The chemical activated char (OS500N900) was prepared according to modified method from Wang et al. (2017b). The oily sludge was impregnated with sodium hydroxide (NaOH) solution in a beaker with water:NaOH:oily sludge equal to 1:1:1 by mass. The mixture was dehydrated in an oven overnight at 105 °C and then pyrolyzed at 500 °C for 30 min under nitrogen atmosphere. The product was heated directly from 500 °C to 900 °C at 10 °C/min and held for 80 min for the activation treatment. The activated char was then washed, dried, and ground similar to non-activated sample.

Hydrothermal treatment of char with NaOH solution was performed based on modified method from Visa et al. (2012). About 10 g of OS500 (without wash and grinding) was added to 100 mL of 2M or 8M NaOH solution. The slurries were then refluxed with stirring at atmospheric pressure and 100 °C for 24 h. At the end of activation period, the product was collected, washed, dried, and ground. The resulting char samples were hereby denoted as OS500N100-2M and OS500N100-8M respectively, according to the NaOH solution

concentration. For comparison, the activation (with 2M NaOH) was conducted using the same procedures as stated above but the reaction was conducted at room temperature (24 °C). The activated sample obtained was denoted as OS500N24-2M.

The preparation of ferric-activated char (FSOS500) followed the method of Yang et al. (2016). About 20 g of oily sludge was mixed with 10 g of ferric sulfate (FeSO₄). The mixture was then pyrolyzed in the same conditions as those used in the OS500 preparation. After cooling, the solid product was washed, dried, and ground before use.

The characteristics of chars were determined and the analytical methods can be found in Section 5.2.3.

6.2.3. Preliminary test

Sorption experiment was conducted in 50-mL centrifuge tubes by mixing 0.1 g of nonactivated char or activated char with 30 mL of 1000 mg/L Cd²⁺, Cu²⁺, Pb²⁺, or Zn²⁺ solution. The mixture was shaken at 200 rpm and room temperature (24 °C) for 48 h. After shaking, all mixtures were subject to nylon filter (0.45- μ m) filtration and the concentration of metal (i.e., Cd²⁺, Cu²⁺, Pb²⁺, or Zn²⁺) in the filtrate was determined by ICP-OES. The initial and final pH values of solutions were recorded by a Mettler Toledo FG2 portable pH meter. The Cd²⁺, Cu²⁺, Pb²⁺, or Zn²⁺ sorption capacity of char or activated char was calculated by eq. (5.1).

6.2.4. Post-sorption analysis

To keep consistency with Chapter 5, the OSDC after Pb^{2+} (or Cd^{2+}) sorption at initial Pb^{2+} concentration of 1600 mg/L (or initial Cd^{2+} concentration of 1000 mg/L) was chosen for the post-sorption analysis. The Pb^{2+} or Cd^{2+} solution contained 0.01 M NaNO₃ as the background electrolyte and the pH of solution was pre-adjusted to 5.0 ± 0.05 . The shaking time of 128 h

was used to achieve equilibrium in sorption experiments. The OSDC after Pb²⁺ (or Cd²⁺) sorption was quickly washed by 20 mL UHQ water and the water was discarded after centrifugation. The remaining solid was oven dried at 60 °C for 48 h and was then identified as post-sorption OSDC (OSDC-Pb or OSDC-Cd). The same procedure was employed to control sample without the presence of Pb²⁺ (or Cd²⁺). The resulting sample was identified as OSDC before sorption (OSDC-B). The net amount of released cation (K⁺, Ca²⁺, Mg²⁺, and Ba²⁺) during Pb²⁺ and Cd²⁺ sorption was determined by the difference of concentration of cations in solution before and after sorption. The OSDC-Pb, OSDC-Cd, and OSDC-B were examined using the XRD, FTIR, and sequential extraction test. The analytical methods and extraction procedures are given in Section 5.2.5.

6.3. Results and discussion

6.3.1. Characteristics of chars

In order to identify the most promising activated char for the subsequent sorption mechanism studies, a preliminary sorption of heavy metal using chars prepared at different pyrolysis temperatures and activation methods was carried out. Preliminary sorption results are shown in Table 6.1. The activated chars showed similar Pb²⁺ removal performance, with the sorption capacities in the range of 251.8–304.6 mg/g. However, among the five activated chars, OS500N100-8M exhibited the best performance in removal of Cu²⁺, Cd²⁺, and Zn²⁺ from solution. The Cd²⁺ sorption capacity was increased by 4.7-fold for OS500N100-8M as compared to that for OS500. Therefore, OS500N100-8M was chosen in this study to further investigate its sorption mechanisms for heavy metals.

The physicochemical properties of chars are summarized in Table 6.2. Non-activated char was not rich in C (3.73–7.33%) and its C concentration decreased as the pyrolysis temperature increased from 300 °C to 700 °C. The decrease of C could be attributed to the transformation of carbonaceous materials into CH₄, CO₂ and other gases or aromatic structures. During pyrolysis, the release of volatile matters led to the loss of surface functional groups elements (H and N). As a result, the content of H decreased from 0.50% at 300 °C to 0.09% at 900 °C, and the content of N decreased from 0.10% at 300 °C to 0.02% at 900 °C (Table 6.2). The ash content of chars increased from 88.8% to 96.3% with increasing pyrolysis temperature from 300 °C to 900 °C, mainly due to decomposition of volatile matters and enrichment of minerals. The pH values of chars at 300–700 °C ranged from 10.7 to 11.3, and then decreased to 9.5 at 900 °C, which is in agreement with the previous result (Zhang et al., 2015). The lower pH value of the char pyrolyzed at 900 °C may be related to its relatively lower concentration of Ca, as compared to that of chars pyrolyzed at 300-700 °C. The Ca and Mg concentration decreased when the pyrolysis temperature increased from 700 °C to 900 °C. On the one hand, the concentrations of elements in chars were determined by acid digestion method (i.e., method 3050 B). It was reported that the elemental recovery using USEPA method 3050 B was affected by a number of factors such as hot plate temperature, refluxing times, and acid additions (Chen and Ma, 1998). Therefore, incomplete recovery might happen for method 3050 B. On the other hand, the chloride (Cl) in the char sample could be incorporated with Ca and Mg to form MgCl₂ or CaCl₂, which volatilized at 700–900 °C (Zhang et al., 2015). The total basicity of chars increased with increasing pyrolysis temperature because of increasing contents of ash. The BET surface area increased gradually from 10.8 m²/g in char at 300 °C to 23.8 m²/g in char at 700 °C. This might be because volatilization was more subtle at higher temperature leading to

more porous char (Zhang et al., 2015). As can be observed from Table 6.2, the increase of pyrolysis temperature from 700 °C to 900 °C caused a reduction of surface area and total pore volume. Similar results has been reported in other studies (Chun et al., 2004; Yang et al., 2016). It was reported that high temperature (above 650 °C) could destroy the pore walls between adjacent pores, leading to decreased surface area (Zou et al., 2013). The activation process improved the development of pores and created new pores. The BET surface area of OS500N100-8M was 32.9 m²/g, which is approximately 1.9 times that of OS500. The total pore volume (PV) of OS500N100-8M was 0.231 cm³/g, which is approximately 3.6 times that of OS500.

	Cu ²⁺		Cd^{2+}		Pb^{2+}	Zn^{2+}			
Chars	$\begin{array}{c} Q_{48h}{}^a \\ mg/g \end{array}$	$pH_f{}^b$	Q _{48h} mg/g	pH_f	$\begin{array}{c} Q_{48h} \\ mg/g \end{array}$	pH_f	Q _{48h} mg/g	pH_f	
OS300	134.5	5.06	44.90	5.98	260.9	5.48	68.35	6.54	
OS500	140.3	4.94	17.56	6.43	297.0	5.67	75.22	6.51	
OS700	173.2	6.07	83.00	5.02	298.4	6.54	75.75	6.18	
OS900	114.3	4.94	15.73	6.14	81.82	5.17	9.153	6.26	
OS500N900	241.5	5.40	62.03	6.11	300.0	ND	72.18	6.50	
OS500N100-2M	184.6	5.21	54.68	5.98	273.9	5.40	55.02	6.45	
OS500N100-8M	256.8	6.01	99.81	6.35	297.5	5.69	87.57	6.53	
OS500N24-2M	154.2	4.93	16.85	6.11	304.6	6.86	81.31	6.54	
FSOS500	19.29	4.64	18.21	6.43	251.8	5.19	14.18	6.43	

Table 6.1. Preliminary sorption results of chars

Note: initial Cu²⁺ solution pH = 4.52; initial Cd²⁺ solution pH = 6.22; initial Pb²⁺ solution pH = 4.53; initial Zn²⁺ solution pH = 5.98; ND: not detected.

^a The amount of heavy metal sorbed per unit mass of char at 48 h (mg/g).

^b Final pH values of solution.

	Eleme	ental co	ntent (‰) ^b						TSA	TSB mmol /g	Ash % ^b	CEC	Microstructures		
Chars	С	Н	Ν	K	Ca	Na	Mg	рН	pH _{PZC}	mmol /g			cmol /kg	S _{BET} m ² /g	PV cm ³ /g	D _P nm
OS300	7.33	0.50	0.10	0.29	7.34	0.02	1.32	11.3	11.67	0.09	4.37	88.8	117.1	10.8	0.069	3.62
OS500	6.11	0.28	0.08	0.37	7.26	0.04	1.35	10.7	11.57	0.07	4.52	90.4	86.95	17.4	0.064	3.63
OS700	3.73	0.42	0.03	0.45	8.55	0.16	1.66	11.2	11.66	0.29	6.10	94.3	255.9	23.8	0.203	3.87
OS900	3.92	0.09	0.02	0.54	6.55	0.25	0.93	9.5	9.96	0.26	6.23	96.3	104.7	6.50	0.034	3.89
OS500N 100-8M	4.54	0.75	0.06	0.20	9.77	2.40	1.43	10.5	10.84	0.14	8.60	89.6	163.3	32.4	0.231	3.85

 Table 6.2. Physicochemical properties of chars^a

^a Values are given as the average of duplicate measurements. ^b On a dry basis.

The nitrogen adsorption-desorption isotherms and pore size distribution of chars are shown in Figures 6.1 and 6.2. According to international union of pure and applied chemistry (IUPAC), the N₂ adsorption/desorption isotherms for all the chars corresponded to type II adsorbents (Sing et al., 1985). As seen from Figure 6.1a and Figure 6.2a, the adsorbed volume of N₂ increased slowly with increasing P/P₀ from 0.0 to 0.8. When the relative pressure P/P₀ approached to 1, the capillary condensation could take place and the adsorbed volume increased rapidly. The average pore diameter (D_p) of chars between 3.62 and 3.89 nm denoted mesopores characteristics. It is interesting that new pores (in the range 3.5–4.5 nm) formed at the expense of the small pores (1.0–3.0 nm) for OS700 (Figure 6.1b). As shown in Figure 6.2b, the total pore volume for activated char was significantly larger than that of non-activated char, which is mainly attributed to the appearance of new pores in the range 10.0–200.0 nm.

The mobility and speciation of heavy metals in OS300-B, OS500-B, OS700-B, OS900-B, and OS500N100-8M were shown in Table D1 in Appendix D. Their water soluble fraction and exchangeable fraction were negligible, suggesting there was no direct risks to plants and humans when OSDCs were applied in water treatment. In fact, there was no Cd (or Pb), Cr, Cu, Ni, and Zn was detected in solution after Pb²⁺ (or Cd²⁺) sorption (initial concentration: Pb²⁺ 1600mg/L; Cd²⁺ 1000 mg/L) except a low concentration of Zn (0.6–0.7 mg/L) was leached out from OS900 after the Pb²⁺ sorption. In this regard, the effect of Pb and Cd originating from OSDCs could be ignored in the sorption studies.



Figure 6.1. (a) Nitrogen adsorption/desorption isotherms and (b) pore size distribution of the OSDCs prepared at different pyrolysis temperatures.



Figure 6.2. (a) Nitrogen adsorption/desorption isotherms and (b) pore size distribution of the non-activated OSDC and activated OSDC obtained at 500 °C.

6.3.2. XRD and FTIR results

The XRD spectra of the OSDCs before Pb^{2+}/Cd^{2+} sorption is shown in Figure D1 (Appendix D). The OS300-B presents mainly muscovite 2M2 (K_{0.77}Al_{1.93}(Al_{0.5}Si_{3.5})O₁₀(OH)₂), barite (BaSO₄), quartz (SiO₂), calcite (CaCO₃), and dolomite (CaMg(CO₃)₂). Calcite and dolomite started to decompose to calcium oxide (CaO) after heating above 500 °C. The peaks of muscovite 2M2 and barite started to disappear above 700 °C, leading to the formation of celsian (BaAl₂Si₂O₈) and barium oxide hydrate (BaO₂ (H₂O)₈). The hydrothermal treatment of OS500 with NaOH solution was performed in order to synthesize zeolite (crystalline aluminum-silicates) which could be an effective sorbent. However, the zeolite was not identified in OS500N100-8M (Figure D1 in Appendix D). This might be because the concentration of aluminum (Al) which is a primary source for forming zeolites was relatively low in oily sludge (Table 5.1). As shown in Figure D1 in Appendix D, the complete conversion of barite to witherite (BaCO₃) was achieved under hydrothermal condition, probably resulting from dissolution-recrystallization (Rendón-Angeles et al., 2008).

The higher pyrolysis temperature and activation led to the disappearance and the formation of certain minerals, which could affect the heavy metal sorption capacities. To further illustrate, the char samples loaded with Pb²⁺ or Cd²⁺ were also characterized using XRD (Figure 6.3). New peaks at 27.080° and 34.155° showed hydrocerussite (Pb₃(CO₃)₂(OH)₂) formed on OS300-Pb, OS500-Pb, OS700-Pb, and OS500N100-8M-Pb. Also, a precipitation of cerussite (PbCO₃) at $2\theta = 24.792^{\circ}$ and 47.016° were observed in OS300-Pb and OS500-Pb. These precipitates formed in Pb²⁺-loaded OSDCs may be the product of the precipitation of Pb²⁺ and the dissolved anions (i.e., OH⁻ and CO₃²⁻) from minerals. No precipitation of Pb-carbonates was detected in OS900-Pb, probably because most of calcite and other carbonate underwent

decomposition at 900 °C. XRD results (Figure 6.3) showed that no precipitate formed on the surface of OSDCs after Cd²⁺ sorption except for OS500N100-8M. Formation of otavite (CdCO₃, at $2\theta = 30.275^{\circ}$ and 23.485°) precipitates was probably related to the existence of witherite (BaCO₃) in OS500N100-8M.

Figure D2 in Appendix D presents the FTIR spectra of OSDC before Pb^{2+} or Cd^{2+} sorption. The peaks at 3385–3425 cm⁻¹ corresponded to hydroxyl stretching (O–H) and disappeared at 900 °C. The band for aliphatic CH₂ (2923 cm⁻¹) disappeared upon heating to 500 °C. At 300– 500 °C, the bands at 777 and 875 cm⁻¹ was assigned to aromatic C–H. The carboxyl C=O (1633 cm⁻¹) became more apparent at 700 °C. The peak at 1007 cm⁻¹, which shifted towards lower wavenumbers as a result of increasing pyrolysis temperature, was assigned to Si–O stretching.

The organic functional groups on the surface of OSDCs before and after Pb²⁺ or Cd²⁺ sorption were also characterized using FTIR (Figure 6.4). The peaks at 1431 and 694 cm⁻¹ (assigned to CO_3^{2-}) of the OS300, were intensified obviously after Pb²⁺ sorption, suggesting formation of lead carbonate which was consistent with that observed in XRD. Similar trends were also observed for OS500, OS700, OS500N100-8M (Figure 6.4). The peaks at 1429 cm⁻¹ corresponding to CO_3^{2-} in the OS500N100-8M was shifted to 1391 cm⁻¹ after it sorbed Cd²⁺, indicating a change in the vibration of C–O bond which was probably due to formation of cadmium carbonate precipitate. Compared with the FTIR spectra of the OS900-B, a new band at 1370 and 1413 cm⁻¹ was observed in the OS900-Pb and OS900-Cd, respectively, indicating a weak formation of Pb- or Cd-carbonate precipitation (Figure 6.4d). But no precipitates of Pb or Cd-carbonate were detected in OS900-Pb and OS900-Cd by XRD (Figure 6.3d), which may be due to the detection limit. The absence of peak associated with CO_3^{2-} for OS900-B (Figure

6.4d) may be due to its low concentration. After Pb^{2+} sorption, the peak at 874 cm⁻¹ (assigned to aromatic C–H) of OS500, and the peak at 860 cm⁻¹ (assigned to aromatic C–H) of OS500N100-8M weakened obviously, confirming the effect of $Pb^{2+}-\pi$ interaction on the Pb^{2+} sorption process. After Cd²⁺ sorption, the peaks at 3385–3425 cm⁻¹ corresponding to O–H vibrations of hydroxyl groups in OS300, OS500, OS700, and OS500N100-8M shifted, likely from the coordination between Cd²⁺ and hydroxyl (–OH) functional groups. However, there was no peak shifting from FTIR results suggesting the coordination between the –OH and Pb^{2+} in OSDCs, except for OS700 and OS500N100-8M.







Figure 6.3. XRD patterns of (a) OS300, (b) OS500, (c) OS700, (d) OS900, and (e) OS500N100-8M before and after Pb^{2+}/Cd^{2+} sorption.



Figure 6.4. FTIR spectra of (a) OS300, (b) OS500, (c) OS700, (d) OS900, and (e) OS500N100-8M before and after Pb²⁺/Cd²⁺ sorption.

6.3.3. Sequential extraction results

The speciation of Pb^{2+} or Cd^{2+} in OSDCs after Pb^{2+} or Cd^{2+} sorption are shown in Table D2 (Appendix D) and Figure 6.5. The recovery percentages from sequential extraction tests are shown in Table D3 (Appendix D). The recoveries of Cd²⁺ from OS500, OS700, OS900, and OS500N100-8M were 80.92-93.52%, while that for OS300 was 65.22%. The recoveries of Pb²⁺ from OSDCs were within 74.15–87.26%. Shen et al. (2016) conducted sequential extraction to determine the speciation of Pb²⁺ on biochar treated soil. The recoveries of the Pb^{2+} were within 61.50–97.28%, which were comparable to the recovery of Pb^{2+} and Cd^{2+} in this study. Figure 6.5a-d demonstrated that physical sorption can be ignored in most of the cases. Only 0–1.34 % of total Pb^{2+} or Cd^{2+} could be extracted from water in all OSDCs except for OS900. The contribution of physical sorption in the OS900 was also very little. The concentration of water-extractable Pb^{2+} accounted for 5.46 % of the total sorbed Pb^{2+} in OS900, while the water-extractable Cd^{2+} accounted for 3.29 % of the total sorbed Cd^{2+} . The carbonate fraction dominated the existence of Pb^{2+} although to a lesser extent in OS900 (79.30%) compared with OS300, OS500, OS700, and OS500N100-8M (92.99–98.06%). Conversely, the exchangeable fraction was greater in OS900 (7.73%) than the other OSDCs (0.28-0.81%). Cd²⁺ was mainly bound to the carbonate fraction (61.35-92.96%) and the exchangeable fraction (5.59-29.78%). The proportion bound to carbonate was highest (92.96%) in OS500N100-8M while the exchangeable fraction (5.59%) was lowest in OS500N100-8M.

Significant concentrations of K⁺, Ca²⁺, Mg²⁺, and Ba²⁺ were released during Pb²⁺/Cd²⁺ sorption (Table 6.3). These cations were mainly released from the minerals (e.g., CaCO₃, CaMg(CO₃)₂, and BaCO₃) on the surface of OSDCs (Lu et al., 2012). Alternatively, it may result from substitution between Pb²⁺ or Cd²⁺ and metal ions (e.g., Ca²⁺, Mg²⁺, and Ba²⁺)

associated with inner-sphere complexation. The formed precipitates and complexes containing Pb^{2+} or Cd^{2+} could be desorbed at step 3 (fraction bound to carbonate) due to acidic environment (Lu et al., 2012; Shen et al., 2017). Hence, the sorption (Q_R) attributed to the release of cations can be described as:

$$Q_{\rm R} = Q_{\rm e} + Q_{\rm p} + Q_{\rm cm} \tag{6.1}$$

Where Q_R is the amount of Pb²⁺ or Cd²⁺ sorption attributed to the release of cations (mg/g), Q_e is the amount of Pb²⁺ or Cd²⁺ existed as exchangeable fraction (mg/g), Q_p is the amount of Pb²⁺ or Cd²⁺ attributed to the precipitation with minerals (mg/g), and Q_{cm} is the amount of Pb²⁺ or Cd²⁺ substituted with metal ions to form inner-sphere complexation (mg/g).

According to the sequential extraction results, the net amount of released cations and eq. (6.1), the contribution of different mechanisms to Pb^{2+} or Cd^{2+} sorption on OSDCs could be estimated as shown in Table 6.4.



Figure 6.5. Sequentially extracted (a) Pb^{2+} and (b) Cd^{2+} amounts in the OSDCs after Pb^{2+} or Cd^{2+} sorption. Fractions of (c) Pb^{2+} and (d) Cd^{2+} in each step of sequential extraction (WS: water soluble fraction, EX: exchangeable fraction, CB: fraction bound to carbonate, OX: fraction bound to Fe-Mn oxides, OM: fraction bound to organic matter, RS: residual fraction).

		The net amoun	nt of released catio	ons (meq/100g) ³	a	Sum of net amount	Maximum metal sorption	R_r
		K ⁺	Ca ²⁺	Mg ²⁺	Ba ²⁺	(mg/g)	capacity (mg/g)	(70)
Pb^{2+}	OS300	0.31 ± 0.00	177.15 ± 12.55	22.74 ± 0.38	-0.12 ± 0.08	207.28 ± 13.31	282.96 ± 3.22	73.3
	OS500	0.27 ± 0.01	229.64 ± 0.79	48.75 ± 0.46	2.78 ± 0.11	291.58 ± 1.40	351.48 ± 2.08	83.0
	OS700	-0.09 ± 0.01	85.56 ± 2.93	51.27 ± 0.76	7.35 ± 0.10	149.28 ± 3.79	261.14 ± 2.02	57.1
	OS900	-0.31 ± 0.02	8.66 ± 0.59	2.30 ± 0.05	5.04 ± 0.31	16.26 ± 0.99	49.68 ± 2.31	32.7
	OS500N100- 8M	0.11 ± 0.00	69.01 ± 2.45	54.51 ± 0.64	115.37 ± 2.00	247.60 ± 0.97	310.00 ± 2.19	79.9
Cd^{2+}	OS300	-0.01 ± 0.05	24.12 ± 9.22	0.61 ± 0.01	0.23 ± 0.06	14.02 ± 5.18	46.67 ± 0.69	30.0
	OS500	0.02 ± 0.02	13.19 ± 0.54	4.32 ± 0.11	0.23 ± 0.02	9.98 ± 0.36	23.95 ± 3.79	41.7
	OS700	-0.15 ± 0.03	46.81 ± 3.12	21.18 ± 0.68	3.86 ± 0.03	40.30 ± 2.06	92.14 ± 3.11	43.7
	OS900	-0.34 ± 0.02	1.61 ± 0.24	$1.41\ \pm 0.06$	2.73 ± 0.37	3.04 ± 0.36	11.05 ± 1.50	27.5
	OS500N100- 8M	0.07 ± 0.07	5.42 ± 0.23	7.33 ± 0.19	109.61 ± 1.93	68.82 ± 1.14	90.06 ± 3.17	76.4

Table 6.3. The release of K⁺, Ca²⁺, Mg²⁺, and Ba²⁺ during Pb²⁺ and Cd²⁺ sorption by OSDCs

^a The net amount of released cations were the difference values between the concentration of K⁺, Ca²⁺, Mg²⁺, and Ba²⁺ released into Pb²⁺ (Cd²⁺) sorption system at 1600 mg/L Pb²⁺ (1000 mg/L Cd²⁺) solution with 0.01M NaNO₃ at pH 5.0 and the corresponding release from OSDC in 0.01M NaNO₃ at pH 5.0.

^b R_r is calculated by dividing the sum of net amount of released cations by the total sorbed Pb²⁺ or Cd²⁺.

		Physical sorption		ysical Cation orption exchange with weak binding		Precipitation		Complexation with mineral oxides of char		Complexation with free functional groups		Cation- π interaction		Others	
		Qw ^a mg/g	R _m ^k %	Qe ^b mg/g	Rm %	Qp ^c mg/g	Rm %	Q _{cm} ^d mg/g	Rm %	Q _{cf} ^e mg/g	Rm %	Q_{π}^{f} mg/g	Rm %	Qo ^g mg/g	Rm %
Pb	OS300	0	0	1.71	0.81	205.57	97.97	/h	0	i	0	_	0	2.90	1.38
	OS500	0	0	1.38	0.45	290.20	93.79	/	0	_	0	13.22	4.27	4.62	1.49
	OS700	0.29	0.13	0.44	0.20	148.84	68.13	/	0	54.32	24.86	_	0	14.59	6.68
	OS900	2.10	5.47	2.97	7.74	13.29	34.63	/	0	17.15	44.68	_	0	2.88	7.50
	OS500N 100-8M ^j	0	0	0.76	0.28	246.84	91.25	/	0	<11.06	<4.09	<11.06	<4.09	11.86	4.38
Cd	OS300	0.41	1.35	6.29	20.66	_	0	7.73	25.39	15.83	52.00	_	0	0.18	0.59
	OS500	0.02	0.10	2.93	15.12	_	0	7.05	36.38	9.26	47.78	_	0	0.12	0.62
	OS700	0.02	0.02	8.79	10.66	_	0	31.51	38.21	41.22	49.99	_	0	0.92	1.12
	OS900	0.33	3.28	3.00	29.82	_	0	0.04	0.40	6.13	60.93	_	0	0.57	5.67
	OS500N 100-8M	0	0	4.71	5.59	64.11	76.12	/	0	14.18	16.84	_	0	1.22	1.45

Table 6.4. Quantitative analysis of sorption mechanisms of Pb^{2+}/Cd^{2+} onto OSDCs

 ${}^{a}Q_{w}$ is the amount of Pb²⁺/Cd²⁺ existed as water soluble fraction. ${}^{b}Q_{e}$ is the amount of Pb²⁺/Cd²⁺ existed as exchangeable fraction. ${}^{c}Q_{p}$ is the sum of net amount of released cations in Pb²⁺/Cd²⁺ sorption – the amount of Pb²⁺ existed exchangeable fraction (if the precipitation is evidenced by XRD/FTIR) ^d Q_{cm} is the sum of net amount of released cations in Cd²⁺ sorption – the amount of Cd²⁺ existed exchangeable fraction (if the precipitation is not

evidenced by XRD/FTIR).
^e Q_{cf} is the amount of Pb^{2+}/Cd^{2+} existed as carbonate fraction – Q_{cm} or Q_p (if the cation- π interaction is not evidenced by FTIR).

 ${}^{f}Q_{\pi}$ is the amount of Pb²⁺ existed as carbonate fraction – Q_{p} (if the cation- π interaction is verified but complexation with free functional groups is not evidenced by FTIR).

 ${}^{g}Q_{o}$ is the amount of $P\dot{b}^{2+}/Cd^{2+}$ existed as Fe-Mn oxides, organic matter, or residual fraction.

^h Not applicable.

ⁱ Not evidenced by XRD and FTIR.

^j $Q_{cf} + Q_{\pi} = 11.06$ mg/g, since both complexation with free functional groups and cation- π interaction were evidenced by FTIR.

^k R_m is calculated by dividing the Q resulted from each mechanism by the total extracted Pb²⁺ (Cd²⁺) in sequential extraction (Qt).

The sum of net amount of released cations (i.e., K⁺, Ca²⁺, Mg²⁺, and Ba²⁺) into Pb²⁺ sorption system was accounted for 73.3%, 83.0%, 57.1%, and 32.7% of the total sorbed Pb^{2+} on OS300, OS500, OS700, and OS900, respectively (Table 6.3). The released K⁺, Ca²⁺, Mg²⁺, and Ba²⁺ dramatically decreased from 291.58 to 16.26 mg Pb²⁺/g with the pyrolysis temperature increasing from 500 to 900 °C. Accordingly, the Pb²⁺ sorption capacity decreased from 351.48 to 49.68 mg/g as the pyrolysis increased from 500 to 900 °C. As shown in the XRD patterns (Figure D1 in Appendix D), CaCO₃ and CaMg(CO₃)₂ decomposed at high temperature $(\geq 700 \text{ °C})$, thereby the amount of CO₃²⁻ released from OS700 and OS900 was much smaller than that from OS500, which could explain the sorption capacity difference among chars prepared at different pyrolysis temperature. These results confirmed that the precipitation with minerals dominated the Pb²⁺ sorption on the low-pyrolysis-temperature chars (\leq 500 °C). The contribution of precipitation to Pb^{2+} sorption decreased with increasing pyrolysis temperature. For example, the sorption capacity attributed to precipitation (Q_p) of OS500 was 290.20 mg/g, accounting for 93.97% of total extracted Pb^{2+} in sequential extraction (Qt), while Qp and Qp/Qt of OS900 were only 13.39 mg/g and 13.29%, respectively (Table 6.4). The contribution of complexation with free carboxyl/hydroxyl functional groups (Q_{cf}) by OS700 and OS900 were higher than OS300 and OS500. The Q_{cf} in OS700 and OS900 reached 54.32 mg/g and 17.15 mg/g, respectively, while the corresponding proportions were 24.86% and 44.68%, respectively. This may be attributed to the higher total surface acidity (TSA) value in OS700 and OS900 (Table 6.2). In the case of OS500N100-8M sample, the Q_p accounted for 91.25% of Qt value, indicating the precipitation is the dominant mechanism for Pb²⁺ sorption. The released Ba²⁺ of OS500N100-8M was 115.37 mg/g, which is approximately 42 times greater

than that of OS500 (2.78 mg/g). This phenomenon may be due to the fact that BaCO₃ was the major carbonate mineral formed in the OS500N100-8M (Figure 6.3e).

For Cd^{2+} sorption, the Q_{cf}/Q_t value of non-activated OSDCs were 47.78–60.93%, suggesting the complexation with free carboxyl/hydroxyl functional groups played a dominant role in Cd^{2+} sorption. The sorption capacity of Cd^{2+} for OS700 (92.14 mg/g) was greater than that of other three non-activated chars (11.05–46.67 mg/g), implying that 700 °C was the optimized pyrolysis temperature for Cd^{2+} sorption. Due to the higher TSA value in OS700 than in other non-activated chars, the Q_{cf} of OS700 increased to 41.22 mg/g compared to that of OS300 and OS500 (9.26–15.83 mg/g). Besides, the amount of Cd^{2+} substituted with metal ions to form complexes (Q_{cm}) in OS700 was obviously larger than that of other non-activated chars, which may be related to its higher CEC value (Table 6.2). After chemical activation, the effect of carboxyl/hydroxyl functional group on Cd^{2+} sorption (Q_{cf}/Q_t) decreased, while the contribution of the precipitation (Q_p/Q_t) to sorption significantly increased. For OS500N100-8M, the Q_p value was 64.11 mg Cd^{2+}/g , accounting for 76.12% of the Q_t value, indicating the precipitation between Cd^{2+} and the minerals could be the dominant mechanism for Cd^{2+} sorption.

Pearson correlation analysis (Table D4 in Appendix D) was conducted to explore the relationship between the OSDCs properties and Pb^{2+}/Cd^{2+} sorption mechanism. No correlations were observed between the ash content and $Q_{p,Pb}$, which was consistent with previous studies (Li et al., 2018; Wang et al., 2015). The minerals that could release dissolved anions (e.g., CO_3^{2-} , OH^- , and PO_4^{3-}) instead of Al_2O_3 and SiO_2 in ash led to the formation of precipitates (Li et al., 2018). Therefore, an increase in ash content could not increase the Pb^{2+} sorption performance in this study. The CEC of OSDCs showed positive correlations with

 $Q_{cm,Cd}$, $Q_{cf,Cd}$, and $Q_{t,Cd}$, implying the CEC values in OSDCs is a good predictor of Cd^{2+} sorption capacities.

6.4. Summary

The Pb²⁺ sorption capacity of OSDCs at different temperatures followed the order of OS500 (351.48 mg/g) > OS300 (282.96 mg/g) > OS700 (261.14 mg/g) > OS900 (49.68 mg/g). For Cd^{2+} , the order of sorption capacity was OS700 (92.14 mg/g) > OS300 (46.67 mg/g) > OS500 (23.95 mg/g) > OS900 (11.05 mg/g). Precipitation with minerals (e.g., CO_3^{2-} and OH^-) dominated the Pb²⁺ sorption on OSDCs except for OS900. Pb²⁺ was more effectively sorbed onto low-pyrolysis-temperature OSDCs (≤500 °C), which was mainly due to their abundant CO_3^{2-} that can precipitate with Pb²⁺. With increasing pyrolysis temperature, the contribution of precipitation to metal sorption reduced due to the decomposition of minerals which could release dissolved anions (e.g., CO_3^{2-} , and OH^{-}). The sorption capacity of Cd^{2+} was less than that of Pb^{2+} and no precipitation was formed during Cd^{2+} sorption by OSDCs. Complexation with free carboxyl/hydroxyl functional groups dominated Cd²⁺ sorption on the OSDCs, while the contribution of interaction with minerals (complexation with mineral oxides and metal ion exchange) was second to functional groups. OS700 had a greater sorption capacity for Cd²⁺ than other OSDCs probably due to its higher effective cation exchange capacity (CEC) (255.9 cmol/kg) and total surface acidity (0.29 mmol/g). Among various activation methods, hydrothermal treatment with NaOH solutions (8M) at 100 °C was determined to be the optimum activation method considering the performance of activated OSDCs in removal Pb^{2+} , Cu^{2+} , Cd^{2+} , and Zn^{2+} from solution. The resultant char (OS500N100-8M) had significantly increased CEC, surface area, and total pore volume compared to the unmodified char (OS500). Moreover, the complete conversion of barite (BaSO₄) to witherite (BaCO₃) after hydrothermal

treatment contributed to the mineral precipitation of Cd^{2+} . As a result, the Cd^{2+} sorption capacity of OS500N100-8M (90.06 mg/g) was over 3 times higher than that of OS500 (23.95 mg/g). Overall, the oily sludge can be converted into value-added char as an effective sorbent for Pb²⁺ and Cd²⁺. Pyrolysis temperature and activation method affected the chemical properties (e.g., H/C, CEC, and ash content), microstructure (e.g., surface area and total pore volume), as well as the mineral components (e.g., CO_3^{2-} , OH^-) in the OSDC, consequently changed the Pb²⁺ and Cd²⁺ sorption capacity and the contribution of different mechanism. However, further research is necessary to evaluate and minimize the environmental risk of preparation and application of OSDCs.

Chapter 7

CONCLUSION AND RECOMMENDATIONS

7.1. Synthesis and conclusion

The effective treatment of oily sludge is a worldwide problem faced by many refineries, pipelines, and oil producing companies. Most common ways to treat oily sludge such as landfills and incinerations are challenged by their unsatisfactory efficiency, high operational cost, and/or possible production of secondary toxic compounds. In fact, oily sludge contains a large amount of combustibles with high heating values. The proper solution to solve the problem of oily sludge requires consideration of the economic benefit and in compliance with environmental standards. This study proposed three effective oily sludge management techniques: (i) IL-enhanced solvent extraction; (ii) co-pyrolysis with wood waste; and (iii) converting oily sludge into sorbent to remove Pb^{2+} and Cd^{2+} from solution.

Solvent extraction is a commonly used approach to recycle petroleum hydrocarbons from oily sludge. However, the organic solvents introduce problems associated with handling volatile, flammable, and toxic material, limiting the extension of this technology to field-scale oily sludge treatment. Chapter 3 proposed an ionic liquid (IL) enhanced solvent extraction method for oily recovery from oily sludge. Compared with conventional solvent extraction, the advantages of IL-enhanced solvent extraction are as follows: (i) the issue associated with solvent loss by volatilization was addressed since the solvent volume was greatly reduced; (ii) the residual IL was completely separated from residual sand/clay after water washing, which is of significance for recycling IL; (iii) there was no evidence of IL and mineral fines existing in the recovered oil after IL-enhanced solvent extraction; and (iv) the process can be economically competitive since IL yielded high oily recovery at low energy consumption and short extraction duration. This work expanded the existing limited knowledge regarding the use of IL in oily sludge treatment. Chromatographic characterization of recovered oil indicated that the IL addition did not promote alteration of the long-chain and heavy petroleum hydrocarbons (PHCs). The break of incrustation and desorption of oil from solid matrices were high at short extraction duration (10 min), low solvent/sludge ratio (4:5 mL/g), and low energy consumption (100 rpm). However, due to the constraint of the small solvent/sludge ratio (4:5 mL/g), not all desorbed oil could be dissolved in a solvent, leaving 29.33% of TPH in the oil-IL interface. The higher solvent/sludge ratio and stronger shearing force could enhance the dissolution of suspended oil into the solvent.

As one of the thermal methods to treat oily sludge, pyrolysis has the advantages of energy recovery (pyrolysis oil and gas), solid waste reduction, and less secondary pollution. More importantly, pyrolysis can immobilize heavy metals in the solid residue. Chapter 4 concluded that co-pyrolysis of oily waste with other biomass waste is an effective approach for both oil recovery and heavy metal immobilization in the obtained solid residue. The co-pyrolysis treatment could achieve more than 50% of total petroleum hydrocarbon (TPH) recovery. The degree of potential ecological risk posed by heavy metals in the solid residue from co-pyrolysis was also reduced from "considerable risk" (RI of 302.50 for untreated oily waste) to "low risk" (RI of 21.96–120.2 for solid residue). This work adds to the current understanding of factors that contribute the oil recovery and heavy metal immobilization during co-pyrolysis treatment. The individual factors of pyrolysis temperature, reaction time, and hog fuel addition on TPH recovery and ecological risk of solid char residue, were studied using a response surface methodology (RSM). In addition, the interaction effects between any two of the aforementioned factors were also studied. Oil recovery and heavy metal immobilization

responded very differently to experimental factors. Specifically, a maximum TPH recovery was obtained at a low temperature (400 °C), but the increase in temperature could reduce the potential ecological risk of heavy metals. The addition of hog fuel into oily waste for co-pyrolysis led to an increased metal immobilization, but the overall oil recovery was decreased. A longer reaction time could favor the pyrolysis conversion, but had little effect on heavy metal immobilization. In this study, a low temperature co-pyrolysis (400 °C) by adding 20% of hog fuel was found as the most effective oily waste disposal strategy with satisfactory oil recovery and an acceptable risk index of 54.1. However, it is important to consider the site specific factors for determination of optimum condition in co-pyrolysis treatment. Environmental testing, including the determination of heavy metal concentration and oil, water, and solid composition, in oily sludge is essential for co-pyrolysis treatment decision making.

Converting oily sludge into sorbent could be regarded as a "win-win" strategy since this conversion not only provides safe disposal of oily sludge, but also allows its reuse in water treatment applications. Chapter 5 investigated the Pb²⁺ and Cd²⁺ sorption capacity and mechanisms by char (OS500) prepared from pyrolysis of oily sludge at 500 °C. The sorption of Pb²⁺ and Cd²⁺ on OS500 was a chemical rather than physical process. Sorption of Pb²⁺ by OS500 was mainly attributed to its precipitation with CO_3^{2-} originating in OS500, while complexation dominated Cd²⁺ sorption on OS500. Chapter 6 investigated the influence of pyrolysis temperature and chemical activation on properties and heavy metal sorption performance of oily sludge-derived chars (OSDCs). With the temperature increasing from 300 °C to 700 °C, the ash content and microstructure development of OSDCs promoted. The best Cd²⁺ sorption performance of OSDC prepared at pyrolysis temperature of 700 °C (OS700) was probably due to its high effective cation exchange capacity (CEC) and total surface acidity.

However, the Pb²⁺ sorption capacity dramatically decreased as the pyrolysis increased from 500 to 900 °C. This is because the minerals such as CaCO₃ and CaMg(CO₃)₂ decomposed at high temperature (\geq 700 °C), thereby the mineral precipitation with Pb²⁺ was inhibited. The hydrothermal treatment (8 M NaOH solution) activated OS500 significantly with respect to surface area, CEC, and total pore volume (PV). The activated OSDC showed a higher sorption capacity for Cd²⁺ than OS500 because conversion of barite (BaSO₄) to witherite (BaCO₃) after hydrothermal treatment favored the precipitation of Cd-carbonate. This work contributed to understand the mechanisms of Pb²⁺ and Cd²⁺ sorption by OSDCs, which is of significant importance to the practical application of OSDCs in water treatment. Pyrolysis temperature and chemical activation were crucial for both heavy metals sorption capacities of OSDCs and the contribution of different mechanisms. Chemical activation significantly contributed to the precipitation of Cd²⁺. With increasing pyrolysis temperature, the contribution of mineral precipitation with Pb²⁺ reduced, while the contribution of functional groups complexation increased.

In summary, the proposed methods could represent environmentally friendly and economically competitive alternatives for the effective treatment of oily sludge. The selection of alternative management methods should be based on a solid understanding of the characteristics of oily sludge. IL-enhanced solvent extraction is a very promising solution to treat oily sludge containing relatively high oil content. This method could not only maximize the benefit of heating values originating from oily sludge, but also reduce the waste volume. Meanwhile, the greater amount of PHCs was recovered as oil, the less amount of unrecovered PHCs was left in residual sand/clay after extraction, indicating the further remediation of residual sand/clay would be easier. Co-pyrolysis with wood waste is recommended to treat oily sludge with a high concentration of heavy metals and a certain amount of TPH. After copyrolysis treatment, TPH was effectively recovered from oily sludge. Pyrolysis temperature and wood waste addition had a positive effect on heavy metal immobilization in solid char. Converting oily sludge into sorbent could be a desirable method to treat oily sludge with relatively low TPH content. It was found that the minerals which could release dissolved anions (i.e., CO_3^{2-} and OH^{-}) played a very important role in Pb^{2+} and Cd^{2+} sorption on OSDCs. In order to evaluate the suitability of converting oily sludge into sorbent, it is essential to identify the crystalline phases in OSDC using XRD.

7.2. Limitations and future research

Although the methods proposed in this study demonstrated promising results, they are all at a lab scale. Before large-scale application, the linkage between treatment performance and laboratory test results needs careful verification.

In this study, cyclohexane was selected as the solvent in IL-enhanced solvent extraction. In fact, any organic solvent that dissolves bitumen but immiscible with the IL will accomplish the separation of oil from oily sludge. The extraction performance is very sensitive to the solvent properties, such as solubility parameter, the distribution of the polar force, dispersion force, and hydrogen-bonding force diameters, and the structure of the solvent. It is also possible that the mixed solvent could achieve higher oil recovery then the pure solvents. Unlike laboratory solvents, the industrial solvents are generally of lower purity and consist of a mixture of related compounds. Therefore, the effect of other solvents or solvent mixtures on the extraction performance in IL-enhance solvent extraction needs to be further investigated.

Since ILs are expensive materials, the future challenge of IL for oil recovery from oily sludge is to customize low-cost but effective ILs. It is recommended to continue more research

works to understand the extraction mechanism of the oil in the presence of IL. In this respect, zeta potential distribution measurements and atomic force microscopy (AFM) could be used to study the surface interactions between the components of oily sludge (e.g., oil and silica). In addition, the near infrared spectroscopy (NIR) could be used to study the effects of ILs on extraction kinetics. To minimize the concerns about the high cost of IL, further research about the reuse of IL need to be conducted.

In co-pyrolysis treatment, there were more than one reactions occurred. Oil recovery took place due to distillation rather than pyrolysis considering the similarities between the composition of the recovered oil and of the oil in the original oily waste. However, the charred biomass formed from pyrolysis did favor the immobilization of heavy metal ions. More work should be done to further study pathway of the formation of co-pyrolysis products and the related mechanism using real oily sludge sample. In doing so, the compositions of noncondensable gas and condensable oil from co-pyrolysis of oily sludge should be analyzed by gas chromatography-mass spectrometry (GC-MS) and gas chromatography-thermal conductivity detector (GC-TCD). The kinetic and thermal conversion behavior of oily sludge and wood waste during co-pyrolysis should be investigated through thermogravimetric analysis (TGA). To better understand the mechanism involved in the immobilization of the metals during co-pyrolysis, the characterization of solid char using X-ray absorption near-edge spectra (XANES), TGA, and XRD is recommended.

The addition of catalysis could not only increase the conversion of oily sludge to desirable products, but also improve the quality of pyrolysis oil. Further study should be focused on the addition of catalysis in the co-pyrolysis process of oily sludge. From an economic point of view, cheap and easily available catalysis or additives such as fly ash and oily sludge ash, should be considered when the raw materials used are wastes.

Once Pb²⁺ and Cd²⁺ were sorbed on OSDC, they are difficult to be released since the majority of them would not leach out into water or MgCl₂ solution. Future studies on the metal recovery and reuse of OSDC is needed in future. Conversely, the metal-loaded OSDC could be solidified to an environmentally safe form. A thermal treatment could be conducted for further stabilization of the sorbed metal. The mineral constituents (e.g., silicon, aluminum, iron, and calcium) of OSDC may potentially act as precursors to incorporate the sorbed metals into the crystal structure through a thermal treatment. The role of mineral constituents in stabilization of sorbed metals would be another venue for further study.

The original contamination of oily sludge might migrate, transform, and volatilize during the preparation process of OSDC, which might become an environmental issue. Further research will include the off-gas treatment in the preparation process and migration and transformation of element in sludge by pyrolysis. To assess the environmental risk of application of OSDCs to water treatment, long-term heavy metal leaching experiment are needed.

The majority of Pb^{2+} was sorbed on OS500 through precipitation, which represented a bound to carbonate fraction. When OS500 is applied to Pb^{2+} contaminated soil, it is expected the OS500 could reduce the bioavailability of Pb^{2+} , and consequently reduced the environmental risks. The stability of the bound to carbonate fraction could be affected by the solubility of formed precipitates and the site conditions such as soil pH. Further sorption studies are necessary to investigate the long-term effectiveness of OS500 as a heavy metal sorbent in soil. Heavy metals such as Pb, Cu, Zn, and Cd may coexist in contaminated waters,

thereby there is a competition for sorption sites on OSDC surface between metals. Future study should explore OSDC potential to treat multi-metal contaminated water. To synthesize zeolites from OSDC, the modification of aluminum/silicon (Al/Si) ratio by adding aluminum oxide (Al₂O₃) during hydrothermal treatment is recommended.

References

- Abnisa, F., Wan Daud, W.M.A., 2015. Optimization of fuel recovery through the stepwise copyrolysis of palm shell and scrap tire. Energy Convers. Manag. 99, 334–345.
- Abnisa, F., Wan Daud, W.M.A., Sahu, J.N., 2011. Optimization and characterization studies on bio-oil production from palm shell by pyrolysis using response surface methodology. Biomass Bioenergy 35, 3604–3616.
- Admon, S., Green, M., Avnimelech, Y., 2001. Biodegradation kinetics of hydrocarbons in soil during land treatment of oily sludge. Bioremediation J. 5, 193–209.
- Ahmad, M., Lee, S.S., Dou, X., Mohan, D., Sung, J.-K., Yang, J.E., Ok, Y.S., 2012. Effects of pyrolysis temperature on soybean stover- and peanut shell-derived biochar properties and TCE adsorption in water. Bioresour. Technol. 118, 536–544.
- Ahmadi, M., Vahabzadeh, F., Bonakdarpour, B., Mofarrah, E., Mehranian, M., 2005. Application of the central composite design and response surface methodology to the advanced treatment of olive oil processing wastewater using Fenton's peroxidation. J. Hazard. Mater. 123, 187–195.
- Akhtar, J., Amin, N.S., 2012. A review on operating parameters for optimum liquid oil yield in biomass pyrolysis. Renew. Sustain. Energy Rev. 16, 5101–5109.
- Alberti, G., Amendola, V., Pesavento, M., Biesuz, R., 2012. Beyond the synthesis of novel solid phases: Review on modelling of sorption phenomena. Coord. Chem. Rev. 256, 28–45.
- Alfutaisi, A., Jamrah, A., Yaghi, B., Taha, R., 2007. Assessment of alternative management techniques of tank bottom petroleum sludge in Oman. J. Hazard. Mater. 141, 557–564.

- Ali, M.F., Abbas, S., 2006. A review of methods for the demetallization of residual fuel oils. Fuel Process. Technol. 87, 573–584.
- Ali, M.F., Alqam, M.H., 2000. The role of asphaltenes, resins and other solids in the stabilization of water in oil emulsions and its effects on oil production in Saudi oil fields. Fuel 79, 1309–1316.
- AL-Saleh, E.S., Obuekwe, C., 2005. Inhibition of hydrocarbon bioremediation by lead in a crude oil-contaminated soil. Int. Biodeterior. Biodegrad. 56, 1–7.
- Al-Zahrani, S.M., Putra, M.D., 2013. Used lubricating oil regeneration by various solvent extraction techniques. J. Ind. Eng. Chem. 19, 536–539.
- Andrade, P.F., Azevedo, T.F., Gimenez, I.F., Filho, A.G.S., Barreto, L.S., 2009. Conductive carbon–clay nanocomposites from petroleum oily sludge. J. Hazard. Mater. 167, 879– 884.
- American Petroleum Institute (API), 2010. Category Assessment Document for Reclaimed Petroleum Hydrocarbons: Residual Hydrocarbon Wastes from Petroleum Refining. US EPA HPV Challenge Program, Washington.
- ASTM D2974-00 Method A, 2000. Standard Test Methods for Moisture, Ash, and Organic Matter of Peat and Other Organic Soils.
- ASTM D2015-85, 1985. Standard Test Method for Gross Calorific Value of Coal and Coke by the Adiabatic Bomb Calorimeter. Philadelphia, PA, USA.
- ASTM D5185-18, 2018. Standard Test Method for Multielement Determination of Used and Unused Lubricating Oils and Base Oils by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES). West Conshohocken, PA, USA.
- ASTM D5291-16, 2016. Standard Test Methods for Instrumental Determination of Carbon, Hydrogen, and Nitrogen in Petroleum Products and Lubricants. West Conshohocken, PA, USA.

- Bagreev, A., Bandosz, T.J., Locke, D.C., 2001. Pore structure and surface chemistry of adsorbents obtained by pyrolysis of sewage sludge-derived fertilizer. Carbon 39, 1971–1979.
- Ball, A.S., Stewart, R.J., Schliephake, K., 2012. A review of the current options for the treatment and safe disposal of drill cuttings. Waste Manag. Res. 30, 457–473.
- Barrett, E.P., Joyner, L.G., Halenda, P.P., 1951. The determination of pore volume and area distributions in porous substances. I. Computations from nitrogen isotherms. J. Am. Chem. Soc. 73, 373–380.
- Bera, A., Belhaj, H., 2016. Ionic liquids as alternatives of surfactants in enhanced oil recovery—A state-of-the-art review. J. Mol. Liq. 224, 177–188.
- Bezerra, M.A., Santelli, R.E., Oliveira, E.P., Villar, L.S., Escaleira, L.A., 2008. Response surface methodology (RSM) as a tool for optimization in analytical chemistry. Talanta 76, 965–977.
- Bhattacharyya, J.K., Shekdar, A.V., 2003. Treatment and disposal of refinery sludges: Indian scenario. Waste Manag. Res. 21, 249–261.
- Bogusz, A., Nowak, K., Stefaniuk, M., Dobrowolski, R., Oleszczuk, P., 2017. Synthesis of biochar from residues after biogas production with respect to cadmium and nickel removal from wastewater. J. Environ. Manage. 201, 268–276.
- Bou Malham, I., Turmine, M., 2008. Viscosities and refractive indices of binary mixtures of 1-butyl-3-methylimidazolium tetrafluoroborate and 1-butyl-2,3-dimethylimidazolium tetrafluoroborate with water at 298 K. J. Chem. Thermodyn. 40, 718–723.
- Boukherissa, M., Mutelet, F., Modarressi, A., Dicko, A., Dafri, D., Rogalski, M., 2009. Ionic liquids as dispersants of petroleum asphaltenes. Energy Fuels 23, 2557–2564.
- Brebu, M., Ucar, S., Vasile, C., Yanik, J., 2010. Co-pyrolysis of pine cone with synthetic polymers. Fuel 89, 1911–1918.

- Breuer, E., Stevenson, A., Howe, J., Carroll, J, Shimmield, G., 2004. Drill cutting accumulations in the Northern and Central North Sea: a review of environmental interactions and chemical fate. Mar. Pollut. Bull. 48, 12–25.
- British Columbia Ministry of Environment (BCMOE), 2016. Hazardous Waste Legislation Guide. Victoria.
- British Petroleum (BP), 2019. British petroleum statistical review of world energy. London.
- Cao, Q., Jin, L., Bao, W., Lv, Y., 2009. Investigations into the characteristics of oils produced from co-pyrolysis of biomass and tire. Fuel Process. Technol. 90, 337–342.
- Cao, X., Harris, W., 2010. Properties of dairy-manure-derived biochar pertinent to its potential use in remediation. Bioresour. Technol. 101, 5222–5228.
- Cao, X., Ma, L., Gao, B., Harris, W., 2009. Dairy-manure derived biochar effectively sorbs lead and atrazine. Environ. Sci. Technol. 43, 3285–3291.
- Cao, Y., Xiao, W., Shen, G., Ji, G., Zhang, Y., Gao, C., Han, L., 2019. Carbonization and ball milling on the enhancement of Pb(II) adsorption by wheat straw: Competitive effects of ion exchange and precipitation. Bioresour. Technol. 273, 70–76.
- Castaldi, F.J., 2003. Tank-based bioremediation of petroleum waste sludges. Environ. Prog. 22, 25–36.
- Cavaco, S.A., Fernandes, S., Quina, M.M., Ferreira, L.M., 2007. Removal of chromium from electroplating industry effluents by ion exchange resins. J. Hazard. Mater. 144, 634– 638.
- Canadian Council of Ministers of the Environment (CCME), 2008a. Canadian Soil Quality Guidelines for Carcinogenic and Other Polycyclic Aromatic Hydrocarbons (PAHs): Environmental and Human Health Effects: Scientific Supporting Document. CCME, Winnipeg.

- Canadian Council of Ministers of the Environment (CCME), 2008b. Canada-Wide Standard for Petroleum Hydrocarbons (PHC) in Soil: Scientific Rationale. CCME, Winnipeg, Manitoba.
- Canadian Council of Ministers of the Environment (CCME), 2001. Reference Method for the Canada-Wide Standard for Petroleum Hydrocarbons in Soil Tier 1 Method. CCME, Winnipeg.
- Canadian Council of Ministers of the Environment (CCME), 1999. Canadian Soil Quality Guidelines for the Protection of Environmental and Human Health. CCME, Winnipeg.
- Chabukdhara, M., Nema, A.K., 2011. Heavy metals in water, sediments, and aquatic macrophytes: river Hindon, India. J. Hazard. Toxic Radioact. Waste 16, 273–281.
- Chang, C.-Y., Shie, J.-L., Lin, J.-P., Wu, C.-H., Lee, D.-J., Chang, C.-F., 2000. Major products obtained from the pyrolysis of oil sludge. Energy Fuels 14, 1176–1183.
- Chen, G., Liu, C., Ma, W., Zhang, X., Li, Y., Yan, B., Zhou, W., 2014. Co-pyrolysis of corn cob and waste cooking oil in a fixed bed. Bioresour. Technol. 166, 500–507.
- Chen, H., Zhai, Y., Xu, B., Xiang, B., Zhu, L., Qiu, L., Liu, X., Li, C., Zeng, G., 2014. Fate and risk assessment of heavy metals in residue from co-liquefaction of Camellia oleifera cake and sewage sludge in supercritical ethanol. Bioresour. Technol. 167, 578– 581.
- Chen, M., Ma, L.Q., 1998. Comparison of four USEPA digestion methods for trace metal analysis using certified and Florida soils. J. Environ. Qual. 27, 1294–1300.
- Chen, T., Zhang, Y., Wang, H., Lu, W., Zhou, Z., Zhang, Y., Ren, L., 2014. Influence of pyrolysis temperature on characteristics and heavy metal adsorptive performance of biochar derived from municipal sewage sludge. Bioresour. Technol. 164, 47–54.
- Chen, X., Chen, G., Chen, L., Chen, Y., Lehmann, J., McBride, M.B., Hay, A.G., 2011. Adsorption of copper and zinc by biochars produced from pyrolysis of hardwood and corn straw in aqueous solution. Bioresour. Technol. 102, 8877–8884.

- Chen, X., Wright, J.V., Conca, J.L., Peurrung, L.M., 1997. Effects of pH on heavy metal sorption on mineral apatite. Environ. Sci. Technol. 31, 624–631.
- Cheng, S., Takahashi, F., Gao, N., Yoshikawa, K., Li, A., 2016a. Evaluation of oil sludge ash as a solid heat carrier in the pyrolysis process of oil sludge for oil production. Energy Fuels 30, 5970–5979.
- Cheng, S., Wang, Y., Gao, N., Takahashi, F., Li, A., Yoshikawa, K., 2016b. Pyrolysis of oil sludge with oil sludge ash additive employing a stirred tank reactor. J. Anal. Appl. Pyrolysis 120, 511–520.
- Chien, S., Clayton, W., 1980. Application of Elovich equation to the kinetics of phosphate release and sorption in soils. Soil Sci. Soc. Am. J. 44, 265–268.
- Chun, Y., Sheng, G., Chiou, C.T., Xing, B., 2004. Compositions and sorptive properties of crop residue-derived chars. Environ. Sci. Technol. 38, 4649–4655.
- Cui, X., Fang, S., Yao, Y., Li, T., Ni, Q., Yang, X., He, Z., 2016. Potential mechanisms of cadmium removal from aqueous solution by Canna indica derived biochar. Sci. Total Environ. 562, 517–525.
- da Rocha, O.R.S., Dantas, R.F., Duarte, M.M.M.B., Duarte, M.M.L., da Silva, V.L., 2010. Oil sludge treatment by photocatalysis applying black and white light. Chem. Eng. J. 157, 80–85.
- da Silva, L.J., Alves, F.C., de França, F.P., 2012. A review of the technological solutions for the treatment of oily sludges from petroleum refineries. Waste Manag. Res. 30, 1016– 1030.
- Debela, F., Thring, R., Arocena, J., 2012. Immobilization of heavy metals by co-pyrolysis of contaminated soil with woody biomass. Water. Air. Soil Pollut. 223, 1161–1170.
- Demirbas, A., 2011. Waste management, waste resource facilities and waste conversion processes. Energy Convers. Manag. 52, 1280–1287.

- Devi, P., Saroha, A.K., 2014. Risk analysis of pyrolyzed biochar made from paper mill effluent treatment plant sludge for bioavailability and eco-toxicity of heavy metals. Bioresour. Technol. 162, 308–315.
- Djedidi, Z., Bouda, M., Souissi, M.A., Cheikh, R.B., Mercier, G., Tyagi, R.D., Blais, J.-F., 2009. Metals removal from soil, fly ash and sewage sludge leachates by precipitation and dewatering properties of the generated sludge. J. Hazard. Mater. 172, 1372–1382.
- Doke, S.M., Yadav, G.D., 2014. Process efficacy and novelty of titania membrane prepared by polymeric sol-gel method in removal of chromium(VI) by surfactant enhanced microfiltration. Chem. Eng. J. 255, 483–491.
- Dubinin, M.M., Radushkevich, L.V., 1947. The equation of the characteristic curve of the activated charcoal. Proc Acad Sci USSR Phys Chem Sect 55, 331–337.
- Elbashir, N.O., Al-Zahrani, S.M., Abdul Mutalib, M.I., Abasaeed, A.E., 2002. A method of predicting effective solvent extraction parameters for recycling of used lubricating oils. Chem. Eng. Process. Process Intensif. 41, 765–769.
- Elektorowicz, M., Habibi, S., 2005. Sustainable waste management: recovery of fuels from petroleum sludge. Can. J. Civ. Eng. 32, 164–169.
- Elektorowicz, M., Habibi, S., Chifrina, R., 2006. Effect of electrical potential on the electrodemulsification of oily sludge. J. Colloid Interface Sci. 295, 535–541.
- Feng, D., Aldrich, C., 2000. Sonochemical treatment of simulated soil contaminated with diesel. Adv. Environ. Res. 4, 103–112.
- Ferrarese, E., Andreottola, G., Oprea, I.A., 2008. Remediation of PAH-contaminated sediments by chemical oxidation. J. Hazard. Mater. 152, 128–139.
- Fisher, J.A., Scarlett, M.J., Stott, A.D., 1997. Accelerated solvent extraction: an evaluation for screening of soils for selected US EPA semivolatile organic priority pollutants. Environ. Sci. Technol. 31, 1120–1127.

Fonts, I., Juan, A., Gea, G., Murillo, M.B., Sánchez, J.L., 2008. Sewage sludge pyrolysis in fluidized bed, 1: Influence of operational conditions on the product distribution. Ind. Eng. Chem. Res. 47, 5376–5385.

Freundlich, H.M.F., 1906. Over the adsorption in solution. J Phys Chem 57, 385–470.

- Frišták, V., Pipíška, M., Lesný, J., Soja, G., Friesl-Hanl, W., Packová, A., 2015. Utilization of biochar sorbents for Cd²⁺, Zn²⁺, and Cu²⁺ ions separation from aqueous solutions: comparative study. Environ. Monit. Assess. 187:4093.
- Fu, F., Wang, Q., 2011. Removal of heavy metal ions from wastewaters: A review. J. Environ. Manage. 92, 407–418.
- Funk, E.W., 1979. Behavior of tar sand bitumen with paraffinic solvents and its application to separations for athabasca tar sands. Can. J. Chem. Eng. 57, 333–341.
- Gascó, G., Blanco, C.G., Guerrero, F., Méndez Lázaro, A.M., 2005. The influence of organic matter on sewage sludge pyrolysis. J. Anal. Appl. Pyrolysis 74, 413–420.
- Ge, M.-L., Zhao, R.-S., Yi, Y.-F., Zhang, Q., Wang, L.-S., 2008. Densities and viscosities of 1-butyl-3-methylimidazolium trifluoromethanesulfonate + H₂O binary mixtures at *T* = (303.15 to 343.15) K. J. Chem. Eng. Data 53, 2408–2411.
- Godinho, D., Dias, D., Bernardo, M., Lapa, N., Fonseca, I., Lopes, H., Pinto, F., 2017. Adding value to gasification and co-pyrolysis chars as removal agents of Cr³⁺. J. Hazard. Mater. 321, 173–182.
- Goertzen, S.L., Thériault, K.D., Oickle, A.M., Tarasuk, A.C., Andreas, H.A., 2010. Standardization of the Boehm titration. Part I. CO₂ expulsion and endpoint determination. Carbon 48, 1252–1261.
- Gong, Y., Zhao, D., Wang, Q., 2018. An overview of field-scale studies on remediation of soil contaminated with heavy metals and metalloids: Technical progress over the last decade. Water Res. 147, 440–460.

- González, J.J., Viñas, L., Franco, M.A., Fumega, J., Soriano, J.A., Grueiro, G., Muniategui, S., López-Mahía, P., Prada, D., Bayona, J.M., Alzaga, R., Albaigés, J., 2006. Spatial and temporal distribution of dissolved/dispersed aromatic hydrocarbons in seawater in the area affected by the Prestige oil spill. Mar. Pollut. Bull. 53, 250–259.
- Greaves, T.L., Weerawardena, A., Fong, C., Krodkiewska, I., Drummond, C.J., 2006. Protic ionic liquids: solvents with tunable phase behavior and physicochemical properties. J. Phys. Chem. B 110, 22479–22487.
- Gupta, A., Garg, A., 2015. Primary sewage sludge-derived activated carbon: characterisation and application in wastewater treatment. Clean Technol. Environ. Policy 17, 1619–1631.
- Guritno, M.A., Sihombing, R., Krisnandi, Y.K., 2016. Synthesis of porous activated carbon from petroleum sludge using mesoporous silica template. Presented at the AIP Conference Proceedings, Depok, Indonesia, p.020040.
- Gustafson, J.B., Tell, J.G., Orem, D., 1997. Selection of Representative TPH Fractions Based on Fate and Transport Considerations, Total Petroleum Hydrocarbon Criteria Working Group series. Amherst Scientific Publishers, Amherst, MA.
- Gutiérrez-Segura, E., Solache-Ríos, M., Colín-Cruz, A., Fall, C., 2012. Adsorption of cadmium by Na and Fe modified zeolitic tuffs and carbonaceous material from pyrolyzed sewage sludge. J. Environ. Manage. 97, 6–13.
- Guzmán-Lucero, D., Flores, P., Rojo, T., Martínez-Palou, R., 2010. Ionic liquids as demulsifiers of water-in-crude oil emulsions: Study of the microwave effect. Energy Fuels 24, 3610–3615.
- Hall, C.A., Howarth, R., Moore III, B., Vörösmarty, C.J., 1978. Environmental impacts of industrial energy systems in the coastal zone. Annu. Rev. Energy 3, 395–475.
- Hansen, C.M., 2007. Hansen Solubility Parameters: A User's Handbook, 2nd ed. CRC press, Boca Raton.

- He, Y.D., Zhai, Y.B., Li, C.T., Yang, F., Chen, L., Fan, X.P., Peng, W.F., Fu, Z.M., 2010. The fate of Cu, Zn, Pb and Cd during the pyrolysis of sewage sludge at different temperatures. Environ. Technol. 31, 567–574.
- Hedayatipour, M., Jaafarzadeh, N., Ahmadmoazzam, M., 2017. Removal optimization of heavy metals from effluent of sludge dewatering process in oil and gas well drilling by nanofiltration. J. Environ. Manage. 203, 151–156.
- Hejazi, R.F., Husain, T., Khan, F.I., 2003. Landfarming operation of oily sludge in arid region—human health risk assessment. J. Hazard. Mater. 99, 287–302.
- Hildebrand, J., Scott, R., 1950. The Solubility of Nonelectrolytes, 3rd ed. Reinhold Publishing Corporation, New York.
- Ho, Y.-S., McKay, G., 1999. Pseudo-second order model for sorption processes. Process Biochem. 34, 451–465.
- Ho, Y.-S., McKay, G., 1998. Sorption of dye from aqueous solution by peat. Chem. Eng. J. 70, 115–124.
- Hogshead, C.G., Manias, E., Williams, P., Lupinsky, A., Painter, P., 2011. Studies of bitumen-silica and oil-silica interactions in ionic liquids. Energy Fuels 25, 293–299.
- Hossain, M.K., Strezov, V., Chan, K.Y., Ziolkowski, A., Nelson, P.F., 2011. Influence of pyrolysis temperature on production and nutrient properties of wastewater sludge biochar. J. Environ. Manage. 92, 223–228.
- Hu, G., Li, J., Hou, H., 2015. A combination of solvent extraction and freeze thaw for oil recovery from petroleum refinery wastewater treatment pond sludge. J. Hazard. Mater. 283, 832–840.
- Hu, G., Li, J., Huang, S., Li, Y., 2016. Oil recovery from petroleum sludge through ultrasonic assisted solvent extraction. J. Environ. Sci. Health Part A 51, 921–929.
- Hu, G., Li, J., Zeng, G., 2013. Recent development in the treatment of oily sludge from petroleum industry: A review. J. Hazard. Mater. 261, 470–490.

- Hu, G., Li, J., Zhang, X., Li, Y., 2017. Investigation of waste biomass co-pyrolysis with petroleum sludge using a response surface methodology. J. Environ. Manage. 192, 234–242.
- Hu, Y.-F., Guo, T.-M., 2005. Effect of the structures of ionic liquids and alkylbenzene-derived amphiphiles on the inhibition of asphaltene precipitation from CO₂-injected reservoir oils. Langmuir 21, 8168–8174.
- Huang, H., Yuan, X., 2016. The migration and transformation behaviors of heavy metals during the hydrothermal treatment of sewage sludge. Bioresour. Technol. 200, 991– 998.
- Huddleston, J.G., Visser, A.E., Reichert, W.M., Willauer, H.D., Broker, G.A., Rogers, R.D., 2001. Characterization and comparison of hydrophilic and hydrophobic room temperature ionic liquids incorporating the imidazolium cation. Green Chem. 3, 156– 164.
- IARC Working Group on the Evaluation of Carcinogenic Risks to Humans (IARC WGECRH), 2012. Arsenic, Metals, Fibres, and Dusts. World Health Organization, Lyon, France.
- IARC Working Group on the Evaluation of Carcinogenic Risks to Humans (IARC WGECRH), 2010. Some Non-heterocyclic Polycyclic Aromatic Hydrocarbons and Some Related Occupational Exposures. World Health Organization, Lyon, France.
- IARC Working Group on the Evaluation of Carcinogenic Risks to Humans (IARC WGECRH), 2006. Inorganic and Organic Lead Compunds, IARC monographs on the evaluation of carcinogenic risks to humans. World Health Organization, Lyon, France.
- IARC Working Group on the Evaluation of Carcinogenic Risks to Humans (IARC WGECRH), 1987. Overall Evaluations of Carcinogenicity: An Updating of IARC Monographs Volumes 1 to 42, IARC monographs on the evaluation of carcinogenic risks to humans. World Health Organization, Lyon, France.
- ICF Consulting, 2000. Overview of Exploration and Production Waste Volumes and Waste Management Practices in the United States. American Petroleum Institute, Washington.

- Inguanzo, M., Dominguez, A., Menéndez, J.A., Blanco, C.G., Pis, J.J., 2002. On the pyrolysis of sewage sludge: the influence of pyrolysis conditions on solid, liquid and gas fractions. J. Anal. Appl. Pyrolysis 63, 209–222.
- Inyang, M., Gao, B., Yao, Y., Xue, Y., Zimmerman, A.R., Pullammanappallil, P., Cao, X., 2012. Removal of heavy metals from aqueous solution by biochars derived from anaerobically digested biomass. Bioresour. Technol. 110, 50–56.
- Islam, M.N., Park, J.-H., 2017. Immobilization and reduction of bioavailability of lead in shooting range soil through hydrothermal treatment. J. Environ. Manage. 191, 172–178.
- Jacobs, F.S., Filby, R.H., 1983. Solvent extraction of oil-sand components for determination of trace elements by neutron activation analysis. Anal. Chem. 55, 74–77.
- Jasmine, J., Mukherji, S., 2019. Impact of bioremediation strategies on slurry phase treatment of aged oily sludge from a refinery. J. Environ. Manage. 246, 625–635.
- Jasmine, J., Mukherji, S., 2015. Characterization of oily sludge from a refinery and biodegradability assessment using various hydrocarbon degrading strains and reconstituted consortia. J. Environ. Manage. 149, 118–125.
- Jin, H., Arazo, R.O., Gao, J., Capareda, S., Chang, Z., 2014. Leaching of heavy metals from fast pyrolysis residues produced from different particle sizes of sewage sludge. J. Anal. Appl. Pyrolysis 109, 168–175.
- Jin, J., Li, Y., Zhang, J., Wu, S., Cao, Y., Liang, P., Zhang, J., Wong, M.H., Wang, M., Shan, S., Christie, P., 2016. Influence of pyrolysis temperature on properties and environmental safety of heavy metals in biochars derived from municipal sewage sludge. J. Hazard. Mater. 320, 417–426.
- Jin, J., Wang, M., Cao, Y., Wu, S., Liang, P., Li, Y., Zhang, J., Zhang, J., Wong, M.H., Shan, S., 2017. Cumulative effects of bamboo sawdust addition on pyrolysis of sewage sludge: biochar properties and environmental risk from metals. Bioresour. Technol. 228, 218– 226.

- Jindarom, C., Meeyoo, V., Kitiyanan, B., Rirksomboon, T., Rangsunvigit, P., 2007a. Surface characterization and dye adsorptive capacities of char obtained from pyrolysis/gasification of sewage sludge. Chem. Eng. J. 133, 239–246.
- Jindarom, C., Meeyoo, V., Rirksomboon, T., Rangsunvigit, P., 2007b. Thermochemical decomposition of sewage sludge in CO₂ and N₂ atmosphere. Chemosphere 67, 1477– 1484.
- José-Alberto, M.-H., Jorge, A., 2011. Current Knowledge and Potential Applications of Ionic Liquids in the Petroleum Industry, in: Ionic Liquids: Applications and Perspectives. InTech.
- Kalra, Y.P., Maynard, D.G., 1991. Methods Manual for Forest Soil and Plant Analysis, Information report. Canadian Forest Service, Edmonton, Alberta.
- Kar, Y., 2011. Co-pyrolysis of walnut shell and tar sand in a fixed-bed reactor. Bioresour. Technol. 102, 9800–9805.
- Karamalidis, A.K., Voudrias, E.A., 2007. Cement-based stabilization/solidification of oil refinery sludge: Leaching behavior of alkanes and PAHs. J. Hazard. Mater. 148, 122– 135.
- Karayildirim, T., Yanik, J., Yuksel, M., Bockhorn, H., 2006. Characterisation of products from pyrolysis of waste sludges. Fuel 85, 1498–1508.
- Khan, F.I., Husain, T., Hejazi, R., 2004. An overview and analysis of site remediation technologies. J. Environ. Manage. 71, 95–122.
- Kilpatrick, P.K., 2012. Water-in-crude oil emulsion stabilization: Review and unanswered questions. Energy Fuels 26, 4017–4026.
- Kim, K.-H., Jahan, S.A., Kabir, E., Brown, R.J.C., 2013. A review of airborne polycyclic aromatic hydrocarbons (PAHs) and their human health effects. Environ. Int. 60, 71–80.
- Kim, W.-K., Shim, T., Kim, Y.-S., Hyun, S., Ryu, C., Park, Y.-K., Jung, J., 2013. Characterization of cadmium removal from aqueous solution by biochar produced from

a giant Miscanthus at different pyrolytic temperatures. Bioresour. Technol. 138, 266–270.

- Kistler, R.C., Widmer, F., Brunner, P.H., 1987. Behavior of chromium, nickel, copper, zinc, cadmium, mercury, and lead during the pyrolysis of sewage sludge. Environ. Sci. Technol. 21, 704–708.
- Kloss, S., Zehetner, F., Dellantonio, A., Hamid, R., Ottner, F., Liedtke, V., Schwanninger, M., Gerzabek, M.H., Soja, G., 2012. Characterization of slow pyrolysis biochars: Effects of feedstocks and pyrolysis temperature on biochar properties. J. Environ. Qual. 41, 990.
- Kołodyńska, D., Wnętrzak, R., Leahy, J.J., Hayes, M.H.B., Kwapiński, W., Hubicki, Z., 2012. Kinetic and adsorptive characterization of biochar in metal ions removal. Chem. Eng. J. 197, 295–305.
- Krerkkaiwan, S., Fushimi, C., Tsutsumi, A., Kuchonthara, P., 2013. Synergetic effect during co-pyrolysis/gasification of biomass and sub-bituminous coal. Fuel Process. Technol. 115, 11–18.
- Kriipsalu, M., Marques, M., Maastik, A., 2008. Characterization of oily sludge from a wastewater treatment plant flocculation-flotation unit in a petroleum refinery and its treatment implications. J. Mater. Cycles Waste Manag. 10, 79–86.
- Kuang, S., Wu, Z., Zhao, L., 2011. Accumulation and risk assessment of polycyclic aromatic hydrocarbons (PAHs) in soils around oil sludge in Zhongyuan oil field, China. Environ. Earth Sci. 64, 1353–1362.
- Kumar, A., Jena, H.M., 2016. Preparation and characterization of high surface area activated carbon from Fox nut (Euryale ferox) shell by chemical activation with H₃PO₄. Results Phys. 6, 651–658.
- Kuriakose, A., Manjooran, S.K.B., 2001. Bitumenous paints from refinery sludge. Surf. Coat. Technol. 145, 132–138.
- Lagergren, S., 1898. Zur theorie der sogenannten adsorption gelöster stoffe. K Sven Vetenskapsakad Handl 24, 1–39.

- Lam, S.S., Russell, A.D., Chase, H.A., 2010. Pyrolysis using microwave heating: a sustainable process for recycling used car engine oil. Ind. Eng. Chem. Res. 49, 10845–10851.
- Langmuir, I., 1918. The adsorption of gases on plane surfaces of glass, mica, and platinum. J. Am. Chem. Soc. 40, 1361–1403.
- Lemos, R.C.B., da Silva, E.B., dos Santos, A., Guimarães, R.C.L., Ferreira, B.M.S., Guarnieri, R.A., Dariva, C., Franceschi, E., Santos, A.F., Fortuny, M., 2010. Demulsification of water-in-crude oil emulsions using ionic liquids and microwave irradiation. Energy Fuels 24, 4439–4444.
- Leung, D.Y.C., Yin, X.L., Zhao, Z.L., Xu, B.Y., Chen, Y., 2002. Pyrolysis of tire powder: influence of operation variables on the composition and yields of gaseous product. Fuel Process. Technol. 79, 141–155.
- Li, A.M., Li, X.D., Li, S.Q., Ren, Y., Shang, N., Chi, Y., Yan, J.H., Cen, K.F., 1999. Experimental studies on municipal solid waste pyrolysis in a laboratory-scale rotary kiln. Energy 24, 209–218.
- Li, B., Yang, L., Wang, C., Zhang, Q., Liu, Q., Li, Y., Xiao, R., 2017. Adsorption of Cd(II) from aqueous solutions by rape straw biochar derived from different modification processes. Chemosphere 175, 332–340.
- Li, C.-T., Lee, W.-J., Mi, H.-H., Su, C.-C., 1995. PAH emission from the incineration of waste oily sludge and PE plastic mixtures. Sci. Total Environ. 170, 171–183.
- Li, H., Dong, X., da Silva, E.B., de Oliveira, L.M., Chen, Y., Ma, L.Q., 2017. Mechanisms of metal sorption by biochars: Biochar characteristics and modifications. Chemosphere 178, 466–478.
- Li, L., Xu, Z., Zhang, C., Bao, J., Dai, X., 2012. Quantitative evaluation of heavy metals in solid residues from sub-and super-critical water gasification of sewage sludge. Bioresour. Technol. 121, 169–175.

- Li, X., Coles, B.J., Ramsey, M.H., Thornton, I., 1995. Sequential extraction of soils for multielement analysis by ICP-AES. Chem. Geol. 124, 109–123.
- Li, X., He, L., Wu, G., Sun, W., Li, H., Sui, H., 2012. Operational parameters, evaluation methods, and fundamental mechanisms: aspects of nonaqueous extraction of bitumen from oil sands. Energy Fuels 26, 3553–3563.
- Li, X., Sun, W., Wu, G., He, L., Li, H., Sui, H., 2011. Ionic liquid enhanced solvent extraction for bitumen recovery from oil sands. Energy Fuels 25, 5224–5231.
- Li, X.D., Poon, C.S., Sun, H., Lo, I.M.C., Kirk, D.W., 2001. Heavy metal speciation and leaching behaviors in cement based solidified/stabilized waste materials. J. Hazard. Mater. 82, 215–230.
- Li, Y., Liu, X., Zhang, P., Wang, X., Cao, Y., Han, L., 2018. Qualitative and quantitative correlation of physicochemical characteristics and lead sorption behaviors of crop residue-derived chars. Bioresour. Technol. 270, 545–553.
- Lillo-Ródenas, M.A., Ros, A., Fuente, E., Montes-Morán, M.A., Martin, M.J., Linares-Solano, A., 2008. Further insights into the activation process of sewage sludge-based precursors by alkaline hydroxides. Chem. Eng. J. 142, 168–174.
- Lima, I.M., Boateng, A.A., Klasson, K.T., 2009. Pyrolysis of broiler manure: Char and product gas characterization. Ind. Eng. Chem. Res. 48, 1292–1297.
- Lin, Q.H., Cheng, H., Chen, G.Y., 2012. Preparation and characterization of carbonaceous adsorbents from sewage sludge using a pilot-scale microwave heating equipment. J. Anal. Appl. Pyrolysis 93, 113–119.
- Line, M.A., Garland, C.D., Crowley, M., 1996. Evaluation of landfarm remediation of hydrocarbon-contaminated soil at the Inveresk Railyard, Launceston, Australia. Waste Manag. 16, 567–570.
- Liu, J., Jiang, X., Zhou, L., Han, X., Cui, Z., 2009. Pyrolysis treatment of oil sludge and modelfree kinetics analysis. J. Hazard. Mater. 161, 1208–1215.

- Liu, J., Song, W., Nie, Y., 2008. Effects of temperature on pyrolysis products of oil sludge. Front. Environ. Sci. Eng. China 2, 8–14.
- Liu, J., Xu, Z., Masliyah, J., 2005. Interaction forces in bitumen extraction from oil sands. J. Colloid Interface Sci. 287, 507–520.
- Liu, P., Liu, W.-J., Jiang, H., Chen, J.-J., Li, W.-W., Yu, H.-Q., 2012. Modification of bio-char derived from fast pyrolysis of biomass and its application in removal of tetracycline from aqueous solution. Bioresour. Technol. 121, 235–240.
- Long, X., Zhang, G., Han, L., Meng, Q., 2013. Dewatering of floated oily sludge by treatment with rhamnolipid. Water Res. 47, 4303–4311.
- Lu, H., Zhang, W., Wang, S., Zhuang, L., Yang, Y., Qiu, R., 2013. Characterization of sewage sludge-derived biochars from different feedstocks and pyrolysis temperatures. J. Anal. Appl. Pyrolysis 102, 137–143.
- Lu, H., Zhang, W., Yang, Y., Huang, X., Wang, S., Qiu, R., 2012. Relative distribution of Pb²⁺ sorption mechanisms by sludge-derived biochar. Water Res. 46, 854–862.
- Luo, M., Lin, H., Li, B., Dong, Y., He, Y., Wang, L., 2018. A novel modification of lignin on corncob-based biochar to enhance removal of cadmium from water. Bioresour. Technol. 259, 312–318.
- Ma, Z., Gao, N., Xie, L., Li, A., 2014. Study of the fast pyrolysis of oilfield sludge with solid heat carrier in a rotary kiln for pyrolytic oil production. J. Anal. Appl. Pyrolysis 105, 183–190.
- Maliszewska-Kordybach, B., Smreczak, B., 2003. Habitat function of agricultural soils as affected by heavy metals and polycyclic aromatic hydrocarbons contamination. Environ. Int. 28, 719–728.
- Marin, J.A., Hernandez, T., Garcia, C., 2005. Bioremediation of oil refinery sludge by landfarming in semiarid conditions: Influence on soil microbial activity. Environ. Res. 98, 185–195.

- Martínez, J.D., Veses, A., Mastral, A.M., Murillo, R., Navarro, M.V., Puy, N., Artigues, A., Bartrolí, J., García, T., 2014. Co-pyrolysis of biomass with waste tyres: Upgrading of liquid bio-fuel. Fuel Process. Technol. 119, 263–271.
- Mazlova, E.A., Meshcheryakov, S.V., 1999. Ecological characteristics of oil sludges. Chem. Technol. Fuels Oils 35, 49–53.
- McGill, M.B., Rowell, M.J., Westlake, D.W.S., 1981. Biochemistry, Ecology, and Microbiology of Petroleum Components in Soil, in: Paul, E.A., Ladd, J.N. (Eds.), Soil Biochemistry. Marcel Dekker, New York, pp. 229–296.
- Mishra, S., Jyot, J., Kuhad, R.C., Lal, B., 2001. Evaluation of inoculum addition to stimulate in situ bioremediation of oily-sludge-contaminated soil. Appl. Environ. Microbiol. 67, 1675–1681.
- Mohammadi, S., Mirghaffari, N., 2015. Optimization and comparison of Cd removal from aqueous solutions using activated and non-activated carbonaceous adsorbents prepared by pyrolysis of oily sludge. Water. Air. Soil Pollut. 226.
- Mohan, D., Kumar, H., Sarswat, A., Alexandre-Franco, M., Pittman Jr, C.U., 2014. Cadmium and lead remediation using magnetic oak wood and oak bark fast pyrolysis bio-chars. Chem. Eng. J. 236, 513–528.
- Monroy, M., Maceda-Veiga, A., de Sostoa, A., 2014. Metal concentration in water, sediment and four fish species from Lake Titicaca reveals a large-scale environmental concern. Sci. Total Environ. 487, 233–244.

Montgomery, D.C., 2017. Design and Analysis of Experiments. John wiley & sons.

- Morera, M., Echeverria, J., Mazkiaran, C., Garrido, J., 2001. Isotherms and sequential extraction procedures for evaluating sorption and distribution of heavy metals in soils. Environ. Pollut. 113, 135–144.
- Morrissey, A., Browne, J., 2004. Waste management models and their application to sustainable waste management. Waste Manag. 24, 297–308.

- Mrayyan, B., Battikhi, M.N., 2005. Biodegradation of total organic carbons (TOC) in Jordanian petroleum sludge. J. Hazard. Mater. 120, 127–134.
- Mullen, C.A., Boateng, A.A., Goldberg, N.M., Lima, I.M., Laird, D.A., Hicks, K.B., 2010. Bio-oil and bio-char production from corn cobs and stover by fast pyrolysis. Biomass Bioenergy 34, 67–74.
- Nazet, A., Sokolov, S., Sonnleitner, T., Makino, T., Kanakubo, M., Buchner, R., 2015. Densities, viscosities, and conductivities of the imidazolium ionic liquids [Emim][Ac], [Emim][FAP], [Bmim][BETI], [Bmim][FSI], [Hmim][TFSI], and [Omim][TFSI]. J. Chem. Eng. Data 60, 2400–2411.
- National Institute for Occupational Safety and Health (NIOSH), 2018. Occupational Health Guidelines for Chemical Hazards. https://www.cdc.gov/niosh/docs/81-123/default.html (accessed 17 August 2019).
- National Institute for Occupational Safety and Health (NIOSH), 1977. Occupational Diseases: A Guide to Their Recognition. Washington.
- Önal, E., Uzun, B.B., Pütün, A.E., 2014. Bio-oil production via co-pyrolysis of almond shell as biomass and high density polyethylene. Energy Convers. Manag. 78, 704–710.
- Pacheco, M., Santos, M.A., 1997. Induction of EROD Activity and Genotoxic Effects by Polycyclic Aromatic Hydrocarbons and Resin Acids on the Juvenile Eel (Anguilla anguillaL.). Ecotoxicol. Environ. Saf. 38, 252–259.
- Painter, P., Williams, P., Lupinsky, A., 2010a. Recovery of bitumen from Utah tar sands using ionic liquids. Energy Fuels 24, 5081–5088.
- Painter, P., Williams, P., Mannebach, E., 2010b. Recovery of bitumen from oil or tar sands using ionic liquids. Energy Fuels 24, 1094–1098.
- Pan, Z., Tian, J., Xu, G., Li, J., Li, G., 2011. Characteristics of adsorbents made from biological, chemical and hybrid sludges and their effect on organics removal in wastewater treatment. Water Res. 45, 819–827.

- Pánek, P., Kostura, B., Čepeláková, I., Koutník, I., Tomšej, T., 2014. Pyrolysis of oil sludge with calcium-containing additive. J. Anal. Appl. Pyrolysis 108, 274–283.
- Park, D.K., Kim, S.D., Lee, S.H., Lee, J.G., 2010. Co-pyrolysis characteristics of sawdust and coal blend in TGA and a fixed bed reactor. Bioresour. Technol. 101, 6151–6156.
- Park, E.-S., Kang, B.-S., Kim, J.-S., 2008. Recovery of oils with high caloric value and low contaminant content by pyrolysis of digested and dried sewage sludge containing polymer flocculants. Energy Fuels 22, 1335–1340.
- Piskorz, J., Scott, D.S., Westerberg, I.B., 1986. Flash pyrolysis of sewage sludge. Ind. Eng. Chem. Process Des. Dev. 25, 265–270.
- Plechkova, N.V., Seddon, K.R., 2008. Applications of ionic liquids in the chemical industry. Chem Soc Rev 37, 123–150.
- Pöykiö, R., Nurmesniemi, H., Kuokkanen, T., Perämäki, P., 2006. The use of a sequential leaching procedure for assessing the heavy metal leachability in lime waste from the lime kiln at a caustizicing process of a pulp mill. Chemosphere 65, 2122–2129.
- Punnaruttanakun, P., Meeyoo, V., Kalambaheti, C., Rangsunvigit, P., Rirksomboon, T., Kitiyanan, B., 2003. Pyrolysis of API separator sludge. J. Anal. Appl. Pyrolysis 68–69, 547–560.
- Qin, L., Han, J., He, X., Zhan, Y., Yu, F., 2015. Recovery of energy and iron from oily sludge pyrolysis in a fluidized bed reactor. J. Environ. Manage. 154, 177–182.
- Ramaswamy, B., Kar, D.D., De, S., 2007. A study on recovery of oil from sludge containing oil using froth flotation. J. Environ. Manage. 85, 150–154.
- Redlich, O., Peterson, D.L., 1959. A useful adsorption isotherm. J. Phys. Chem. 63, 1024–1024.
- Ren, X., Liang, B., Liu, M., Xu, X., Cui, M., 2012. Effects of pyrolysis temperature, time and leaf litter and powder coal ash addition on sludge-derived adsorbents for nitrogen oxide. Bioresour. Technol. 125, 300–304.

- Rendón-Angeles, J.C., Matamoros-Veloza, Z., López-Cuevas, J., Pech-Canul, M.I., Yanagisawa, K., 2008. Stability and direct conversion of mineral barite crystals in carbonated hydrothermal fluids. J. Mater. Sci. 43, 2189–2197.
- Renou, S., Givaudan, J.G., Poulain, S., Dirassouyan, F., Moulin, P., 2008. Landfill leachate treatment: Review and opportunity. J. Hazard. Mater. 150, 468–493.
- Revised Regulations of Ontario, 1990. Environmental Protection Act Regulation 347: General Waste Management. https://www.ontario.ca/laws/regulation/900347 (accessed 17 August 2019).
- Rincón, J., Cañizares, P., García, M.T., 2005. Regeneration of used lubricant oil by polar solvent extraction. Ind. Eng. Chem. Res. 44, 4373–4379.
- Robertson, S.J., McGill, W.B., Massicotte, H.B., Rutherford, P.M., 2007. Petroleum hydrocarbon contamination in boreal forest soils: a mycorrhizal ecosystems perspective. Biol. Rev. 82, 213–240.
- Rogers, R.D., Seddon, K.R., 2003. Ionic liquids-solvents of the future? Science 302, 792-793.
- Ros, A., Lillo-Ródenas, M.A., Fuente, E., Montes-Morán, M.A., Martín, M.J., Linares-Solano, A., 2006. High surface area materials prepared from sewage sludge-based precursors. Chemosphere 65, 132–140.
- Roy, S., Labelle, S., Mehta, P., Mihoc, A., Fortin, N., Masson, C., Leblanc, R., Châteauneuf, G., Sura, C., Gallipeau, C., Olsen, C., Delisle, S., Labrecque, M., Greer, C.W., 2005. Phytoremediation of heavy metal and PAH-contaminated brownfield sites. Plant Soil 272, 277–290.
- Saha, S., Sarkar, P., 2012. Arsenic remediation from drinking water by synthesized nanoalumina dispersed in chitosan-grafted polyacrylamide. J. Hazard. Mater. 227–228, 68– 78.
- Said, W., Lewis, D., 1991. Quantitative assessment of the effects of metals on microbial degradation of organic chemicals. Appl Env. Microbiol 57, 1498–1503.

- Sakthivel, S., Velusamy, S., Gardas, R.L., Sangwai, J.S., 2014. Eco-efficient and green method for the enhanced dissolution of aromatic crude oil sludge using ionic liquids. RSC Adv 4, 31007–31018.
- Saltalı, K., Sarı, A., Aydın, M., 2007. Removal of ammonium ion from aqueous solution by natural Turkish (Yıldızeli) zeolite for environmental quality. J. Hazard. Mater. 141, 258–263.
- Samaksaman, U., Kuo, J.-H., Peng, T.-H., Wey, M.-Y., 2016. Effect of co-contaminated soil mixtures as fixed/fluidized bed media on pollutants emission under thermal treatment. Int. J. Environ. Sci. Technol. 13, 519–528.
- Samanya, J., Hornung, A., Apfelbacher, A., Vale, P., 2012. Characteristics of the upper phase of bio-oil obtained from co-pyrolysis of sewage sludge with wood, rapeseed and straw. J. Anal. Appl. Pyrolysis 94, 120–125.
- Schmid, A., Kollmer, A., Mathys, R.G., Witholt, B., 1998. Developments toward large-scale bacterial bioprocesses in the presence of bulk amounts of organic solvents. Extremophiles 2, 249–256.
- Schmidt, H., Kaminsky, W., 2001. Pyrolysis of oil sludge in a fluidised bed reactor. Chemosphere 45, 285–290.
- Schulz, H., Glaser, B., 2012. Effects of biochar compared to organic and inorganic fertilizers on soil quality and plant growth in a greenhouse experiment. J. Plant Nutr. Soil Sci. 175, 410–422.
- Schwab, A.P., Su, J., Wetzel, S., Pekarek, S., Banks, M.K., 1999. Extraction of petroleum hydrocarbons from soil by mechanical shaking. Environ. Sci. Technol. 33, 1940–1945.
- Seddon, K.R., Stark, A., Torres, M.-J., 2002. Viscosity and Density of 1-Alkyl-3-Methylimidazolium Ionic Liquids, in: Abraham, M.A., Moens, L. (Eds.), Clean Solvents. pp. 34–49.

- Seredych, M., Bandosz, T.J., 2006. Removal of copper on composite sewage sludge/industrial sludge-based adsorbents: The role of surface chemistry. J. Colloid Interface Sci. 302, 379–388.
- Shen, G., Lu, Y., Zhou, Q., Hong, J., 2005. Interaction of polycyclic aromatic hydrocarbons and heavy metals on soil enzyme. Chemosphere 61, 1175–1182.
- Shen, L., Zhang, D.-K., 2003. An experimental study of oil recovery from sewage sludge by low-temperature pyrolysis in a fluidised-bed☆. Fuel 82, 465–472.
- Shen, Z., McMillan, O., Jin, F., Al-Tabbaa, A., 2016. Salisbury biochar did not affect the mobility or speciation of lead in kaolin in a short-term laboratory study. J. Hazard. Mater. 316, 214–220.
- Shen, Z., Zhang, Y., Jin, F., McMillan, O., Al-Tabbaa, A., 2017. Qualitative and quantitative characterisation of adsorption mechanisms of lead on four biochars. Sci. Total Environ. 609, 1401–1410.
- Shi, W., Liu, C., Ding, D., Lei, Z., Yang, Y., Feng, C., Zhang, Z., 2013a. Immobilization of heavy metals in sewage sludge by using subcritical water technology. Bioresour. Technol. 137, 18–24.
- Shi, W., Liu, C., Shu, Y., Feng, C., Lei, Z., Zhang, Z., 2013b. Synergistic effect of rice husk addition on hydrothermal treatment of sewage sludge: Fate and environmental risk of heavy metals. Bioresour. Technol. 149, 496–502.
- Shie, J., Chang, C., Lin, J., Wu, C., Lee, D., 2000. Resources recovery of oil sludge by pyrolysis: kinetics study. J. Chem. Technol. Biotechnol. 75, 443–450.
- Shie, J.-L., Lin, J.-P., Chang, C.-Y., Lee, D.-J., Wu, C.-H., 2003. Pyrolysis of oil sludge with additives of sodium and potassium compounds. Resour. Conserv. Recycl. 39, 51–64.
- Shie, J.-L., Lin, J.-P., Chang, C.-Y., Shih, S.-M., Lee, D.-J., Wu, C.-H., 2004. Pyrolysis of oil sludge with additives of catalytic solid wastes. J. Anal. Appl. Pyrolysis 71, 695–707.

- Shinogi, Y., Kanri, Y., 2003. Pyrolysis of plant, animal and human waste: physical and chemical characterization of the pyrolytic products. Bioresour. Technol. 90, 241–247.
- Silva, E.B., Santos, D., Alves, D.R.M., Barbosa, M.S., Guimarães, R.C.L., Ferreira, B.M.S., Guarnieri, R.A., Franceschi, E., Dariva, C., Santos, A.F., Fortuny, M., 2013. Demulsification of heavy crude oil emulsions using ionic liquids. Energy Fuels 27, 6311–6315.
- Sing, K.S., Everett, D.H., Haul, R., Moscou, L., Pierotti, R.A., Rouquerol, J., Siemieniewska, T., 1985. Reporting physisorption data for gas/solid systems with special reference to the determination of surface area and porosity. Pure Appl Chem 57, 603–619.
- Singh, B., Singh, B.P., Cowie, A.L., 2010. Characterisation and evaluation of biochars for their application as a soil amendment. Aust. J. Soil Res. 48, 516–525.
- Sips, R., 1948. On the structure of a catalyst surface. J Chem Phys 16, 490–495.
- Sınağ, A., Gülbay, S., Uskan, B., Uçar, S., Özgürler, S.B., 2010. Production and characterization of pyrolytic oils by pyrolysis of waste machinery oil. J. Hazard. Mater. 173, 420–426.
- Smith, K.M., Fowler, G.D., Pullket, S., Graham, N.J.D., 2009. Sewage sludge-based adsorbents: A review of their production, properties and use in water treatment applications. Water Res. 43, 2569–2594.
- Song, Y., Tahmasebi, A., Yu, J., 2014. Co-pyrolysis of pine sawdust and lignite in a thermogravimetric analyzer and a fixed-bed reactor. Bioresour. Technol. 174, 204–211.
- Subramanian, D., Wu, K., Firoozabadi, A., 2015. Ionic liquids as viscosity modifiers for heavy and extra-heavy crude oils. Fuel 143, 519–526.
- Sui, H., Zhang, J., Yuan, Y., He, L., Bai, Y., Li, X., 2016. Role of binary solvent and ionic liquid in bitumen recovery from oil sands. Can. J. Chem. Eng. 94, 1191–1196.
- Sullivan, A.P., Kilpatrick, P.K., 2002. The effects of inorganic solid particles on water and crude oil emulsion stability. Ind. Eng. Chem. Res. 41, 3389–3404.
- Taguchi, G., Chowdhury, S., Wu, Y., 2005. Taguchi's Quality Engineering Handbook. John Wiley & Sons Hoboken, New Jersey.
- Tahhan, R.A., Abu-Ateih, R.Y., 2009. Biodegradation of petroleum industry oily-sludge using Jordanian oil refinery contaminated soil. Int. Biodeterior. Biodegrad. 63, 1054–1060.
- Taiwo, E.A., Otolorin, J.A., 2009. Oil Recovery from Petroleum Sludge by Solvent Extraction. Pet. Sci. Technol. 27, 836–844.
- Tan, G., Wu, Y., Liu, Y., Xiao, D., 2018. Removal of Pb(II) ions from aqueous solution by manganese oxide coated rice straw biochar A low-cost and highly effective sorbent. J. Taiwan Inst. Chem. Eng. 84, 85–92.
- Tchounwou, P.B., Yedjou, C.G., Patlolla, A.K., Sutton, D.J., 2012. Heavy Metal Toxicity and the Environment, in: Luch, A. (Ed.), Molecular, Clinical and Environmental Toxicology. Springer, Basel, pp. 133–164.
- Tempkin, M.I., Pyzhev, V., 1940. Kinetics of ammonia synthesis on promoted iron catalyst. Acta Phys. Chim. USSR 12, 327–356.
- Tessier, A., Campbell, P.G., Bisson, M., 1979. Sequential extraction procedure for the speciation of particulate trace metals. Anal. Chem. 51, 844–851.
- Thangalazhy-Gopakumar, S., Al-Nadheri, W.M.A., Jegarajan, D., Sahu, J.N., Mubarak, N.M., Nizamuddin, S., 2015. Utilization of palm oil sludge through pyrolysis for bio-oil and bio-char production. Bioresour. Technol. 178, 65–69.
- Thurnau, R.C., 1996. Low-temperature desorption treatment of co-contaminated soils: TCLP as an evaluation technique. J. Hazard. Mater. 48, 149–169.

Tian, Y., Li, J., Yan, X., Whitcombe, T., Thring, R., 2019. Co-pyrolysis of metal contaminated oily waste for oil recovery and heavy metal immobilization. J. Hazard. Mater. 373, 1–10.

- Tong, X., Li, J., Yuan, J., Xu, R., 2011. Adsorption of Cu(II) by biochars generated from three crop straws. Chem. Eng. J. 172, 828–834.
- Tourvieille, J.-N., Larachi, F., Duchesne, C., Chen, J., 2017. NIR hyperspectral investigation of extraction kinetics of ionic-liquid assisted bitumen extraction. Chem. Eng. J. 308, 1185–1199.
- Trakal, L., Šigut, R., Šillerová, H., Faturíková, D., Komárek, M., 2014. Copper removal from aqueous solution using biochar: Effect of chemical activation. Arab. J. Chem. 7, 43–52.
- Uchimiya, M., Klasson, K.T., Wartelle, L.H., Lima, I.M., 2011a. Influence of soil properties on heavy metal sequestration by biochar amendment: 1. Copper sorption isotherms and the release of cations. Chemosphere 82, 1431–1437.
- Uchimiya, M., Lima, I.M., Thomas Klasson, K., Chang, S., Wartelle, L.H., Rodgers, J.E., 2010. Immobilization of heavy metal ions (CuII, CdII, NiII, and PbII) by broiler litter-derived biochars in water and soil. J. Agric. Food Chem. 58, 5538–5544.
- Uchimiya, M., Wartelle, L.H., Klasson, K.T., Fortier, C.A., Lima, I.M., 2011b. Influence of Pyrolysis Temperature on Biochar Property and Function as a Heavy Metal Sorbent in Soil. J. Agric. Food Chem. 59, 2501–2510.
- USEPA, 2015. National Primary Drinking Water Regulations. https://www.epa.gov/groundwater-and-drinking-water/national-primary-drinking-water-regulations (accessed 17 August 2019).
- USEPA, 2012. Hazardous Waste Listings, a User-Friendly Reference Document.
- USEPA Method 3051A, 2007a. Microwave Assisted Acid Digestion of Sediments, Sludges, Soils, and Oils.

USEPA Method 8015C, 2007b. Nonhalogenated Organics by Gas Chromatography.

USEPA Method 3540C, 1996a. Soxhlet Extraction.

USEPA Method 3050B, 1996b. Acid Digestion of Sediments, Sludges, and Soils.

- van Oudenhoven, J.A.C.M., Copper, G.R., Cricchi, G., Gineste, J., Pötzl, R., Vissers, J., Martin, D.E., 1995. Oil refinery waste disposal methods, quantities and costs 1993 survey. Conservation of Clean Air and Water in Europe (CONCAWE), Brussels.
- Visa, M., Isac, L., Duta, A., 2012. Fly ash adsorbents for multi-cation wastewater treatment. Appl. Surf. Sci. 258, 6345–6352.
- Wake, H., 2005. Oil refineries: a review of their ecological impacts on the aquatic environment. Estuar. Coast. Shelf Sci. 62, 131–140.
- Wang, J., Lin, B.-C., Huang, Q.-X., Ma, Z.-Y., Chi, Y., Yan, J.-H., 2017a. Aromatic hydrocarbon production and catalyst regeneration in pyrolysis of oily sludge using ZSM-5 zeolites as catalysts. Energy Fuels 31, 11681–11689.
- Wang, J., Liu, T.-L., Huang, Q.-X., Ma, Z.-Y., Chi, Y., Yan, J.-H., 2017b. Production and characterization of high quality activated carbon from oily sludge. Fuel Process. Technol. 162, 13–19.
- Wang, R., Liu, J., Gao, F., Zhou, J., Cen, K., 2012. The slurrying properties of slurry fuels made of petroleum coke and petrochemical sludge. Fuel Process. Technol. 104, 57–66.
- Wang, R.-Z., Huang, D.-L., Liu, Y.-G., Zhang, C., Lai, C., Zeng, G.-M., Cheng, M., Gong, X.-M., Wan, J., Luo, H., 2018. Investigating the adsorption behavior and the relative distribution of Cd²⁺ sorption mechanisms on biochars by different feedstock. Bioresour. Technol. 261, 265–271.
- Wang, T., Zhang, C., Zhao, R., Zhu, C., Yang, C., Liu, C., 2014. Solvent extraction of bitumen from oil sands. Energy Fuels 28, 2297–2304.
- Wang, Z., Guo, Q., Liu, X., Cao, C., 2007. Low temperature pyrolysis characteristics of oil sludge under various heating conditions. Energy Fuels 21, 957–962.

- Wang, Z., Liu, G., Zheng, H., Li, F., Ngo, H.H., Guo, W., Liu, C., Chen, L., Xing, B., 2015. Investigating the mechanisms of biochar's removal of lead from solution. Bioresour. Technol. 177, 308–317.
- Weber, W.J., Morris, J.C., 1963. Kinetics of adsorption on carbon from solution. J. Sanit. Eng. Div. 89, 31–60.
- Williams, P., Lupinsky, A., Painter, P., 2010. Recovery of bitumen from low-grade oil sands using ionic liquids. Energy Fuels 24, 2172–2173.
- Wu, J., Dabros, T., 2012. Process for solvent extraction of bitumen from oil Sand. Energy Fuels 26, 1002–1008.
- Wu, X., Cobbina, S.J., Mao, G., Xu, H., Zhang, Z., Yang, L., 2016. A review of toxicity and mechanisms of individual and mixtures of heavy metals in the environment. Environ. Sci. Pollut. Res. 23, 8244–8259.
- Xiao, X., Chen, Z., Chen, B., 2016. H/C atomic ratio as a smart linkage between pyrolytic temperatures, aromatic clusters and sorption properties of biochars derived from diverse precursory materials. Sci. Rep. 6.
- Xiu, S., Shahbazi, A., Shirley, V., Cheng, D., 2010. Hydrothermal pyrolysis of swine manure to bio-oil: Effects of operating parameters on products yield and characterization of bio-oil. J. Anal. Appl. Pyrolysis 88, 73–79.
- Xu, G., Yang, X., Spinosa, L., 2015. Development of sludge-based adsorbents: Preparation, characterization, utilization and its feasibility assessment. J. Environ. Manage. 151, 221–232.
- Xu, L., Jiang, Y., Qiu, R., 2018. Parametric study and global sensitivity analysis for copyrolysis of rape straw and waste tire via variance-based decomposition. Bioresour. Technol. 247, 545–552.
- Xu, N., Wang, W., Han, P., Lu, X., 2009. Effects of ultrasound on oily sludge deoiling. J. Hazard. Mater. 171, 914–917.

- Xu, X., Cao, X., Zhao, L., Wang, H., Yu, H., Gao, B., 2013. Removal of Cu, Zn, and Cd from aqueous solutions by the dairy manure-derived biochar. Environ. Sci. Pollut. Res. 20, 358–368.
- Yang, H., Wang, Y., Ding, M., Hu, B., Ren, S., 2012. Water-assisted solvent extraction of bitumen from oil sands. Ind. Eng. Chem. Res. 51, 3032–3038.
- Yang, L., Nakhla, G., Bassi, A., 2005. Electro-kinetic dewatering of oily sludges. J. Hazard. Mater. 125, 130–140.
- Yang, X., Xu, G., Yu, H., Zhang, Z., 2016. Preparation of ferric-activated sludge-based adsorbent from biological sludge for tetracycline removal. Bioresour. Technol. 211, 566–573.
- Yang, Y.F., Feng, C.P., Inamori, Y., Maekawa, T., 2004. Analysis of energy conversion characteristics in liquefaction of algae. Resour. Conserv. Recycl. 43, 21–33.
- Yongbin, J., Jiejie, H., Yang, W., 2004. Effects of calcium oxide on the cracking of coal tar in the freeboard of a fluidized bed. Energy Fuels 18, 1625–1632.
- Yuan, H., Lu, T., Zhao, D., Huang, H., Noriyuki, K., Chen, Y., 2013. Influence of temperature on product distribution and biochar properties by municipal sludge pyrolysis. J. Mater. Cycles Waste Manag. 15, 357–361.
- Yuan, S., Dai, Z., Zhou, Z., Chen, X., Yu, G., Wang, F., 2012. Rapid co-pyrolysis of rice straw and a bituminous coal in a high-frequency furnace and gasification of the residual char. Bioresour. Technol. 109, 188–197.
- Zhai, Y., Wei, X., Zeng, G., Zhang, D., Chu, K., 2004. Study of adsorbent derived from sewage sludge for the removal of Cd²⁺, Ni²⁺ in aqueous solutions. Sep. Purif. Technol. 38, 191– 196.
- Zhang, B., Xiong, S., Xiao, B., Yu, D., Jia, X., 2011. Mechanism of wet sewage sludge pyrolysis in a tubular furnace. Int. J. Hydrog. Energy 36, 355–363.

- Zhang, C., Shan, B., Tang, W., Zhu, Y., 2017. Comparison of cadmium and lead sorption by Phyllostachys pubescens biochar produced under a low-oxygen pyrolysis atmosphere. Bioresour. Technol. 238, 352–360.
- Zhang, F.-S., Nriagu, J.O., Itoh, H., 2005. Mercury removal from water using activated carbons derived from organic sewage sludge. Water Res. 39, 389–395.
- Zhang, J., Li, J., Thring, R.W., Hu, X., Song, X., 2012. Oil recovery from refinery oily sludge via ultrasound and freeze/thaw. J. Hazard. Mater. 203–204, 195–203.
- Zhang, J., Lü, F., Zhang, H., Shao, L., Chen, D., He, P., 2015. Multiscale visualization of the structural and characteristic changes of sewage sludge biochar oriented towards potential agronomic and environmental implication. Sci. Rep. 5, 9406.
- Zhang, T., Zhu, X., Shi, L., Li, J., Li, S., Lü, J., Li, Y., 2017. Efficient removal of lead from solution by celery-derived biochars rich in alkaline minerals. Bioresour. Technol. 235, 185–192.
- Zhang, W., Mao, S., Chen, H., Huang, L., Qiu, R., 2013. Pb(II) and Cr(VI) sorption by biochars pyrolyzed from the municipal wastewater sludge under different heating conditions. Bioresour. Technol. 147, 545–552.
- Zhao, S., Feng, C., Yang, Y., Niu, J., Shen, Z., 2012. Risk assessment of sedimentary metals in the Yangtze Estuary: New evidence of the relationships between two typical index methods. J. Hazard. Mater. 241–242, 164–172.
- Zolfaghari, G., Esmaili-Sari, A., Anbia, M., Younesi, H., Amirmahmoodi, S., Ghafari-Nazari, A., 2011. Taguchi optimization approach for Pb(II) and Hg(II) removal from aqueous solutions using modified mesoporous carbon. J. Hazard. Mater. 192, 1046–1055.
- Zou, J., Dai, Y., Wang, X., Ren, Z., Tian, C., Pan, K., Li, S., Abuobeidah, M., Fu, H., 2013. Structure and adsorption properties of sewage sludge-derived carbon with removal of inorganic impurities and high porosity. Bioresour. Technol. 142, 209–217.
- Zubaidy, E.A.H., Abouelnasr, D.M., 2010. Fuel recovery from waste oily sludge using solvent extraction. Process Saf. Environ. Prot. 88, 318–326.

Zuo, W., Jin, B., Huang, Y., Sun, Y., 2014. Characterization of top phase oil obtained from copyrolysis of sewage sludge and poplar sawdust. Environ. Sci. Pollut. Res. 21, 9717– 9726.

APPENDIX A

Table A1. Mass balance calculation of the F2, F3, and F4 fractions of TPH for orthogonal experiments

 of solvent extraction alone

E	xp. No.	F2 _o	F2t	F2 _b	F3 _o	F3 _t	F3 _b
	1	(µg)	(µg)	(µg)	(µg)	(µg)	(µg)
1	Rep1	105,869	97,816	4,657	148,833	120,486	16,551
	Rep2	106,609	93,683	5,066	149,873	113,599	18,709
	Rep3	106,102	95,226	3,621	149,160	115,632	18,784
2	Rep1	106,905	104,586	3,911	150,289	120,657	16,237
	Rep2	106,863	10,0243	3,399	150,230	114,618	17,441
	Rep3	106,102	100,362	1,985	149,160	120,210	17,865
3	Rep1	106,440	91,596	4,182	149,635	125,413	15,440
	Rep2	105,172	91,204	4,418	147,852	116,729	15,004
	Rep3	105,743	91,517	4,957	148,655	118,453	17,743
4	Rep1	105,700	101,445	902	148,595	129,972	7,357
	Rep2	105,996	99,683	745	149,011	120,081	10,748
	Rep3	107,138	106,462	1,641	150,616	124,304	14,271
5	Rep1	106,525	102,535	2,081	149,754	128,291	11,655
	Rep2	105,827	99,858	1,436	148,773	121,563	10,583
	Rep3	107,053	96,722	2,660	150,497	130,621	13,291
6	Rep1	106,673	81,048	3,396	149,962	124,989	13,008
	Rep2	106,948	96,484	3,197	150,349	123,480	11,663
	Rep3	105,256	102,705	2,078	147,971	126,867	14,095
7	Rep1	105,362	79,100	2,002	148,120	137,957	8,616
	Rep2	104,728	111,885	1,163	147,228	131,963	9,674
	Rep3	106,271	107,745	1,515	149,398	136,297	11,864
8	Rep1	104,051	83,927	1,435	146,277	125,923	11,001
	Rep2	106,102	107,317	2,889	149,160	127,029	12,996
	Rep3	106,123	99,805	1,825	149,190	132,324	9,029
9	Rep1	106,652	95,827	2,862	149,932	131,858	9,157
	Rep2	106,673	103,002	2,296	149,962	136,641	10,080
_	Rep3	106,800	120,085	1,411	150,141	139,262	8,620

 $F(2/3/4)_{o}$: mass of F2/F3/F4 fractions of TPH in the original oily sludge sample;

 $F(2/3/4)_t$: mass of F2/F3/F4 fractions of TPH in the recovered oil;

 $F(2/3/4)_b$: mass of F2/F3/F4 fractions of TPH in the residual sand/clay;

 $F(2/3/4)_s$: sum of $F(2/3/4)_t$ and $F(2/3/4)_b$;

TPH_s: sum of $F2_t$, $F2_b$, $F3_t$, $F3_b$, $F4_t$, and $F4_b$;

TPH_o: sum of F2_o, F3_o, and F4_o.

Ez	xp. No.	F4 _o	F4 _t	F4 _b	$F2_s/$	F3 _s /	F4 _s /	TPHs/
		(µg)	(µg)	(µg)	F2o	F3 _o	F4 _o	TPHo
1	Rep1	39,267	26,898	11,192	0.97	0.92	0.97	0.94
	Rep2	39,542	26,118	12,025	0.93	0.88	0.96	0.91
	Rep3	39,354	24,042	11,095	0.93	0.90	0.89	0.91
2	Rep1	39,652	29,657	11,152	1.01	0.91	1.03	0.96
	Rep2	39,636	29,439	10,760	0.97	0.88	1.01	0.93
	Rep3	39,354	29,627	9,550	0.96	0.93	1.00	0.95
3	Rep1	39,479	31,291	9,978	0.90	0.94	1.05	0.94
	Rep2	39,009	33,667	10,579	0.91	0.89	1.13	0.93
	Rep3	39,220	30,430	8,800	0.91	0.92	1.00	0.93
4	Rep1	39,205	36,083	4,241	0.97	0.92	1.03	0.95
	Rep2	39,314	33,437	8,908	0.95	0.88	1.08	0.93
	Rep3	39,738	33,333	6,588	1.01	0.92	1.00	0.96
5	Rep1	39,510	37,674	6,964	0.98	0.93	1.13	0.98
	Rep2	39,252	38,278	6,480	0.96	0.89	1.14	0.95
	Rep3	39,706	35,857	5,849	0.93	0.96	1.05	0.96
6	Rep1	39,565	40,064	5,496	0.79	0.92	1.15	0.90
	Rep2	39,667	36,636	6,740	0.93	0.90	1.09	0.94
	Rep3	39,040	34,328	6,127	1.00	0.95	1.04	0.98
7	Rep1	39,079	44,443	5,182	0.77	0.99	1.27	0.95
	Rep2	38,844	36,452	5,863	1.08	0.96	1.09	1.02
	Rep3	39,416	38,858	6,522	1.03	0.99	1.15	1.03
8	Rep1	38,593	39,451	5,564	0.82	0.94	1.17	0.93
	Rep2	39,354	37,254	6,215	1.04	0.94	1.10	1.00
	Rep3	39,361	37,371	5,345	0.96	0.95	1.09	0.97
9	Rep1	39,557	42,315	4,181	0.93	0.94	1.18	0.97
	Rep2	39,565	42,057	4,924	0.99	0.98	1.19	1.01
	Rep3	39,612	37,753	5,669	1.14	0.98	1.10	1.05
				Average	0.95	0.93	1.08	0.96

Table A1. Mass balance calculation of the F2, F3, and F4 fractions of TPH for orthogonal experiments of solvent extraction alone (continued)

 $F(2/3/4)_o$: mass of F2/F3/F4 fractions of TPH in the original oily sludge sample;

 $F(2/3/4)_t$: mass of F2/F3/F4 fractions of TPH in the recovered oil;

F(2/3/4)_b: mass of F2/F3/F4 fractions of TPH in the residual sand/clay;

 $F(2/3/4)_s$: sum of $F(2/3/4)_t$ and $F(2/3/4)_b$;

TPH_s: sum of F2_t, F2_b, F3_t, F3_b, F4_t, and F4_b;

TPH_o: sum of F2_o, F3_o, and F4_o.

		50	52	50	52	52			52
	Exp.	F2o	F2t	F2 _i	F2b	F3o	F3t	F3i	F3b
	No.	(µg)	(µg)	(µg)	(µg)	(µg)	(µg)	(µg)	(µg)
1	Rep1	105,341	78,621	18,324	710	148,090	98,182	37,636	10,853
	Rep2	107,497	80,939	26,914	661	151,121	102,186	43,929	11,166
	Rep3	105,806	93,527	22,459	657	148,744	101,161	42,726	11,766
2	Rep1	105,320	77,363	17,634	737	148,060	105,123	34,762	9,659
	Rep2	104,791	66,603	13,988	978	147,317	105,949	43,430	10,420
	Rep3	106,482	96,918	15,843	679	149,695	111,224	35,393	11,908
3	Rep1	105,447	86,525	11,372	410	148,239	115,224	26,216	7,502
	Rep2	105,193	87,197	16,765	612	147,882	112,516	36,823	9,785
	Rep3	105,595	85,474	10,795	201	148,447	113,586	30,676	12,047
4	Rep1	107,582	91,128	13,250	635	151,240	110,960	39,374	9,193
	Rep2	105,806	92,027	11,853	238	148,744	106,100	42,328	9,279
	Rep3	104,960	82,947	6,520	208	147,555	105,687	41,431	12,473
5	Rep1	107,053	90,705	13,556	495	150,497	115,875	31,023	8,038
	Rep2	105,700	83,990	15,302	740	148,595	113,091	32,281	9,242
	Rep3	104,516	90,602	12,000	197	146,931	104,409	31,658	13,913
6	Rep1	107,095	90,032	8,147	812	150,557	113,313	31,430	11,220
	Rep2	107,201	76,835	17,204	188	150,705	100,882	38,155	8,816
	Rep3	104,580	76,035	10,706	526	147,020	105,760	25,943	17,432
7	Rep1	105,320	95,031	10,767	215	148,060	108,837	29,403	7,933
	Rep2	106,398	85,364	8,702	355	149,576	102,902	25,985	9,173
	Rep3	104,749	75,054	14,839	186	147,258	94,846	35,125	12,831
8	Rep1	106,377	105,510	3,605	399	149,546	122,904	21,351	7,173
	Rep2	106,398	87,722	6,239	317	149,576	118,831	22,586	4,369
	Rep3	106,863	88,730	10,127	787	150,230	104,311	29,355	14,738
9	Rep1	104,876	81,642	4,378	382	147,436	123,428	26,409	6,607
	Rep2	106,208	97,020	17,188	185	149,308	118,540	29,321	3,822
	Rep3	106,017	87,683	8,841	819	149,041	115,452	19,670	14,425

Table A2. Mass balance calculation of the F2, F3, and F4 fractions of TPH for orthogonal experiments of IL-enhanced solvent extraction process

 $F(2/3/4)_o$: mass of F2/F3/F4 fractions of TPH in the original oily sludge sample;

 $F(2/3/4)_t$: mass of F2/F3/F4 fractions of TPH in the recovered oil from top oil layer;

 $F(2/3/4)_i$: mass of F2/F3/F4 fractions of TPH in the recovered oil from oil-IL interface;

F(2/3/4)_b: mass of F2/F3/F4 fractions of TPH in the residual sand/clay;

 $F(2/3/4)_s$: sum of $F(2/3/4)_t$, $F(2/3/4)_i$ and $F(2/3/4)_b$;

TPH_s: sum of F2_t, F2_i, F2_b, F3_t, F3_i, F3_b, F4_t, F4_i, and F4_b;

TPH_o: sum of F2_o, F3_o, and F4_o.

F	n No	F4.	F4.	F4:	F41	F2./	F3_/	$F \Delta_a /$	TPH _c /
Ľ	zh. 140.	тто (по)	ידי (ווס)	יד ז (ווס)	סד <u>ו</u> (ווס)	$F2_{\circ}$	F3_	$F4_{\circ}$	
1	Ren1	39 071	12 897	21 739	10.653	0.93	0.99	1 16	0.99
1	Rep1	39 871	17,075	21,757	5 061	1.01	1.04	1.10	1.05
	Rep2	39 244	13 412	21,037	7 276	1.01	1.01	1.10	1.05
2	Rep3	39,063	16 113	20,704	9 674	0.91	1.05	1.07	1.07
2	Rep1	38 867	21 248	20,704	4 540	0.71	1.01	1.19	1.00
	Rep2	39 495	17 858	18 664	7 028	1.07	1.00	1.23	1.00
3	Rep3	39 111	19,651	19,004	8 721	0.93	1.00	1.10	1.07
5	Rep1	39,016	24 887	23 012	3 628	0.99	1.00	1.25	1.01
	Rep2	39 165	19.039	17 529	5,020	0.99	1.00	1.52	1.00
Δ	Rep3	39,902	17,055	25 876	6 635	0.91	1.05	1.07	1.01
т	Rep1	39,702	17,112 22 173	23,870	4 082	0.98	1.05	1.24	1.05
	Rep2	38 930	16 766	22,417	5 801	0.98	1.00	1.24	1.00
5	Rep3	39,706	19,700	21,440	6 914	0.05	1.00	1.15	1.01
5	Rep1	39,700	25 819	19 717	5 255	0.95	1.03	1.20	1.04
	Rep2	38 766	18 489	18 747	6 3 7 4	0.95	1.04	1.50	1.04
6	Rep3	30,700	22 355	21 023	8 203	0.90	1.02	1.11	1.02
0	Rep1 Rep1	39,722	22,333	21,723 21,723	5 293	0.92	0.08	1.32	0.00
	Rep2	38 780	20,702	2+,++1 15 751	5,275	0.83	1.01	1.55	0.99
7	Rep3	30,767	20,303	10,731	7 254	1.01	0.00	1.00	1.02
/	Rep1 Rep1	30,003	21,032	15,230	3 960	0.80	0.99	1.22	0.03
	Rep2 Rep3	39,403	15 800	18 737	5,900 6 181	0.89	0.92	1.08	0.93
0	Dop1	20,456	24 786	17 544	0,101	1.02	1.01	1.05	1.05
0	Rep1 Dop2	20 462	24,700	12 775	7,222 5,416	0.80	1.01	1.20	1.03
	Rep2 Dop2	39, 4 03 20,626	10.050	15,775	7 700	0.03	0.97	1.23	0.98
0	Rep3	29,030	19,039 26 021	10,010	7,709	0.93	0.99	1.06	0.90
9	Rep1	20,099	20,951	17,014	0,100	0.82	1.00	1.30	1.01
	Rep2	20,273	51,440 22.265	13,192	4,901 8 026	1.00	1.02	1.32	1.00
	керэ	39,322	22,203	12,089	0,020	0.92	1.00	1.09	0.98
					Average	0.94	1.02	1.20	1.03

Table A2. Mass balance calculation of the F2, F3, and F4 fractions of TPH for orthogonal experiments of IL-enhanced solvent extraction process (continued)

 $F(2/3/4)_0$: mass of F2/F3/F4 fractions of TPH in the original oily sludge sample;

 $F(2/3/4)_t$: mass of F2/F3/F4 fractions of TPH in the recovered oil from top oil layer;

 $F(2/3/4)_i$: mass of F2/F3/F4 fractions of TPH in the recovered oil from oil-IL interface;

F(2/3/4)_b: mass of F2/F3/F4 fractions of TPH in the residual sand/clay;

 $F(2/3/4)_s$: sum of $F(2/3/4)_t$, $F(2/3/4)_i$ and $F(2/3/4)_b$;

 TPH_s : sum of $F2_t$, $F2_i$, $F2_b$, $F3_t$, $F3_i$, $F3_b$, $F4_t$, $F4_i$, and $F4_b$;

TPHo: sum of F2o, F3o, and F4o.

Sources of variation	SS ^a	DF ^b	Mean square	<i>F</i> -value	Prob > F	Significance
For TPH recovery						Ē
(A) So/Sl ratio	494.59	2	247.30	30.21	< 0.001	**
(B) Shaking speed	1.72	2	0.86	0.10	0.90	
(C) Extraction duration	70.03	2	35.01	4.28	0.03	*
Error	147.32	18	8.18			
Total	730.67	26				
For F2 recovery						
(A) So/Sl ratio	100.54	2	50.27	0.88	0.43	
(B) Shaking speed	32.46	2	16.23	0.28	0.76	
(C) Extraction duration	258.73	2	129.37	2.26	0.13	
Error	1030.96	18	57.28			
Total	1784.37	26				
For F3 recovery						
(A) So/Sl ratio	470.02	2	235.01	64.30	< 0.001	**
(B) Shaking speed	11.20	2	5.60	1.53	0.24	
(C) Extraction duration	35.42	2	17.71	4.85	0.02	*
Error	65.79	18	3.66			
Total	632.08	26				
For F4 recovery						
(A) So/Sl ratio	3415.07	2	1707.54	91.33	< 0.001	**
(B) Shaking speed	276.35	2	138.17	7.39	0.0045	**
(C) Extraction duration	227.23	2	113.62	6.08	0.0096	**
Error	336.54	18	18.70			
Total	4522.00	26				

Table A3. ANOVA for TPH, F2, F3, and F4 recovery in solvent extraction alone

^a Sum of squares; ^b Degree of freedom; * Significant (P < 0.05); ** Highly significant (P < 0.01)

Sources of variation	SS ^a	DF ^b	Mean square	F-value	$\operatorname{Prob} > F$	Significance
For TPH recovery						
(A) So/Sl ratio	1.79	2	0.89	0.05	0.95	
(B) IL/Sl ratio	89.16	2	44.58	2.32	0.13	
(C) Shaking speed	28.00	2	14.00	0.73	0.50	
Error	345.68	18	19.20			
Total	554.09	26				
Part 1: TPH recovery	v in top o	il laye	r			
(A) So/Sl ratio	139.83	2	69.92	4.01	0.036	*
(B) IL/Sl ratio	125.79	2	62.90	3.61	0.048	*
(C) Shaking speed	135.12	2	67.56	3.87	0.040	*
Error	313.87	18	17.44			

Table A4. ANOVA for TPH recovery in IL-enhanced solvent extraction process

Sources of variation	SS ^a	DF ^b	Mean square	F-value	$\operatorname{Prob} > F$	Significance
Total	761.49	26				
Part 2: TPH recovery	v in oil-IL	interf	face			
(A) So/Sl ratio	111.44	2	55.72	7.99	0.0033	**
(B) IL/Sl ratio	17.69	2	8.84	1.27	0.31	
(C) Shaking speed	284.74	2	142.37	20.42	< 0.001	**
Error	125.48	18	6.97			
Total	575.12	26				
Sum of squares; ^b Degree	of freedom	m; * Si	gnificant (P < 0.	05); ** Hig	shly significa	ant (P < 0.01)

^a Sum of squares; ^b Degree of freedom; * Significant (P < 0.05); ** Highly significant (P < 0.01)

APPENDIX B

SRC Sample Exp. No.1 Exp. No.2 Exp. No.3 Exp. No.4 Exp. No.5 Extractable fractions (mg/kg) 325.47 ± 8.21 0.71 ± 0.11 20.41 ± 4.45 11.94 ± 0.59 F1 13.79 ± 2.50 20.34 ± 5.83 Cu F2 157.94 ± 8.92 101.16 ± 1.27 97.81 ± 8.41 154.07 ± 3.85 134.58 ± 8.92 230.86 ± 6.15 101.28 ± 3.12 155.61 ± 16.56 104.34 ± 1.30 176.50 ± 9.11 168.50 ± 2.62 168.18 ± 24.03 F3 96.79 ± 6.04 525.52 ± 0.37 476.30 ± 31.14 F4 397.51 ± 3.75 453.60 ± 52.01 393.93 ± 44.31 F5 37 ± 2 116 ± 16 318 ± 24 215 ± 41 77 ± 32 220 ± 5 Cr F1 5.06 ± 0.07 0.20 ± 0.28 0.00 0.00 0.00 0.00 1.18 ± 0.06 F2 24.83 ± 0.79 11.17 ± 0.11 10.14 ± 0.65 1.77 ± 0.23 3.58 ± 0.47 85.12 ± 2.59 47.27 ± 3.96 5.41 ± 0.01 40.17 ± 0.97 5.73 ± 0.52 21.47 ± 2.28 F3 648.10 ± 6.53 F4 807.79 ± 50.02 248.03 ± 22.25 747.93 ± 156.16 693.62 ± 109.65 528.02 ± 31.07 53 ± 4 140 ± 54 846 ± 22 271 ± 18 385 ± 52 430 ± 29 F5 677.44 ± 6.59 10.45 ± 1.92 3.47 ± 0.68 6.42 ± 1.41 2.82 ± 0.42 16.00 ± 4.73 Ni F1 F2 64.00 ± 7.01 29.94 ± 1.24 18.15 ± 0.78 26.20 ± 0.66 11.95 ± 0.35 49.50 ± 3.31 22.21 ± 3.66 73.14 ± 8.12 36.35 ± 0.06 56.33 ± 0.87 23.54 ± 1.20 57.88 ± 7.71 F3 25.62 ± 2.25 389.58 ± 3.02 447.62 ± 38.74 401.22 ± 11.16 362.06 ± 25.99 366.92 ± 22.83 F4 F5 44 ± 0 505 ± 10 597 ± 40 581 ± 8 688 ± 24 494 ± 23 128.72 ± 2.69 0.00 0.00 0.00 0.00 0.00 Pb F1 77.45 ± 5.75 F2 159.30 ± 8.17 72.56 ± 3.58 66.95 ± 7.72 87.15 ± 0.88 54.59 ± 4.08 F3 278.78 ± 1.02 187.33 ± 18.52 114.09 ± 1.40 164.61 ± 0.74 65.46 ± 3.21 156.17 ± 16.50 177.97 ± 8.03 573.10 ± 26.33 F4 344.36 ± 31.22 587.21 ± 54.94 656.16 ± 97.38 462.44 ± 43.06 56 ± 1 127 ± 11 524 ± 40 181 ± 13 260 ± 42 242 ± 32 F5

Table B1. Concentrations of extractable fractions of heavy metals in the oily waste (SRC) and its solid residues

Sam	ple	SRC	Exp. No.1	Exp. No.2	Exp. No.3	Exp. No.4	Exp. No.5
Zn	F1	669.33 ± 6.37	19.04 ± 3.45	0.49 ± 0.12	12.54 ± 2.73	3.67 ± 0.30	18.16 ± 4.62
	F2	64.83 ± 7.99	53.34 ± 2.28	23.00 ± 1.57	51.03 ± 0.57	25.12 ± 1.89	55.80 ± 3.74
	F3	21.94 ± 3.79	144.35 ± 10.93	77.82 ± 1.49	128.81 ± 5.09	38.61 ± 0.88	109.18 ± 10.08
	F4	30.23 ± 1.36	510.34 ± 12.46	321.73 ± 21.15	576.48 ± 44.89	632.79 ± 102.75	446.92 ± 26.90
	F5	100 ± 0	327 ± 22	729 ± 21	351 ± 37	437 ± 57	399 ± 25

Table B1. Concentrations of extractable fractions of heavy metals in the oily waste (SRC) and its solid residues (continued)

Sampl	e	Exp. No.6	Exp. No.7	Exp. No.8	Exp. No.9	Exp. No.10
Extrac	table f	ractions (mg/kg)				
Cu	F1	14.03 ± 2.14	1.10 ± 0.34	1.23 ± 0.12	4.19 ± 0.44	1.21 ± 0.16
	F2	221.09 ± 16.43	142.00 ± 4.17	87.10 ± 2.74	89.27 ± 4.37	102.40 ± 6.86
	F3	188.99 ± 2.91	91.01 ± 0.28	109.98 ± 14.72	150.47 ± 4.31	120.55 ± 8.86
	F4	411.11 ± 17.42	477.13 ± 64.31	532.35 ± 3.73	497.10 ± 35.35	516.80 ± 91.48
	F5	86 ± 39	175 ± 11	209 ± 14	245 ± 26	200 ± 8
Cr	F1	0.00	0.00	0.00	0.00	0.00
	F2	10.86 ± 0.99	1.27 ± 0.07	1.28 ± 0.04	1.63 ± 0.02	1.22 ± 0.07
	F3	43.22 ± 2.58	5.29 ± 0.29	5.34 ± 1.12	6.70 ± 0.88	5.72 ± 0.65
	F4	703.96 ± 33.79	179.95 ± 3.63	230.58 ± 17.65	552.05 ± 24.92	296.06 ± 11.84
	F5	259 ± 30	791 ± 3	800 ± 19	527 ± 26	736 ± 12
Ni	F1	6.51 ± 1.49	7.97 ± 2.69	5.97 ± 1.31	3.04 ± 0.60	2.90 ± 0.34
	F2	37.81 ± 2.12	27.79 ± 0.44	25.45 ± 1.00	11.15 ± 0.31	16.55 ± 1.31
	F3	59.89 ± 3.80	24.52 ± 0.55	38.61 ± 7.82	25.77 ± 2.88	28.34 ± 3.46
	F4	401.43 ± 12.19	495.67 ± 25.79	498.35 ± 6.08	373.09 ± 27.28	469.01 ± 1.26

Samp	le	Exp. No.6	Exp. No.7	Exp. No.8	Exp. No.9	Exp. No.10
	F5	513 ± 20	424 ± 22	4701 ± 4	677 ± 24	524 ± 4
Pb	F1	0.00	0.00	0.00	0.00	0.00
	F2	107.27 ± 6.31	47.61 ± 1.13	56.02 ± 0.78	53.56 ± 1.76	64.01 ± 5.46
	F3	186.62 ± 6.17	154.73 ± 4.50	114.94 ± 21.23	73.84 ± 5.50	116.44 ± 13.55
	F4	497.94 ± 34.78	309.30 ± 11.39	352.60 ± 20.68	532.85 ± 2.20	401.07 ± 10.22
	F5	178 ± 22	421 ± 6	466 ± 41	378 ± 9	409 ± 18
Zn	F1	15.05 ± 2.49	0.86 ± 0.16	0.83 ± 0.04	2.94 ± 0.41	0.86 ± 0.12
	F2	64.43 ± 4.04	35.00 ± 0.36	23.00 ± 0.71	25.77 ± 0.46	27.89 ± 2.21
	F3	136.32 ± 11.47	124.39 ± 6.99	86.16 ± 19.79	46.46 ± 5.71	87.20 ± 12.87
	F4	490.85 ± 23.39	278.39 ± 19.58	347.46 ± 19.67	519.63 ± 3.25	372.23 ± 5.62
	F5	358 ± 5	585 ± 12	628 ± 40	544 ± 10	599 ± 5

Table B1. Concentrations of extractable fractions of heavy metals in the oily waste (SRC) and its solid residues (continued)

Sampl	e	Exp. No.11	Exp. No.12	Exp. No.13	Exp. No.14	Exp. No.15			
Extractable fractions (mg/kg)									
Cu	F1	32.23 ± 4.16	2.83 ± 0.42	4.87 ± 0.31	4.48 ± 0.28	2.98 ± 0.39			
	F2	247.78 ± 16.02	188.36 ± 1.08	99.32 ± 4.37	108.12 ± 7.48	108.48 ± 9.94			
	F3	187.37 ± 7.36	162.35 ± 47.40	173.49 ± 11.63	165.76 ± 18.31	149.17 ± 1.16			
	F4	337.29 ± 0.21	432.79 ± 4.64	489.38 ± 13.83	472.23 ± 36.07	493.32 ± 13.57			
	F5	69 ± 5	97 ± 12	163 ± 2	167 ± 11	158 ± 25			
Cr	F1	0.00	0.00	0.00	0.00	0.00			
	F2	10.49 ± 0.84	2.82 ± 0.14	1.81 ± 0.05	2.01 ± 0.20	2.32 ± 0.17			
	F3	58.34 ± 0.24	11.74 ± 1.33	8.16 ± 0.58	8.16 ± 0.62	8.33 ± 0.54			

Samp	le	Exp. No.11	Exp. No.12	Exp. No.13	Exp. No.14	Exp. No.15
	F4	625.04 ± 1.15	457.33 ± 1.80	530.77 ± 14.62	567.19 ± 79.83	531.51 ± 9.11
	F5	270 ± 2	502 ± 1	529 ± 14	513 ± 79	508 ± 8
Ni	F1	32.95 ± 3.45	6.73 ± 0.35	2.75 ± 0.32	3.89 ± 0.63	4.05 ± 0.05
	F2	48.05 ± 2.92	33.88 ± 0.32	12.77 ± 1.23	14.20 ± 1.79	16.85 ± 7.01
	F3	72.46 ± 2.42	40.23 ± 5.21	31.07 ± 2.01	31.59 ± 2.40	31.31 ± 1.60
	F4	339.20 ± 5.70	380.91 ± 9.92	354.27 ± 7.02	351.00 ± 28.00	371.17 ± 12.00
	F5	473 ± 3	515 ± 5	648 ± 5	646 ± 25	614 ± 15
Pb	F1	4.35 ± 0.32	0.00	0.00	0.00	0.00
	F2	149.04 ± 8.92	68.85 ± 0.51	60.91 ± 4.90	57.87 ± 7.72	65.04 ± 6.60
	F3	223.15 ± 10.93	150.58 ± 23.23	82.98 ± 4.69	82.69 ± 5.19	82.95 ± 2.68
	F4	455.56 ± 6.02	409.90 ± 11.36	546.30 ± 26.51	537.51 ± 60.50	522.86 ± 13.04
	F5	87 ± 8	300 ± 11	338 ± 17	347 ± 48	325 ± 22
Zn	F1	42.75 ± 4.58	5.35 ± 0.28	2.97 ± 0.11	3.03 ± 0.24	3.50 ± 0.01
	F2	76.56 ± 4.70	51.32 ± 0.63	30.10 ± 1.67	29.84 ± 3.23	38.15 ± 3.08
	F3	145.86 ± 18.47	102.68 ± 18.60	57.43 ± 1.87	56.51 ± 1.86	57.80 ± 4.23
	F4	453.45 ± 10.08	414.52 ± 21.50	515.58 ± 4.50	503.28 ± 35.63	512.39 ± 14.88
	F5	290 ± 8	446 ± 3	509 ± 1	512 ± 31	476 ± 22



Figure B1. FT-IR spectra of the feedstock and solid residues after pyrolysis (SRC: solid residue sample from control experiment without pyrolysis treatment; SROx: solid residue from oily waste pyrolysis alone at X ($^{\circ}$ C) temperature and reaction time = 75 min; SROHx: solid residue from co-pyrolysis of oily waste and hog fuel at X ($^{\circ}$ C) temperature and reaction time = 75 min and hog fuel at X ($^{\circ}$ C) temperature and reaction time = 75 min and hog fuel at X ($^{\circ}$ C) temperature and reaction time = 75 min and hog fuel at X ($^{\circ}$ C) temperature and reaction time = 75 min and hog fuel at X ($^{\circ}$ C) temperature and reaction time = 75 min and hog fuel addition = 20%

APPENDIX C

		Concentration (mg/kg)							
Fractions	Cd	Pb	Cr	Cu	Ni	Zn			
F1: Water soluble	_a	—	_	_	_	_			
F2: Exchangeable		_	—	5.9	_	—			
F3: Bound to carbonate		_	8.5	54.5	_	115.5			
F4: Bound to Fe-Mn oxides	_	_	_	27.9	_	_			
F5: Bound to organic matter	_	_	_	68.5	_	71.7			
F6: Residual	_	_	8.5	2.5	1.6	2.4			

Table C1. Sequential extraction results of OS500-B

^a Below detection limit.

F1–F5 detection limit (mg/L): Cd (0.06), Pb (0.9), Cr (0.06), Cu (0.1), Ni (0.2) Zn (0.3); F6 detection limit (mg/kg): Cd (0.6), Pb (9), Cr (0.6), Cu (1), Ni (2), and Zn (3).

Fractions	OS500-Pb		OS500-Cd		
	mg/g	%	mg/g	%	
F1: Water soluble	_a	0.00	$0.02\pm\!0.00$	0.11	
F2: Exchangeable	1.38 ± 0.52	0.45	2.93 ± 0.09	15.12	
F3: Bound to carbonate	303.42 ± 11.90	98.06	16.31 ± 0.67	84.15	
F4: Bound to Fe-Mn oxides	4.51 ± 0.35	1.46	0.12 ± 0.01	0.62	
F5: Bound to organic matter	_	0.00	_	0.00	
F6: Residual	0.11 ± 0.01	0.04	_	0.01	

Table C2. Sequential extraction results of OS500-Pb and OS500-Cd

^a Below detection limit.

F1–F5 detection limit (mg/L): Cd (0.06), Pb (0.9);

F6 detection limit (mg/kg): Cd (0.6), Pb (9).

Sample	Sum from each step in sequential extraction (mg/g)	Sorbed amount from equilibrium study (mg/g)	Recovery (%)
OS500-Pb	309.41 ± 12.18	351.48 ± 2.08	88.03
OS500-Cd	19.38 ± 0.75	23.95 ± 3.79	80.92

Table C3. Recovery of sequential extraction results of OS500-Pb and OS500-Cd



Figure C1. Determination of pH_{PZC} for OS500. Thick straight line represents $pH_{initial} = pH_{final}$ line.



Figure C2. Intraparticle diffusion plot for the sorption of (a) Pb^{2+} and (b) Cd^{2+} on OS500 (0.1g char in 30 mL solution (0.01 M NaNO₃), initial Pb^{2+} (or Cd^{2+}) concentration 1600 (1000) mg/L; room temperature 24 °C; initial solution pH 5).



Figure C3. Isotherms of (1) Pb²⁺ and (2) Cd²⁺ sorption onto OS500 (0.1g char in 30 mL solution (0.01 M NaNO₃); contact time 128 h; room temperature 24 °C; initial solution pH 5).

APPENDIX D

Sam	ple	OS300-B	OS500-B	OS700-B	OS900-B	OS500N100-8M-B
Extra	actable	e fractions (mg	g/kg)			
Cd	F1	_a	_	_	_	_
	F2	_	_	_	_	_
	F3	_	_	_	_	_
	F4	_	_	_	_	_
	F5	_	_	_	_	_
	F6	_	_	_	_	_
Pb	F1	_	_	_	_	_
	F2	_	_	_	_	_
	F3	_	_	_	_	_
	F4	_	_	_	_	_
	F5	_	_	_	_	_
	F6	_	_	_	_	_
Cr	F1	-	-	_	_	_
	F2	_	_	_	_	_
	F3	8.4	8.5	12.3	8.7	18.6
	F4	_	_	16.6	24.5	17.1
	F5	_	_	_	_	_
	F6	7.6	8.5	8.9	5.0	5.1
Cu	F1	_	_	_	_	_
	F2	_	5.9	_	_	_
	F3	53.7	54.5	36.7	16.9	43.8
	F4	53.8	27.9	77.3	64.3	106.7
	F5	38.0	68.5	34.0	60.7	30.4
	F6	2.2	2.5	3.1	2.0	1.5
Ni	F1	_	_	_	_	_
	F2	_	_	_	_	_
	F3	_	_	31.0	_	_
	F4	_	_	_	_	-
	F5	_	_	_	_	-
	F6	3.1	1.6	_	1.4	1.4

Table D1. Sequential extraction results of OSDCs before Pb^{2+}/Cd^{2+} sorption

Sam	ple	OS300-B	OS500-B	OS700-B	OS900-B	OS500N100-8M-B
Extra	actable	e fractions (m	g/kg)			
Zn	F1	_	_	_	_	_
	F2	_	_	_	_	_
	F3	79.1	115.5	104.9	125.5	28.3
	F4	_	_	_	_	_
	F5	64.8	71.7	77.4	_	_
	F6	7.4	2.4	_	4.1	1.8

^aBelow detection limit. F1–F5 detection limit (mg/L): Cd (0.06), Pb (0.9), Cr (0.06), Cu (0.1), Ni (0.2) Zn (0.3); F6 detection limit (mg/kg): Cd (0.6), Pb (9), Cr (0.6), Cu (1), Ni (2), and Zn (3).

Table D2. Sequential extraction results of Pb-loaded/Cd-loaded OSD

Chars	Fractions	Loaded with Pb ²⁺		Loaded with Cd ²⁺	
_		mg/g	%	mg/g	%
OS300	1	_a	0.00	0.41 ± 0.08	1.34
	2	1.71 ± 0.13	0.81	6.29 ± 0.33	20.66
	3	205.22 ± 1.38	97.81	23.56 ± 1.72	77.40
	4	2.86 ± 0.04	1.36	0.18 ± 0.02	0.59
	5	_	0.00	_	0.00
	6	0.04 ± 0.00	0.02	_	0.00
OS500	1	_	0.00	0.02 ± 0.00	0.11
	2	1.38 ± 0.52	0.45	2.93 ± 0.09	15.12
	3	303.42 ± 11.90	98.06	16.31 ± 0.67	84.15
	4	4.51 ± 0.35	1.46	0.12 ± 0.01	0.62
	5	_	0.00	—	0.00
	6	0.11 ± 0.01	0.04	—	0.01
OS700	1	0.29 ± 0.06	0.13	0.02 ± 0.00	0.03
	2	0.44 ± 0.21	0.20	8.79 ± 1.16	10.65
	3	203.16 ± 6.91	92.99	72.73 ± 2.75	88.21
	4	13.64 ± 1.53	6.24	0.82 ± 0.60	0.99
	5	0.39 ± 0.02	0.18	0.06 ± 0.01	0.07
	6	0.56 ± 0.08	0.26	0.04 ± 0.00	0.05
OS900	1	2.10 ± 0.39	5.46	0.33 ± 0.07	3.29
	2	2.97 ± 0.20	7.73	3.00 ± 0.25	29.78
	3	30.44 ± 2.23	79.30	6.17 ± 0.19	61.35
	4	2.83 ± 0.51	7.37	0.55 ± 0.02	5.42

Chars	Fractions	Loaded with Pb ²⁺		Loaded with Cd ²⁺	
_		mg/g	%	mg/g	%
	5	_	0.00	_	0.00
	6	0.05 ± 0.00	0.14	0.02 ± 0.00	0.15
OS500N100-8M	1	_	0.00	_	0.00
	2	0.76 ± 0.57	0.28	4.71 ± 0.25	5.59
	3	257.90 ± 7.91	95.34	78.29 ± 6.24	92.96
	4	11.58 ± 0.18	4.28	1.22 ± 0.02	1.45
	5	0.25 ± 0.02	0.09	_	0.00
	6	0.03 ± 0.00	0.01	_	0.00

^a Below detection limit.

Fraction 1–5 detection limit (mg/L): Cd (0.06), Pb (0.9); Fraction 6 detection limit (mg/kg): Cd (0.6), Pb (9)

	Sum from each step	Sorbed amount	
Sample	in sequential	from equilibrium	Recovery
	extraction (mg/g)	study (mg/g)	(%)
OS300-Pb	209.82 ± 1.29	282.96 ± 3.22	74.15
OS500-Pb	309.41 ± 12.18	351.48 ± 2.08	88.03
OS700-Pb	218.48 ± 8.58	261.14 ± 2.02	83.66
OS900-Pb	38.38 ± 2.76	49.68 ± 2.31	77.25
OS500N100-8M-Pb	270.52 ± 7.91	310.00 ± 2.19	87.26
OS300-Cd	30.44 ± 1.99	46.67 ± 0.69	65.22
OS500-Cd	19.38 ± 0.75	23.95 ± 3.79	80.92
OS700-Cd	82.46 ± 3.88	92.14 ± 3.11	89.49
OS900-Cd	10.06 ± 0.33	11.05 ± 1.50	91.04
OS500N100-8M-Cd	84.22 ± 6.30	90.06 ± 3.17	93.52

Table D3. Recovery of sequential extraction results of Pb-loaded/Cd-loaded (OSDCs
------------------------------------------------------------------------------	--------------

	S _{BET}	PV	Ash%	CEC	H/C	Q _{p,Pb}	Q _{t,Pb}	Q _{cm,Cd} ^a	$Q_{cf,Cd}$	Q _{t,Cd}
\mathbf{S}_{BET}	1.00									
PV	0.88	1.00								
Ash%	-0.08	0.16	1.00							
CEC	0.73	0.97^{*}	0.34	1.00						
H/C	0.82	0.95	-0.12	0.90	1.00					
Qp, Pb	0.48	0.10	-0.85	-0.15	0.25	1.00				
Qt,Pb	0.68	0.32	-0.73	0.07	0.43	0.97^{*}	1.00			
$Q_{cm,Cd}{}^a$	0.89	1.00^{**}	0.11	0.95*	0.96*	0.15	0.36	1.00		
$Q_{cf,Cd}$	0.81	0.99^{*}	0.14	0.98^{*}	0.97^{*}	0.04	0.25	0.99^{*}	1.00	
Q _{t,Cd}	0.83	0.99**	0.12	0.97^{*}	0.97^{*}	0.08	0.29	0.99**	1.00**	1.00

Table D4. Pearson correlation coefficient matrix between OSDCs properties and Pb²⁺/Cd²⁺ sorption mechanism

^a OS500N100-8M was not included; ^{*} Significant (P < 0.05); ^{**} Highly significant (P < 0.01).



Figure D1. XRD patterns of OSDCs before Pb^{2+}/Cd^{2+} sorption (OSDC-B). Minerals with peaks labeled: M, Muscovite 2M2, $K_{0.77}Al_{1.93}(Al_{0.5}Si_{3.5})O_{10}(OH)_2$; B, Barite, BaSO₄; Q, Quartz, SiO₂; C, Calcite, CaCO₃; D, Dolomite, CaMg(CO₃)₂; O, Calcium oxide, CaO; Cl, Celsian, BaAl₂Si₂O₈; Bo, Barium oxide hydrate, BaO₂ (H₂O)₈; F, Ferritungstite, (W, Fe)(O,OH)₃; W, Witherite, BaCO₃.



Figure D2. FTIR spectra of OSDC before Pb²⁺/Cd²⁺ sorption (OSDC-B).