Commercial Douglas fir biochar based multifunctional exotic adsorbents for water remediation

Chanaka Navarathna
chanaka89@yahoo.com

Follow this and additional works at: https://scholarsjunction.msstate.edu/td

Recommended Citation
https://scholarsjunction.msstate.edu/td/5191

This Dissertation - Open Access is brought to you for free and open access by the Theses and Dissertations at Scholars Junction. It has been accepted for inclusion in Theses and Dissertations by an authorized administrator of Scholars Junction. For more information, please contact scholcomm@msstate.libanswers.com.
Commercial Douglas fir biochar based multifunctional exotic adsorbents for water remediation

By

Chanaka Navarathna

Approved by:

Todd E. Mlsna (Major Professor)
Charles U. Pittman Jr.
David O. Wipf
Debra A. Mlsna
Dongmao Zhang
Joseph Emerson (Graduate Coordinator)
Rick Travis (Dean, College of Arts & Sciences)

Submitted to the Faculty of Mississippi State University in Partial Fulfillment of the Requirements for the Degree of PhD in Chemistry in the Department of Chemistry (College of Arts & Sciences)

Mississippi State, Mississippi

August 2021
Providing safe drinking water and wastewater remediation are constant worldwide challenges. Adsorption is an attractive alternative to conventional techniques such as coagulation, precipitation (chemically or electrochemically), hybrid membranes, and ion-exchange for the purification of water. Biochar-based composite sorbents are increasingly popular because a range of surface chemical and physical treatments can impart performance and environmental benefits to the material. This is ideal for rural areas where more costly conventional methods may not be readily available or affordable. This dissertation focused on three different projects involving high surface area (~700 m²/g) Douglas fir biochar based multifunctional engineered adsorbents. Chapter II focuses on arsenic (III) adsorptive removal onto magnetic iron oxide dispersed onto biochar. This chapter highlights the adsorptive and redox properties of biochar composites for pollutant toxicity reduction. Chapter III focuses on pollutant toxicity neutralization after adsorption, simultaneous adsorption, and multi-phase adsorption. A MIL-53-MOF magnetite/magnetic biochar composite model system was used to demonstrate simultaneous chromium (VI) adsorption and organic pollutant rhodamine (RhB) degradation. Chapter IV is focused on tailoring the biochar to change its physical properties
(enhance hydrophobicity) to achieve a specific pollutant treatment requirement (buoyancy). Oil spill remediation was used as a model example for this purpose and lauric acid-decorated magnetite biochar composite was introduced. The composites and their pollutant-loaded analogues were extensively characterized using BET, SEM, TEM, EDS, XRD, VSM, PZC, Elemental analysis, TGA, DSC, FT-IR and XPS.
DEDICATION

This dissertation is dedicated to my parents, the love of my life, and Dr. Charles U. Pittman Jr.

*For supporting and encouraging me to believe in myself*
ACKNOWLEDGEMENTS

Firstly, I would like to express my deepest appreciation to my advisor, Dr. Todd Mlsna, for the continuous support for my research, his patience, motivation, and immense knowledge. Very special gratitude goes out to Dr. Charles U. Pittman Jr for support and guidance.

I would also like to thank all my committee members, Dr. David O. Wipf, Dr. Dongmao Zhang, and Dr. Deb Mlsna, for their comments and suggestions. In addition, I would like to thank my teaching coordinator, Dr. Sean Stokes, for all his support for my instrument teaching career. Furthermore, I would like to thank Dr. Dinesh Mohan, Dr. E Barbery Hassan, Dr, Rooban, Dr. Felio Perez, Ms. Renel Anderson, Dr. Xuefeng Zhang, and Ms. Jacinta Alchouron, and all my collaborators for their valuable assistance.

My special thanks to fantastic undergraduate researchers who have given so much of their time to assist my experiments in numerous ways. I appreciate their hard work and effort. Also, I would thank all my lab mates, past and present, who in diverse ways have made an enormous contribution towards the successful completion of my Ph.D. program.

Last but by no means least, I am grateful to my family members and Hasini, who have encouraged me through moral and emotional support in my life. I am also grateful to my friends, especially, Akila, Sunith, Prashan, Tharindu, and Randika, who have supported me along the way.
# TABLE OF CONTENTS

DEDICATION .......................................................................................................................... ii  
ACKNOWLEDGEMENTS ......................................................................................................... iii  
LIST OF TABLES ....................................................................................................................... viii  
LIST OF FIGURES ..................................................................................................................... x  
LIST OF SCHEMES ................................................................................................................... xv  

CHAPTER

I. INTRODUCTION ..................................................................................................................... 1  
   1.1 Adsorption for water remediation ................................................................. 1  
   1.2 Carbonaceous materials .............................................................................. 2  
      1.2.1 Activated carbon ................................................................. 2  
      1.2.2 Biochar ................................................................. 3  
         1.2.2.1 Biochar preparation and features ......................................... 4  
         1.2.2.2 Biochar engineering strategies to enhance adsorption ......... 8  
            1.2.2.2.1 Advantages of preparing biochar composites .......... 9  
            1.2.2.2.2 Fe-based biochar composites .................................. 10  
            1.2.2.2.3 Biochar for oil remediation .................................. 11  
   1.3 Dissertation objectives and broader impact in water remediation .......... 13  
   1.4 REFERENCES ................................................................................................. 15  

II. REMOVAL OF ARSENIC(III) FROM WATER USING MAGNETITE  
   PRECIPITATED ONTO DOUGLAS FIR BIOCHAR ....................................................... 24  
   2.1 Abstract ........................................................................................................ 24  
   2.2 Introduction .................................................................................................... 25  
   2.3 Methods and materials ............................................................................. 27  
      2.3.1 Materials ............................................................................. 27  
      2.3.2 Preparation of magnetically modified biochar ......................... 27  
      2.3.3 Characterization of BC, MBC and As(III)-laden MBC ............... 28  
      2.3.4 Batch sorption studies ......................................................... 29  
      2.3.5 Competitive batch sorption studies ........................................ 30  
      2.3.6 Fixed-bed column breakthrough and stripping regeneration studies .... 30  
      2.3.7 Sample preparation for XPS studies on arsenic redox effects ....... 31
III. RHODAMINE B ADSORPTIVE REMOVAL AND PHOTOCATALYTIC DEGRADATION ON MIL-53-FE MOF/MAGNETIC MAGNETITE/BIOCHAR COMPOSITES ................................................. 60

3.1 Abstract ............................................................................................................. 60
3.2 Introduction ......................................................................................................... 61
3.3 Materials and methods ....................................................................................... 64
  3.3.1 Synthesis of MIL-53 Fe MOF and MOF-MBC composite ......................... 64
  3.3.2 Adsorption kinetics and isotherm experiments ........................................... 65
  3.3.3 Characterization of BC, MBC, MIL-53-Fe MOF and MOF-MBC ............ 67
3.4 Results and discussion ......................................................................................... 69
  3.4.1 Characterization of MIL-53-Fe MOF, MBC, and MOF-MBC ................. 69
    3.4.1.1 Surface morphology ........................................................................ 69
    3.4.1.2 X-ray diffraction analysis ............................................................... 71
  3.4.2 FTIR analysis ................................................................................................ 72
    3.4.2.1 Elemental, proximate and surface area analysis .............................. 75
    3.4.2.2 Thermogravimetric analysis (TGA) .............................................. 77
    3.4.2.3 X-ray photoelectron Spectroscopy (XPS) .................................... 78
  3.4.3 Adsorption kinetics and isotherms on MOF-MBC ..................................... 84
    3.4.3.1 pH dependence of Rh B adsorption .............................................. 84
    3.4.3.2 Kinetics .......................................................................................... 86
    3.4.3.3 Isotherms and thermodynamics of adsorption ............................... 86
    3.4.3.4 Comparison of adsorbents for simultaneous removal of Rh B and Cr(VI) ................................................................. 87
    3.4.3.5 Degradation product identification .............................................. 91
    3.4.3.6 Iron leaching experiments ............................................................ 92
    3.4.3.7 Comparison of adsorbents for Rh B sorption and photocatalytic degradation ................................................................. 93
3.5 Conclusions ......................................................................................................... 94
3.6 REFERENCES .................................................................................................... 96
IV. BIOCHAR ADSORBENTS WITH ENHANCED HYDROPHOBICITY FOR OIL SPILL REMOVAL ......................................................... 102

4.1 Abstract .................................................................................................................. 102
4.2 Introduction ............................................................................................................. 103
4.3 Methods and Materials ......................................................................................... 105
  4.3.1 Preparation of magnetite-bearing magnetic biochar, lauric acid-decorated biochar and two types of lauric acid-decorated and magnetite-bearing magnetic biochar analogues ........................................ 105
  4.3.2 Characterization methods .................................................................................. 107
  4.3.3 The lauric acid wt % effect on BC sinking and oil uptake .............................. 110
  4.3.4 Oil recovery and adsorbent recycling ............................................................... 110
  4.3.5 Sorption experiments ....................................................................................... 111
4.4 Results .................................................................................................................... 112
  4.4.1 Characterization results .................................................................................... 112
    4.4.1.1 Effect of lauric acid (LA) and LA wt % on BC for sinking .................... 112
    4.4.1.2 Surface morphology ............................................................................... 114
    4.4.1.3 Surface area and elemental analysis ...................................................... 115
    4.4.1.4 FTIR analysis ....................................................................................... 118
    4.4.1.5 XRD analysis and explanation of particle sizes of precipitated Fe_{3}O_{4} 119
    4.4.1.6 Contact angle (CA) measurements ....................................................... 121
    4.4.1.7 Thermal analysis ................................................................................... 123
    4.4.1.8 Magnetic moment (M) experiments ....................................................... 125
  4.4.2 Adsorption results ............................................................................................ 127
    4.4.2.1 pH dependence of sorption .................................................................... 127
    4.4.2.2 Sorption kinetics .................................................................................. 128
    4.4.2.3 Sorption isotherms ............................................................................... 128
    4.4.2.4 Effect of sea water and temperature on crude oil uptake ..................... 132
  4.4.3 Adsorbent sustainability .................................................................................... 133
    4.4.3.1 Effect of Lauric acid dose ...................................................................... 133
    4.4.3.2 Oil recovery and adsorbent recycling .................................................... 134
    4.4.3.3 Heating values .................................................................................... 134
    4.4.3.4 Comparison of adsorbents ................................................................... 137
4.5 Conclusion ............................................................................................................. 138
4.6 REFERENCES ....................................................................................................... 140

APPENDIX

A. REMOVAL OF ARSENIC(III) FROM WATER USING MAGNETITE
   PRECIPITATED ONTO DOUGLAS FIR BIOCHAR .............................................. 145

A.1 Characterization of BC, MBC and As-laden MBC .............................................. 146
  A.1.1 Point of zero charge (PZC) measurements .................................................. 146
  A.1.2 Surface Morphological characterization ....................................................... 146
  A.1.3 X-ray powder diffraction (XRD) and X-ray photoelectron spectroscopy
       (XPS) .............................................................................................................. 147
LIST OF TABLES

Table 2.1 Thermodynamic parameters for the adsorption of As(III) by MBC from 20-40 °C.a .........................................................................................................................39

Table 2.2 Comparative evaluation of various adsorbents for As(III) and As(V) removal at room temperature (22-25 °C)a ..................................................................................43

Table 3.1 Elemental, proximate analysis and surface area data for BC, MBC, MOF, MOF-MBC and Rh-laden MOF-MBC ........................................................................................................77

Table 3.2 High resolution (HR) C1s, O1s and Fe2p XPS data for BC, MBC, MIL-53-Fe MOF, MOF-MBC and Rh B-laden MOF-MBC ...................................................................................82

Table 3.3 Comparative evaluation of various adsorbents/catalysts for Rh B sorption and degradationa .................................................................................................................................93

Table 4.1 Elemental, proximate analysis and surface area data for adsorbents and oil-laden adsorbents. a,b,c ..........................................................................................................................117

Table 4.2 Contact angle data for BC, LBC, MBC, MLBC and LMBC .........................................................................................................................123

Table 4.3 Saturation magnetization (or Magnetic moments) (M) values vs Fe3O4 crystallite particle sizes from XRD and Debye-Scherrer equation ......................................................127

Table 4.4 Summary of oil uptake (transmission, machine and engine oils) for BC, LBC, MBC, LMBC and MLBC over the pH 1-13 range (25 °C, 1 h equilibration) ..............128

Table 4.5 Sips isotherm model data for transmission, machine and engine oils at 25 °C (pH = 7 and 1 hour equilibration).a,b ............................................................................................................130

Table 4.6 Comparison to oil absorbents in the literature .........................................................................................................................138

Table A.1 Calculation for iron oxide (Fe3O4) yield .................................................................................................................................150

Table A.2 Isotherm data fits for adsorption of As(III) on MBC at 20, 25 and 40 °C, pH = 7, 1 h equilibration time. b .....................................................................................................................151

Table A.3 C1s and O1s XPS binding energies for inorganic and organic or polymeric carbonates, aldehydes, ketones and carboxylic acids. .............................................................................152
Table A.4  Amounts of Fe chemical contents found in surface regions of MBC before and after As(III) adsorption XPS

Table A.5  O1s and Fe2p core level binding energies for MBC (pH 7) samples and atomic charges of their adsorbent surface species.

Table A.6  HR-XPS data for As(III)- and As(V)-laden MBC prepared at pH 2, 7, 12 under oxic and anoxic conditions

Table C.2  Low resolution (LS) survey scan XPS data for biochar (BC), lauric acid-coated biochar (LBC), Fe$_3$O$_4$-modified biochar (MBC), lauric acid-biochar modified with Fe$_3$O$_4$ (LMBC) and Fe$_3$O$_4$-modified biochar coated with lauric acid (MLBC) and their crude oil-laden analogues.

Table C.3  High resolution (HR) C1s deconvoluted XPS data for biochar (BC), lauric acid-coated biochar (LBC), Fe$_3$O$_4$-modified biochar (MBC), lauric acid-biochar modified with Fe$_3$O$_4$ (LMBC) and Fe$_3$O$_4$-modified biochar coated with lauric acid (MLBC) and their crude oil-laden analogues.

Table C.4  High resolution (HR) O1s deconvoluted XPS data for biochar (BC), lauric acid-coated biochar (LBC), Fe$_3$O$_4$-modified biochar (MBC), lauric acid-biochar modified with Fe$_3$O$_4$ (LMBC) and Fe$_3$O$_4$-modified biochar coated with lauric acid (MLBC) and their crude oil-laden analogues.
LIST OF FIGURES

Figure 1.1 Biochar based multifunctional adsorbents for water treatment ...........................................11

Figure 2.1 SEM micrographs of BC (a) and MBC (b-d) and TEM and TEM-EDX elemental mapping images of (e) BC (f) MBC (g) As-loaded MBC (h) As-loaded MBC, focused on a magnetite aggregate. Gray and black particles are BC and MBC composites lying on the copper grid. As-loaded MBC samples were prepared using pH 7, 12 mg/L [As(III)] solutions (25 mL) equilibrated with 50 mg of MBC for 1h at 25 °C (2 g/L dose). ..........................................................32

Figure 2.2 pH dependence of As(III) (10 mg/L) adsorption onto BC and MBC (at 25 °C and 1 h equilibration) and fractional composition curves for As(III) speciation. (Error bars represent the standard deviation of 3 replicates). Note that the $H_4AsO_4^+$ speciation is not shown in the graph due to the unavailability of equilibrium constants for $H_4AsO_4^-$ formation. ..................................................35

Figure 2.3 a) Normalized adsorption vs time for initial As(III) concentrations of 5, 10, 20 mg/L (at 25 °C and pH 7), b) Fits to the Sips isotherm of As(III) adsorption on MBC at 20, 25 and 40 °C (pH = 7, 1 h equilibration time) (Error bars represent the standard deviation of 3 replicates) and c) van’t Hoff plot of lnKs vs 1/T for the As(III) adsorption on MBC from 20-40 °C. ....................38

Figure 2.4 a) Breakthrough curve for As(III) adsorption onto MBC and b) desorption curve for As(III) (particle size, 300-500 µm range) .................................................................41

Figure 2.5 HR-XPS deconvolutions of MBC’s C1s, O1s and Fe2p (a), (c) and (g) spectra, respectively, before As(III) adsorption and also As(III)-laden MBC’s C1s, O1s and Fe2p (b), (d) and (h) spectra, respectively. Deconvolution of As2p (e) and As3d (f) spectra for arsenic-laden MBC, initially prepared by As(III) adsorption are also given. (CPS – counts per second). Note that the As3p third peak was not identified due to its low signal to noise ratio. Experimental data is not distinguishable from curve fittings in C1s, O1s and Fe2p HR-XPS due to their high signal to noise ratio. .................................................................46

Figure 3.1 Structure of MIL-53-Fe MOF ..........................................................................................63

Figure 3.2 Schematic representation of a) MOF-MBC and b) the chemical structure of rhodamine B ......................................................................................................................64
Figure 3.3  SEM images of a), b) MIL-53-Fe MOF c) MBC and d) MOF-MBC ......................70

Figure 3.4  XRD data for MBC, MIL-53-Fe MOF and MOF-MBC ........................................72

Figure 3.5  FT-IR characterization of MBC, MIL-53-Fe MOF, Rh B, MOF-MBC and Rh-laden MOF-MBC .............................................................................................................74

Figure 3.6  Thermogravimetric analysis profiles of BC, MBC, MIL-53-Fe MOF and MOF-MBC (10 °C/min heating rate under 100 mL/min N₂) ........................................78

Figure 3.7  Low resolution (LS) survey scan XPS spectra for BC, MBC, MIL-53-Fe MOF, MOF-MBC and Rh B-laden MOF-MBC (CPS – counts per second). ..............79

Figure 3.8  High resolution (HR) C1s, O1s and Fe2p XPS spectra for a) BC, b) MBC, c) MIL-53-Fe MOF, d) MOF-MBC and e) Rh B-laden MOF-MBC (CPS – counts per second). The Roman numerals given on the C1s and O1s HR XPS spectra correspond to those assigned in Table 2. *Due to the complex nature of Fe2p, the curve-resolved peaks are not labeled here. These HR-XPS figs are given in expanded form in the supporting materials (Figures B.3, B.4, B.5, B.6 and B.7) with the assignments shown. ..............................................................83

Figure 3.9  pH dependence of aqueous Rh B adsorption onto MOF-MBC (50.0 mg MOF-MBC dose, 20 mL of 50 ppm Rh B, 1 h equilibration, 200 rpm agitation at 25 °C) ........................................................................................................85

Figure 3.10  Effect of contact time on Rh B adsorption at 25 °C onto MOF-MBC (50.0 mg dose MOF-MBC, 50 ppm Rh B (20 mL), pH = 6, and 200 rpm agitation) ..........86

Figure 3.11  Adsorption isotherms at 10, 25 and 40 °C of Rh B uptake on MOF-MBC and thermodynamics (50.0 mg MOF-MBC, 3 h equilibration, pH = 6, 20 mL solution and 200 rpm agitation) .............................................................................87

Figure 3.12  Comparison of adsorbents for removal of Rh B (~104 µM) and Cr(VI) (~231 µM) (1:2 mole ratio) (50.0 mg adsorbent, 3 h equilibration, pH = 6, 20 mL solution, 25 °C and 200 rpm agitation) .............................................................................89

Figure 3.13  Pseudo first order plots for photodegradation of Rh B (50.0 mg catalytic adsorbent, pH = 6, 25 °C and 20 mL of the solution) and (b) Rh B in the presence of Cr(VI) during adsorption on BC, MBC, MIL-53-Fe MOF and MOF-MBC (Initial Rh B and Cr(VI) concentrations were each 50 mg/L before sorptive equilibrium). .............................................................................91
Figure 4.1 a) Lauric acid surface uptake on BC, where outer surface and large pores are made hydrophobic, blocking water access to substantial pore volume further below the surface where lauric acid cannot penetrate; b) oil molecules adhering to lauric acid adsorbed at the biochar surfaces. More oil adsorbs to lauric acid, to already adsorbed oil and to hydrophobic biochar surface regions. Finally, oil takes up more oil building a thick coating; c1) Neat biochar sinks in water; c2) biochar after decoration with lauric acid floats and c3) effect of lauric acid dose on BC sinking (Lauric acid weight % (wt/wt %); 0.125 M = 2.0 %, 0.5 M = 1.2 % and 0.5 M = 3.9 %).

Figure 4.2 SEM-micrographs of a) BC, b) LBC, c) MBC, d) LMBC, e) MLBC and f) oil-laden LBC (8 g oil/g adsorbent).

Figure 4.3 a) FT-IR characterization, b) XRD data and c) thermogravimetric analysis profiles (10 °C/min heating rate under 100 mL/min N₂) of lauric acid, BC, LBC, MBC, LMBC and MLBC.*The amorphous biochar peak is due to aromatic plane region separations.

Figure 4.4 a) pH dependences of oil uptake (at 25 °C and 1 h of equilibration), b) Normalized uptake vs time plots (at 25 °C and pH 7) and c) Sips isotherm fits of oil sorption (25 °C, pH = 7, 1 h of equilibration) for BC, LBC, MBC, LMBC and MLBC.

Figure 4.5 Crude oil uptake by BC, LBC, MBC, LMBC and MLBC, b) temperature dependence of crude oil uptake and c) FT-IR of LBC before and after crude oil uptake vs neat crude oil (In each experiment 0.25 g of each adsorbent and 8.0 g of crude oil were equilibrated for 1 h at 25 °C water layer and pH = 7). *Characterization results are only presented for LBC and crude-oil laden LBC as the results for other adsorbents and crude-oil laden adsorbents were similar.

Figure 4.6 a) Effect of lauric acid dose on BC sinking and and crude oil uptake (Lauric acid weight %; 0.125 M = 2.0 %, 0.5 M = 1.2 % and 0.5 M = 3.9 %), b) crude oil uptake-recovery data for LBC and MLBC (25 °C, 1 hour in simulated sea water) and c) bomb calorimeter heating values for oils, adsorbents and oil-laden adsorbents.

Figure A.1 SEM-EDX spectra of (a) BC, (b) MBC and (c) arsenic-loaded MBC. As-loaded MBC samples were prepared using pH 7, 25.0 mL of 12 mg/L As(III) solution equilibrated with 50 mg of MBC for 1 h at 25 °C (2 g/L dose). The EDX-measured surface region weight percent of carbon dropped from ~84% on BC to ~58% on MBC due to Fe₃O₄ particle deposition. The weight percent of Fe varies at different surface locations due to aggregation and other factors inducing heterogeneity (eg ~26% Fe in (c) at a different location. The much smaller As coverage (0.10 wt%) in (c) could not account for this size drop in surface region %Fe.
Figure A.2 STEM-EDX spectra (a) BC, (b) MBC and (c), (d) arsenic-loaded MBC. Ars- 
loaded MBC samples were prepared using pH 7, 25.0 mL of 12 mg/L As(III) 
solution equilibrated with 50 mg of MBC for 1 h at 25 °C (2 g/L dose). .................159

Figure A.3 The powder XRD spectrum of MBC ........................................................................................................160

Figure A.4 As(III) isotherm data and fitted models a) Langmuir, b) Freundlich and c) 
Sips for As(III) adsorption on MBC. At 25 °C and pH = 7, 1 h equilibration 
time. (Error bars represent the standard deviation of 3 replicates) .........................161

Figure A.5 Dimensionless separation factor (RL) at the temperatures a) 20 °C, b) 25 °C 
and c) 40 °C. Where q_e is the equilibrium capacity of As(III) on MBC and Ce 
is the equilibrium As(III) concentration ..................................................................................162

Figure A.6 Concentrations of As(III) in MBC-treated waste water samples (25.0 mL) 
after 1 h contact with 100.0 mg of MBC at 25 °C at pH 7. Standard deviation 
for the average of 3 replicates of samples A, B and C are 0.02, 0.08 and 0.024 
mg/L, respectively. Note that the actual, speciation of oxyanions is not 
presented. Zinc concentrations in sample A and B are ~0.4 mg/L. Chemical 
laboratory heavy metal contains Cd^{2+}, Pb^{2+}, Cu^{2+}, Fe^{3+} and chromate. 4NA = 
4-nitroniline and SA = salicylic acid) ........................................................................163

Figure A.7 XPS survey spectra of MBC(a) after As(III) adsorption at pH 7 and (b) 
before As(III) adsorption. (CPS – counts per second) .................................................164

Figure A.8 Proposed complexes of AsO_3 trigonal pyramid on FeO_6 octahedra and FeO_4 
tetrahedra .........................................................................................................................................165

Figure A.9 HR-XPS for As(III)- and As(V)-laden MBC under anoxic (pH 2, 7 and 12 
and oxic conditions pH = 7). The anoxic conditions were maintained using 
argon purged solutions in the sorption studies ........................................................................166

Figure B.1 TEM images and element mapped TEM images of a) MBC, b) MIL-53-Fe 
MOF, c) MOF-MBC and d) Rh B-laden MOF-MBC ............................................................171

Figure B.2 TEM-EDX spectra (a) MOF, (b) MBC and (c) MOF-MBC and (d) Rh-laden 
MOF-MBC .....................................................................................................................................172

Figure B.3 Resolved and assigned HR-XPS spectra for C1s, O1s and Fe2p for BC (CPS 
– counts per second) ..................................................................................................................173

Figure B.4 Resolved and assigned HR-XPS spectra for C1s, O1s and Fe2p for MBC 
(CPS – counts per second) ...........................................................................................................174

Figure B.5 Resolved and assigned HR-XPS spectra for C1s, O1s and Fe2p for MIL-53- 
Fe MOF (CPS – counts per second) ..........................................................................................175
Figure B.6  Resolved and assigned HR-XPS spectra for C1s, O1s and Fe2p for MOF-MBC (CPS – counts per second). .......................................................................................................................... 176

Figure B.7  Resolved and assigned HR-XPS spectra for C1s, O1s and Fe2p for Rh B-laden MOF-MBC (CPS – counts per second). .......................................................................................................................... 177

Figure B.8  LC-UV Chromatograms for the separation of Rh B from its degradation products for the photocatalysis experiments (in the presence of Cr(VI)) with (a) no catalyst, (b) BC, (c) MBC, (d) MIL-53-Fe MOF and (e) MOF-MBC (UV detection wavelength = 254 nm). .......................................................................................................................... 178

Figure B.9  ESI mass spectra for chromatographic peaks [in the presence of Cr(VI)]; (a) no catalyst, (b) BC, (c) MBC, (d) MIL-53-Fe MOF and (e) MOF-MBC .......................................................... 179

Figure B.10 Leaching of iron from the adsorbents, BC MBC, MIL-53-Fe MOF and MOF-MBC at pH 1-13 into (a) aqueous Rh B (50 mg/L) and (b) aqueous Rh B + Cr(VI) (50 mg/L) (Each adsorbent 50 mg in 25.0 mL water at the indicated pH was stirred for 3 hrs time at 200 rpm in a shaker) .......................................................................................................................... 180

Figure C.1 Differential scanning calorimetric (DSC) analysis profiles (10 °C/min heating rate under 50 mL/min N2) of lauric acid, biochar (BC), lauric acid-coated biochar (LBC), Fe3O4-modified biochar (MBC), lauric acid-biochar modified with Fe3O4 (LMBC) and Fe3O4-modified biochar coated with lauric acid (MLBC) ......................................................................................................................... 182

Figure C.2 Magnetic moments of lauric acid-coated biochar (LBC), lauric acid coated magnetic biochar (LMBC) and magnetic biochar-coated with lauric acid (MLBC) at 5 and 300 K by VSM ......................................................................................................................... 183

Figure C.3 Low resolution (LS) survey scan XPS spectra for biochar (BC), lauric acid-coated biochar (LBC), Fe3O4-modified biochar (MBC), lauric acid-biochar modified with Fe3O4 (LMBC) and Fe3O4-modified biochar coated with lauric acid (MLBC) and their crude oil-laden analogues (CPS – counts per second). ...... 185

Figure C.4 High resolution (HR) C1s deconvoluted XPS spectra for (a) biochar (BC), (b) lauric acid-coated biochar (LBC), (c) Fe3O4-modified biochar (MBC), (d) lauric acid-biochar modified with Fe3O4 (LMBC) and (e) Fe3O4-modified biochar coated with lauric acid (MLBC) and (f-j) their crude oil-laden analogues (CPS – counts per second) ......................................................................................................................... 187

Figure C.5 High resolution (HR) O1s deconvoluted XPS spectra for (a) Biochar (BC), (b) lauric acid-coated biochar (LBC), (c) Fe3O4-modified biochar (MBC), (d) lauric acid-biochar modified with Fe3O4 (LMBC) and (e) Fe3O4-modified biochar coated with lauric acid (MLBC) and (f-j) their crude oil-laden analogues (CPS – counts per second) ......................................................................................................................... 189
LIST OF SCHEMES

Scheme 2.1 Mechanism of As(III) sorption. Structure 9 ([72])..........................................................50

Scheme 4.1 Preparation of magnetite-coated magnetic biochar char (MBC), lauric acid-coated biochar (LBC), lauric acid-coated magnetite-bearing biochar (LMBC) and magnetite-bearing magnetic biochar coated with lauric acid (MLBC). ..........107

Scheme 4.2 Capping growth of nano Fe$_3$O$_4$ particles during their formation during LMBC synthesis in pH 10 solution. This capping does not occur during MBC synthesis and would be less likely in MLBC synthesis..................................................121

Scheme A.1 As(III)-magnetite hydrogen bonding effects .................................................................167
CHAPTER I
INTRODUCTION

(Published in ACS Symp. Ser. Am. Chem. Soc. 2020, 1352, Chapter 11, 197-251)

(In press Elsivier, Sustainable Biochar for Water and Wastewater Treatment)

1.1 Adsorption for water remediation

Providing safe drinking water and waste remediation is a current, major challenge worldwide. Adsorption is an attractive alternative to conventional techniques such as coagulation, precipitation (chemically or electrochemically), hybrid membranes, ion-exchange. Adsorption is a surface phenomenon that can be discussed in terms of physical and chemical adsorption surface forces that attract analytes [1]. Strong interactions between the adsorbate and the adsorbent in chemical adsorption include covalent bonds formed during chemisorption and ionic bond formation. Physical adsorption interactions are weaker and include hydrogen bonding, dipole-dipole, π-stacking, and van der Waals attraction. Charged molecules are more readily adsorb onto charged surfaces than neutral molecules. Adsorption is widely employed because of its cost-effectiveness, high removal efficiency, ease of operation and environmental sustainability. This is ideal for rural areas, and it generates lower environmental impacts than conventional technologies [2, 3]. Traditional adsorbents include activated alumina, activated carbon, and iron oxide-based sorbents. Recent attention has been given to low-cost sorbents produced from accessible and abundant natural sources such as clays, iron oxides, zeolites [3, 4],
soils [5-7], bio-sorbents or non-living biomass [8, 9], and low-cost carbonaceous materials or biochars [10, 11].

1.2 Carbonaceous materials

Carbonaceous products such as activated carbon and biochar show preferred activity towards adsorbing contaminants, and as a result have been widely studied for removing a large variety of pollutants from wastewater and residues [12, 13]. These substances’ high availability and high efficacy due to their large surface area and porosity makes them preferable to other sorbents for the purpose of removing oil. Research focuses in recent years have shifted from activated charcoal to include biochar (BC). It has been found that BC could be a sorbent with a potentially greater scope with purposes such as oil spill cleanup, metal removal in wastewater, soil amendment, and as a purifier for air contaminated with volatile organic compounds [12-15]. The sorption capacity of BC can even be further improved by modifying the surface area and microporosity [16, 17].

1.2.1 Activated carbon

AC is used for water remediation because it provides a high surface area, a well-developed pore structure, and an abundance of surface functional groups that interact with adsorbates. Typically, AC feedstocks such as agricultural and industrial waste are cheap, but their activation is expensive. They are activated chemically or physically. Rice husk [18], coconut shell, sugarcane bagasse [19], tea waste, palm tree cobs, potato peel, and bean pod waste [20] are widely used in AC production.

However, AC is not widely used for anionic contaminant removal. The surfaces of ACs are most likely to be negatively charged at pH ~ 7; therefore, electrostatic repulsion causes low
removal capacities [21], Sorbents combining ACs and metal oxides/hydroxides have been developed to solve this problem [21, 22]. Nevertheless, aqueous pollutant removal from modified AC is still expensive. Manufacturing AC is costly, and modifications add extra cost. Low-cost and effective alternative sorbents are still required.

1.2.2 Biochar

Biochar is defined by the International Biochar Initiative (IBI), as “a solid material obtained from the thermochemical conversion of biomass (mainly municipal or agricultural waste products, such as hay, bagasse, switchgrass, corn stover, woodchips, rice hulls, animal manure, or even sewage sludge, which otherwise would be disposed of) in an oxygen-limited environment” (IBI, 2010).

For example, biochars for arsenic removal have been produced from different biomass residues and agricultural wastes including bamboo culms [23], Japanese oak wood [24], red oak, switchgrass [25], corn straw [26, 27], cotton stalks [28], banana pith [29], rice straw [30], white birch [31] spent coffee grounds [32], rice and wheat husks [33], etc. Additionally, non-conventional feedstocks such as bones [34], algae [35], tires [36], and municipal solid waste and sewage sludge [37-39] have been used.

Biochar is produced in large quantities from many biomass sources to have a wide range of properties. Some biochars are co-products of thermochemical conversions to biofuel by fast pyrolysis to bio-oil and or curing gasification to syngas. As a result of being derived from waste products, BC production is considered a carbon-neutral process. Therefore, biochar production successfully helps in waste management and carbon and energy recovery as bio-oil and synthetic gas [15].
Biochar can have high surface areas (~800 m²/g) [40] a variety of pore diameter distributions, internal pore volumes and different surface functional groups, making it a good candidate for contaminated water remediation. Their nano-particle dispersed analogues (iron oxides, layered double hydroxides, metal organic frameworks, etc.) have been long-studied and are effective at adsorbing organic and inorganic pollutants from aqueous solution including pharmaceuticals [41, 42], agricultural waste [43], pesticides, heavy metals [40] and metalloids/metal and oxyanions (arsenate, arsenite, phosphates) [44], phenolics, dyes [45] and oil [46].

1.2.2.1 Biochar preparation and features

Biochar adsorption capacities depend on pyrolysis conditions and feedstock type [47]. Sorption capacity usually increases with increasing biomass pyrolysis temperature because higher surface areas are obtained with lower char yields.

Biochar is a rich source of carbon with greater proportions of aromatic and condensed aromatic structures and has greater stability compared to other organic sorbents. The condensed aromatic portion consists of different structural motifs like graphite, amorphous carbon produced under lower pyrolysis temperature, and turbostratic carbon formed under high temperatures [47].

The properties of biochar, which is produced by a thermal decomposition under oxygen-limited conditions and at temperatures below 700 °C, differ depending upon the biomass or the raw materials used and on the pyrolysis conditions as well [15, 48]. The ash content, moisture content, fixed carbon fraction, percentage of volatile substances; lignin, cellulose, and hemicellulose content, particle size, and content of inorganic substances are all dependent on the biomass type [49, 50]. With the increasing temperature and residence time of the pyrolysis process, the carbon content, surface area, porosity, and the energy of BC goes up [15]. Zhou et
al. suggested the following structure transitions for BC depending on the temperature; 1) transition BC with crystalline nature of the biomass feedstock or conserved solid; (2) amorphous, an arbitrary mixture of thermally altered molecules and emerging aromatic polycondensates; (3) composite BCs with poorly structured graphene mounds fixed in their amorphous phase; and (4) turbastic BC mainly composed of disordered graphite crystallites [51]. The lignin content increases the porosity of biochar. The BC properties will also change depending on the source of biomass, amount of water, particle size, and biomass shape [48].

During pyrolysis, the biomass is first dried. Further heating then releases volatile matter or condensable organic substances from the mass. Gaseous phase molecules undergo several reactions, including cracking and polymerization, which affects the final product [52]. This gaseous phase polymerization is believed to undergo a secondary char formation, increasing the mass of char. For that reason, during the process of making BC, the biomass is subjected to heating at a lower rate for a longer amount of time (slow pyrolysis). This contrasts with fast pyrolysis, where the biomass is heated and cooled rapidly to obtain liquid oil as the final product (however, it should be noted that even in fast pyrolysis, some BC is still obtained as a byproduct). During the conventional (slow pyrolysis) method of charcoal preparation, which is the most common type of BC, slow pyrolysis at 500 °C is carried out in a charcoal pit for several weeks until the desired product is achieved. Usually, the temperatures in pyrolysis are between 300 °C to 700 °C with a resident time of 60-240 min [52]. Torrefaction is the pyrolysis between 200-300 °C which is also known as mild pyrolysis or high temperature drying, where the BC produced exhibits properties similar to (stable to rotting for a long time) the biomass from which it was derived [53]. BC yield is mainly expressed through the following parameters: 1) mass yield, 2) energy yield and 3) fixed carbon content. Mass yield indicates the percentage of original
biomass remaining in the final product after pyrolysis. Biomasses with high water content will result in low mass yield, normally indicating their unsuitability as starting materials. In contrast, biomass rich with lignin will result in high yield due to its structural stability compared to cellulose and hemicellulose [54]. The energy yield parameter specifies the amount of energy remaining in the solid residue from the biomass after pyrolysis, and fixed carbon content is the ratio between the fixed carbon content in the product to the fixed carbon content in the total organic matter [52, 55].

Studies have been carried out to observe the temperature dependence on the yields of different biochar. When the pyrolysis temperature of date-seed BC was increased from 350 °C to 550 °C, an increase of 64.4% to 82.2% was observed in carbon content. However, the reduction of BC yield was ~27% to ~22% [56]. On the contrary, when the temperature of wastewater sludge was raised from 300 °C to 400 °C, the carbon content decreased from 25.6% to 20.2% and remained constant as the temperature was further raised to 700 °C. The reason for such an observation could be the high content of carbonic volatile matter in the biomass which can be gasified easily under elevated temperatures [15, 57]. When the temperature of poultry litter was raised from 300 °C to 600 °C, a similar behavior was obtained for carbon content (38% to 32.5%) with increased ash content from 48% to 60% explaining the reduction of carbon content [58]. Pitch pine wood chips exhibited increased carbon contents of 63.9%, 70.7 %, and 90.5% at 300 °C, 400 °C, and 500 °C, respectively, from fast pyrolysis [59]. When the carbon content and the yield was compared for sugarcane bagasse for slow and fast pyrolysis, there was no linear relationship between the char percentage and the pyrolysis temperatures. This proved the fact that BC yield was reduced at high temperature [60]. Oxytree pruning, sawdust, and municipal waste have shown high BC yields of 98%, 94%, and 89%, respectively [61, 62].
Pyrolysis removes polar functional groups on the surface of BC and makes them hydrophobic, enhancing the adsorption capacity of organic pollutants and oils. The hydrophobic surface of the pores will repel water from entering, and the water repellant activity of BC can be further increased by torrefaction. However, further heating can decompose the aliphatic functional groups and hence BC can also become less hydrophobic. Increased porosity at high temperatures will allow more water to be absorbed [52].

The feedstock type defines many of the initial biochar textural properties, while pyrolysis temperature determines the final physicochemical properties [52]. Higher temperatures remove greater amounts of volatile compounds, promoting a more graphene-like structure and higher pore volumes, pore distributions, and surface areas. Additionally, composition and surface chemistry vary. As ash content increases, C content decreases, organic oxygen-containing surface groups decrease and pH$_{PZC}$ increases as pyrolysis temperature rises. The O/C ratio decreases with temperature as aromaticity rises, and the surface becomes more hydrophobic. Biochars produced at higher pyrolysis temperatures (600-800 ºC) are usually more effective for pollutant adsorption than those prepared at low temperatures (300-500 ºC) [11, 63]. For instance, Niazi, Bibi [64] found that perilla leaf biochar produced at 700 ºC had better As(III) and As(V) sorption capacities than when produced at 300 ºC. The former had a higher surface area, smaller pore sizes, and higher aromaticity. However, biochars produced at lower pyrolysis temperatures can be more effective [65] when considering the crucial role of polar functional groups with a higher oxyanion affinity (mainly –OH, –SH) or those which promote pollutant removal through electrostatic attraction, ion exchange, and surface complexation [11].
1.2.2.2 Biochar engineering strategies to enhance adsorption

It has been well-accepted that pristine biochars are less effective than modified or the so-called engineered biochars for pollutant removal. Indeed, currently few articles report the sorption capacities of the pristine material, and the modified counterparts are directly characterized and used. For example, enhanced arsenic sorption capacities of modified biochars have been attributed to improvements in both textural properties and surface chemistry; higher porosity and surface areas, along with an increase in desired functional groups or compounds with higher affinity to As [11].

Because pristine biochars have shown relatively low pollutant removal efficiencies, several engineering strategies have been studied to enhance sorption capacities (Figure 1.1). Activation processes (e.g., acid, base, peroxide, gas, and steam) cause chemical modifications of BC that significantly alter the surface area and surface functional groups (e.g., amine, ethers, sulfonates, hydroxides, esters, phenols, and ketones) [66], thereby enhancing the sorption capacity [67]. Some of the more frequent pre- or post-pyrolysis modifications [68] are treatments with alkali or acidic solutions such as KOH [69] and H₃PO₄ [28], oxidation with HNO₃ [70, 71], functionalization with particular surface groups (e.g., thiols) [72] and/or impregnation with metals or metal oxide/hydroxides nanoparticles to produce composites, such as Zn [73], Mn [34], Ti [74], Ca [75], Al [76, 77], Fe [78] or their mixtures [79-81].

The higher sorption capacities of chemically and physically modified biochars contrast with pristine counterparts. Activating agents have positive effects on textural parameters such as surface area, pore volume, and pore size distribution, which facilitate diffusion of pollutants into the adsorbent pores. Interestingly, low adsorption capacities have been found for some materials
with high specific surfaces and porosity, indicating that many factors can govern the adsorption process besides textural parameters: biochar surface functional groups being among these [65].

1.2.2.2.1 Advantages of preparing biochar composites

Biochar-based composite sorbents are increasingly popular [63] since the surface chemical and physical treatments offer technical and environmental benefits [82]. First, most treatments have affinity for metals and metallic compounds or phases [78, 83]. Second, using biochars to support and disperse metallic or oxide/hydroxide nanoparticles with affinity to pollutants reduces the self-agglomeration of these particles when used alone, enhancing adsorption capacities [84]. Moreover, the porous carbonaceous BC skeleton provides mechanical strength, which is essential for column-based adsorption processes. Also, the biochar carbonaceous phase can adsorb additional sorbates. Providing multiple surface phases allows the simultaneous adsorption of other contaminants [85]. Third, the resultant composites can be endowed with a magnetic response (e.g. magnetite phase), enabling easy recovery of the pollutant-loaded adsorbents from solution using an external magnetic field [86]. Hence, these easy-to-produce magnetic nano-dispersions present reusability potential after several application cycles. Additionally, from an environmental point of view, fewer hazardous chemicals and less energy are needed for biochar-based adsorption versus some other methods. Finally, nanoparticles are regarded as an emerging class of pollutants, so their direct incorporation in water is highly discouraged [78]. Tiny adsorbent particles also lead to high pressure drops in columns. Therefore, supporting high surface area nanoparticles on much larger carrier biochar particles, allows easier flow through columns while still exposing the polluted water to nanoparticle surfaces.
1.2.2.2 Fe-based biochar composites

Fe-based biochar composites are the most studied modified BC materials in the past decade. Different iron species can be obtained, from zero-valent iron (ZVI) to iron oxide/hydroxide nanoparticles such as magnetite, maghemite, and hematite, prepared both ex-situ and in situ [11, 87]. Biochar loading is performed traditionally by wetness impregnation and co-precipitation. Briefly, the general procedure consists of a soaking step with impregnating solutions containing Fe, most frequently FeCl₃, Fe(NO₃)₃ and Fe₂(SO₄)₃ followed by a drying step. In the co-precipitation method, a further reducing (NaBH₄) or precipitating agent (NaOH, KOH, NH₄OH) are added to the suspension before the drying step. A thermal conversion to promote nZVI or oxide particle nucleation and growth on the surface of the biochar can also be performed [88, 89]. Additionally, iron oxide compounds or nanoparticles can be produced separately and then physically mixed together with the feedstock or biochar in order to achieve the Fe-based composite after co-pyrolysis [89].

For the instance, addition of Fe(NO₃)₃ from solution to the surface of empty fruit bunches (e.g., remains of palm oil fruit) [90] and rice husk BCs increased As(III) adsorption capacities from 18.9 to 31.4 mg/g and 19.3 to 30.7 mg/g, respectively [90]. Furthermore, a Fe–Mn oxide loaded on corn stem BC and formed through direct pyrolysis of corn stem with Fe(NO₃)₃ and KMnO₄ showed 8.25 mg/g adsorption for As(III) [91]. The higher capacity of this modified corn stem BC was due to the enhanced specific surface area (208 m²/g) compared with the surface area of pristine corn stem BC (61 m²/g) as more surface was available for As(III) oxidation and adsorption. Furthermore, adsorption is enhanced mostly by iron oxide deposits, in which As(III) has a strong affinity to As(V).
The Mn oxides (Mn$_3$O$_4$ and Mn$_2$O$_3$) present cause the oxidation of As(III) to As(V) [91]. Similar trends were observed for iron oxide (FeO, Fe$_2$O$_3$, and Fe$_3$O$_4$) and oxyhydroxide (FeOOH) impregnated BC when prepared by Hu et al [92]. Large shifts in the XPS Fe2p, As3d, O1s, and C1s binding energies support an As adsorption mechanism governed by chemisorption [92]. Furthermore, reduction of Fe(III) to Fe(II) drives the oxidation of As(III) to As(V) during adsorption. Strong As interactions with surface metal hydroxyl functions (Fe–OH and Mn–OH) form stable iron–arsenate surface complexes [93].

**Figure 1.1** Biochar based multifunctional adsorbents for water treatment

### 1.2.2.2.3 Biochar for oil remediation

Even though synthetic sorbents show high absorptivity/adsorptivity towards oils, there are a few drawbacks such as their high cost, reduced biodegradability, and operating complexity. Therefore, organic sorbents are much preferred over other types of sorbents due to their high abundance, low cost, high degradability, and a reduced threat to nature [12, 94]. Rice straw, corn
cob, sawdust, and fibers such as wood fiber, cotton fiber, kapok fiber, wool fiber, kenaf fiber, and cattail fiber, milkweed, rice husk, coconut husk, hay, feathers, and bagasse are examples of some organic sorbents used for oil spill cleanup [94]. According to Adebajo et al. organic fibrous sorbents have higher adsorption capacities than most natural and synthetic sorbents and low densities, allowing them to float on the surface, increasing the sorption activity [95]. The negative aspect of these materials is the high water uptake during the process. Passila., 2004 explained the concept of biological adsorption filters, where it was mentioned that due to low hydrophobicity, the effectiveness of the microporous structure of the sorbents to adsorb oil over water is reduced [96]. In contrast, the waxy coating surrounding the sorbent surface in kapok fibers increases the hydrophobicity; hence, it shows higher oil sorption capacity. Choi et al., Deschamps et al., and Lim et al. reported that the oil sorption capacity of kapok, cotton, and milkweed floss is between 20-50 g of oil per gram of sorbent [97, 98]. Natural organic sorbents can adsorb oil about 3-15 times their weight [16].

The high availability of carbonaceous materials and their high efficacy due to large surface area and porosity makes the usage of carbonaceous materials for the removal of oil preferable to other sorbents. From activated charcoal progressively, the focus was directed towards biochar (BC), obtained by pyrolysis of plant-and animal-based biomass at elevated temperatures and under reduced oxygen concentrations, as a potential sorbent with a greater scope; i.e; for oil spill cleanup, metal removal in wastewater, for agricultural soil amendment and remediation and as a purifier for air contaminated with volatile organic compounds [12-15]. The sorption capacity of BC can be enhanced by increasing the surface area and microporosity [16, 17]. Even though BC is a promising adsorbent, it also has the shortcoming of adsorbing water
and sinking in water. Hence the removal of BC becomes difficult from water, no matter how good an adsorbent it is.

The sorption capacity of BC has enhanced during steam activation, hydrothermal carbonization, magnetization, and by oxidation with strong oxidizing agents such as KMnO₄ and H₂O₂ [16, 99-102]. A small amount of work has been carried out in the applications of BC for oil spill cleanup. Composites modified with magnetic materials such as superparamagnetic iron oxide nanoparticles have shown enhanced oil cleanup and fast recovery of the sorbents [103].

1.3 Dissertation objectives and broader impact in water remediation

Some disadvantages of using adsorption include competitive adsorption; influence of the complex natural water matrix; difficulty in predicting overall column performance; the need to scale the process; frequent adsorbent regeneration or replacement; disposal of toxic adsorbent wastes; and removal of some other contents of concern (including microbes) [104]. These require additional time and remediation costs. Modifications can be performed to expand the adsorption and activation capacities as well as the physical and chemical properties of BC. Siddik et al., 2012 suggested that by attaching lauric acid to BC, the hydrophobicity can be increased by increasing the water contact angle. These modified compounds with increased buoyancy become better adsorbents than unmodified BC [99]. Magnetization by magnetite iron oxide nanoparticle deposition onto BC and lauric acid-modified BC allowed for the recovery of the exhausted adsorbent by a magnetic field as an alternative to filtration.

This dissertation focused on three different projects on developing commercial Douglas fir biochar based multifunctional engineered adsorbents to address aforementioned issues. Chapter II focuses on arsenic (III) adsorptive removal onto iron oxide dispersed magnetic biochar. This chapter highlights the adsorptive and redox properties of biochar composites for pollutant
toxicity reduction. Chapter III focuses on pollutant toxicity neutralization after adsorption, simultaneous adsorption, and multi-phase adsorption. The MIL-53-MOF magnetite/magnetic biochar composite model system was used to demonstrate simultaneous chromium (VI) adsorption and organic pollutant (RhB) degradation. Chapter IV is focused on tailoring the biochar to change its physical properties (enhance hydrophobicity) to achieve specific pollutant treatment requirement (buoyancy). Oil spill remediation was used as a model example for this purpose and lauric acid decorated magnetite biochar composite was introduced.

Low-cost engineered biochar adsorbents could serve in large-scale water treatment to adsorb pollutants where the cost of activated carbon makes their use impossible [105]. The operation cost is reduced significantly if the adsorbent is readily available, easily recovered, recyclable from solution and is cheap. Wood, agricultural byproducts, and energy crops provide an abundant and renewable supply of lignocellulosic feeds for biorefineries. Herein, this *paradigm* uses a solid char byproduct from chemical and energy production, where the cost of the heat and manufacturing process is born by another products (syn gas here). This process produces a high carbon waste char with unique properties, which might also work with other biomass feeds. Renewable wood feed for chemicals and adsorbents closer to carbon neutral vs fossil fuels and vs use of activated carbon, if biofuel production from fast pyrolysis (to bio-oil) developed in the future.
1.4 REFERENCES


CHAPTER II

REMOVAL OF ARSENIC(III) FROM WATER USING MAGNETITE PRECIPITATED ONTO DOUGLAS FIR BIOCHAR

(Published in J. Environ. Manage. 2019, 250, 109429)

2.1 Abstract

Magnetic Fe$_3$O$_4$/Douglas fir biochar composites (MBC) were prepared with a 29.2% wt. Fe$_3$O$_4$ loading and used to treat As(III)-contaminated water. Toxicity of As(III) (inorganic) is significantly greater than As(V) and more difficult to remove from water. Removal efficiency was optimized verses pH, contact time and initial concentration. Column sorption and regeneration were also studied. Adsorption was analyzed with three isotherm models at 20, 25 and 40 °C. The Sips isotherm showed the best fit at 25 °C with a 5.49 mg/g adsorption capacity, which is comparable with other adsorbents. MBC gave faster kinetics (~1-1.5 h) at pH 7 and ambient temperature than previous adsorbents. The Gibbs free energy ($\Delta G$) of this spontaneous As(III) adsorption was -35 kJ/mol and $\Delta H = 70$ kJ/mol was endothermic. Experiments were performed on industrial and laboratory wastewater samples in the presence of other co-existing contaminants (pharmaceutical residues, heavy metals ions and oxi-anions). The composite reduced the arsenic concentrations below the WHO’s safe limit of 0.2 mg/L for waste water discharge. X-ray photoelectron spectroscopy (XPS) studies found As(III) and less toxic As(V) on Fe$_3$O$_4$ surfaces indicating adsorbed (or adsorbing) As(III) oxidation occurred upon contact with O$_2$ and possibly dissolved Fe(III) or upon drying under oxic conditions. Under anoxic
conditions magnetite to maghemite transformation drives the oxidation. A pH-dependent surface chemisorption mechanism was proposed aided by XPS studies vs pH.

2.2 Introduction

Arsenic (As) is a labile trace element that can undergo oxidation, reduction, methylation, volatilization, adsorption, and desorption in soil [1]. Arsenic occurs as As(V), As(III), As(0) and As(−III) oxidation states [2, 3]. Arsenite (AsO$_3^{3−}$) and arsenate (AsO$_4^{3−}$) dominates under oxidizing environment [4]. As(III) is more reactive and has higher human toxicity than As(V), but its adsorption from water is less studied [5]. Inorganic arsenic compounds are often more toxic than organic arsenic compounds [6]. In US and EU approximately 70% of the arsenic in natural water originates due to agrochemicals; insecticides, herbicides and pigments [7, 8]. Arsenic bearing minerals are also a significant source of ground water and drinking water contamination with widespread health consequences specially in Asian and Latin American regions [9].

The background levels of As in most US and European drinking waters are $\leq$1 µg/L [10]. However, approximately 10% of the population drink water that exceed this level [10]. In Asia the background levels are often higher than 10 µg/L [11]. Arsenic is an acute poison (100-300 mg) to humans and animals [12]. Chronic exposure to inorganic arsenic (As(III) and As(V)) can cause skin, bladder and lung cancers [13], developmental effects, neurotoxicity, diabetes, nephrotoxicity, chronic kidney disease (CKD), and cardiovascular disease [14, 15]. Arsenates may replace the activity of phosphate in certain biochemical reactions [5]. The WHO and US EPA, maximum permissible inorganic arsenic levels in safe drinking and discharge waste water are 10 µg/L and 0.2 mg/L, respectively. [16]. Ion-exchange [17], membrane methods (reverse osmosis) [18], coagulation [19], reaction with metal salts and lime followed by filtration [4], and
Adsorption [20] were demonstrated or are in-use for arsenic-contaminated water remediation [21]. However, these methods are not always efficient, environmentally friendly or cost-effective [20]. Arsenic can be adsorbed on Al, Fe and Mn oxides and hydroxides [22-27] and clay (Kaolinite) surfaces [23, 28]. However, adsorption, limitations include particle agglomeration, weak mechanical strength and flow limits in columns. These limit widespread application of adsorption [29].

Biochars (BCs) can be used as a support material for small particles of other adsorbents to prevent particle agglomeration [29, 30]. BC’s are easily produced from low cost readily available renewable biomass [31]. BC properties, including substantial surface area, porosity, and chemical functionality [32] promote adsorption of toxic heavy metals [33, 34], metalloids and both organic and pharmaceutical residues from water [21, 35-39]. Typical water treatment adsorption processes use adsorbent-packed columns, however, magnetized BC-based water treatment also allows batch sorption, where the exhausted adsorbent can be rapidly retrieved using magnets and regenerated [36]. Tiny, high surface area adsorbent particles, like nano-sized metal oxides, exhibit very high surface areas for adsorption but create large pressure drops in columns. Thus, their dispersion on high surface area, larger biochar particles speeds column flow while providing an added adsorbent surface for other pollutants. BC production is a carbon negative process because the carbon still remaining in BC, produced by biomass pyrolysis, is sequestered for long periods instead of returning to the atmosphere as CO$_2$ during biomass decay [40].

The specific objectives of this work were to 1) prepare Douglas fir BC/magnetite (Fe$_3$O$_4$) composite, 2) test its sorption kinetics and isotherms for As(III) and 3) investigate the possible As(III) adsorption mechanisms and As(III) to As(V) redox effects on magnetite surfaces.
2.3 Methods and materials

2.3.1 Materials

The chemical reagents (arsenic standards, sodium ortho arsenite, acids, bases and auxiliaries) used were in analytical grade (purchased from Sigma-Aldrich, Fischer and Inorganic Ventures). The pH adjustments were made using 1 M, 0.1 M and 0.01 M HCl and NaOH solutions. Sorption experiments under specific constant temperatures were conducted in a water bath shaker (DAIHAN MaXturdy™). Douglas fir biochar (BC) (Biochar Supreme Inc. Environment Ultra) was used in the sorption studies [34-36, 41]. Biochar was produced as a by-product from gasification of timber industry waste wood (Douglas fir). Auger fed, chipped (∼3 inch) green wood (12-15% moisture by weight) was introduced into an air-fed updraft gasifier at 800–1000 °C, with a residence time of 1-10 sec in the hot zone with little or no air. Large biochar particles (∼2 cm) were collected, thoroughly washed several times with water, dried at room temperature (2 days), ground, sieved to a particle size range of 0.1–0.6 mm and stored in closed vessels until needed.

2.3.2 Preparation of magnetically modified biochar

The magnetized biochar composite (MBC) was synthesized via a modified method described in our previous work [36]. A 1:1 (Fe$^{2+}$ : Fe$^{3+}$) molar ratio of FeCl$_3$ and Fe$_2$(SO$_4$)$_3$·7H$_2$O was used at a 1:1 BC:total iron salt mass ratio. The amount of iron salts versus the BC weight seems high, but Fe$_3$O$_4$ has a much higher density (∼5.15 g/cm$^3$) [42] than the highly porous lower particle density (∼0.4 g/cm$^3$) [43] of BC. A substantial coverage of tiny dispersed iron oxide particles on biochar surface was sought to provide a high Fe$_3$O$_4$ surface area. These salts were dissolved in water separately; then and the combined salt solutions were thoroughly mixed into a biochar aqueous suspension. The pH was raised to 10 by adding 10 M
NaOH solution, dropwise. After mixing for 1 h, the resulting suspension was aged at 22-25 °C, nucleating Fe₃O₄ nanoparticles in solution and possibly at the BC surface. The particles attached to BC and continued to develop for 24 h. The Fe₃O₄/BC hybrid (MBC) was filtered, thoroughly washed with distilled water followed by three ethanol washes to remove organic residues, vacuum filtered and dried overnight at 50 °C in a hot air vacuum oven.

2.3.3 Characterization of BC, MBC and As(III)-laden MBC

The instrumentation and methodologies are detailed in Appendix A.1. The points of zero charge (PZC) of MBC (~6.50) and BC (~9.20) were determined using the pH drift method [44]. MBC and BC surface architectures were examined using a JEOL JSM-6500F FE-Scanning electron microscopy (SEM) at 5kV coupled with an energy dispersive X-ray (EDX) detector. EDX analyses employed a Zeiss, EVO 40 scanning electron microscope with a BRUKER EDX system. Transmission electron microscopy (TEM) studies were undertaken using a TEM JEOL model 2100. STEM/EDX analyses were carried out using an Oxford X-max-80 detector. XRD patterns for both MBC and BC were obtained using a Rigaku ultima III instrument (using Cu-Kα (λ =1.54 Å) [The Institute for Imaging & Analytical Technologies (FAT)]. XPS analyses were performed using a Thermo Scientific K-Alpha XPS system (University of Memphis Materials Science Lab). The surface areas of MBC and BC were examined using a TriStar II Plus 3030 surface area analyzer using BET N₂ adsorption isotherms (~273 K). Ash analysis was done by weighing the mass of ash produced after incinerating 1 g of each MBC and BC in a muffle furnace at 650 °C for 15 h. Fe contents in BC and MBC were determined using AAS under the flame mode. The MBC has a total ash content of 31.3% and 20.9% Fe via FAAS versus 2.1% ash and no detectable Fe (by FAAS). Further analytical and iron oxide deposition yields are given in the Appendix A2.1.
2.3.4 Batch sorption studies

The effects of the solution pH on As(III) adsorption by both MBC and BC were studied using 10 mg/L (81.3 µM) As(III) (arsenite) solutions at 25 °C from pH 2 to 12 (at intervals of 2 pH units). As(III) adsorption kinetics on MBC were examined by equilibrating 50.0 mg of MBC with 25.0 mL of three different As(III) concentrations (5, 10 and 20 mg/L) in 50 mL polypropylene vials at 25 °C and pH 7. These vials were shaken at 200 rpm in a water bath shaker, withdrawn at respective time intervals. The contents filtered immediately using a 0.22 µm filter and analyzed for As(III) using atomic absorption spectrophotometer (AAS) [Hitachi Zeeman Polarized, ZA3000 equipped with a hydride generator (HF-4) (HGAAS) with a limit of quantification (LOQ) of 15 µg/L As(III)]. Isotherm experiments at As(III) concentrations of 1 to 12 mg/L (25 mL) were equilibrated with MBC (50 mg), followed by neutralization with drop-wise addition of HCl and NaOH solutions.

Competitive adsorption on wastewater samples and the breakthrough column analysis experiments required lower detection limits. Hence, they were conducted using an inductively coupled plasma mass spectrophotometer (ICP-MS) (PerkinElmer SCIEX, ELAN DRC II) with a LOQ of 0.1 µg/L.

The amount of adsorbents removed \( (q_e) \) was calculated using equation 2.1.

\[
q_e = \frac{V(C_0 - C_e)}{M}
\]  

(2.1)

Here, \( C_0 \) and \( C_e \) are initial and equilibrium analyte solution concentrations (mg/L), \( V \) is the solution volume (L), and \( M \) is the total mass of adsorbent added (g).
2.3.5 **Competitive batch sorption studies**

4-Nitroaniline (4NA), salicylic acid (SA), chromate, selenate, molybdate, phosphate, nitrate, fluoride, cadmium and lead (1 ppm of each in the final solution) were spiked into a zinc-containing wastewater sample originating from an industry in Seattle, WA together with As(III) (4 ppm in final solution). Sorptions were conducted at pH 7.0 and 25 °C (1 h equilibration, 25 mL volume and 4 g/L MBC dose). These experiments were then repeated on both industrial waste water (IWW) and heavy metal waste (HMW) from the Mississippi State Chemical Laboratory samples containing traces of As(III) and other contaminants, using 100 mg of MBC in 25.0 mL of the waste water. Samples were filtered, processed and preserved prior to the ICP-MS analysis as described in previously [45]. Arsenic contents were pre-determined for both IWW and HMW before spiking with 4 ppm As(III) and were 0.000266 mg/L and 0.4 mg/L respectively. The results are given in section 2.4.6.

2.3.6 **Fixed-bed column breakthrough and stripping regeneration studies**

Breakthrough studies were performed for a 10 mg/L As(III) solution (pH = 7 at 25 °C) passing through a laboratory scale MBC glass wool-plugged fixed-bed column (length = 5 cm and dia = 1.1 cm) packed with ~2.5 g of MBC (300-500 µm MBC particle sizes containing ~18.1 nm primary Fe₃O₄ particles and a wide range of primary particle aggregates up to ~7 µm dispersed on the biochar surface). The column was packed using a warm mixture of MBC-water after removing any low density MBC that floats due to trapped air. The mixture was slowly added to the column through a glass funnel. The MBC packed column was vibrated to ensure an even packing and remove air bubbles. Approximately 0.5 L of As(III) solution was passed through the column during the experiment, while the flow-rate was maintained at 2 mL/min.
The fixed bed was stripped with 0.5 M KH$_2$PO$_4$ at pH ~ 4.5 (~2 mL/min flow rate), as described by Tuutijärvi [46]. The regenerated column was then recycled through three sorption-stripping cycles, by loading As(III) using a ~0.5 L of 10 mg/L As(III) solution and then stripping with ~0.6 L of 0.5 M KH$_2$PO$_4$.

2.3.7 Sample preparation for XPS studies on arsenic redox effects.

MBC samples were isolated after As(III) and As(V) adsorption under both oxic and anoxic conditions. Samples were prepared in oxic conditions at initial pH values of 2, 7 and 12 for both As(III) and As(V). Anoxic samples were prepared at pH7 in argon-purged solutions. All samples employed 50 mg of MBC equilibrated with 25 mL of 25 mg/L of either As(III) or As(V) for 1 h. Anoxic samples were dried in inert nitrogen and helium in a BET degasser for 2 h, while the samples prepared in oxic environment were oven-dried in air at 40 °C for 2 h.

2.4 Results

2.4.1 Biochar elemental analyses, surface areas and morphologies

Scanning electron micrographs for BC and MBC (Figure 2.1 b-d) show the morphological changes due to widely distributed iron oxide precipitation, observed as primary Fe$_3$O$_4$ particles (18.1±3.9 nm diameter) often clustered or aggregated (~2-7 µm) on the surface. Primary particle sizes were calculated at minimally aggregated particle regions (~1650 x 1334 nm$^2$ spot size) on rescaled TEM images by imageJ software-derived histograms of the particle distribution for these spots. Primary particles are also easily seen on particle aggregate surfaces. Biochar serves as an effective dispersing matrix [29]. The x1700 magnification SEM of BC is shown in Figure 1a to illustrate its morphology and provide a contrast to the surface observed after deposition of magnetite. The fraction of primary particles found in larger aggregates was
reduced by depositing smaller weight fractions of Fe$_3$O$_4$ onto biochar. SEM-EDX confirmed a decrease in surface carbon content going from BC to MBC, due to Fe$_3$O$_4$ covering portions of MBC’s carbonaceous surface (Appendix, Figure A.1). BC and MBC surface areas were 670.4 m$^2$/g and 320.1 m$^2$/g respectively, while micropore volumes were 0.242 cm$^3$/g (BC) and 0.139 cm$^3$/g (MBC). The loss of 350 m$^2$/g of surface area going from BC to MBC indicates iron oxide blocks access to N$_2$ adsorption onto a portion of the biochar’s microporous and macroporous surface during BET measurements (Figure 2.1) [34].

![SEM micrographs of BC (a) and MBC (b-d) and TEM and TEM-EDX elemental mapping images of (e) BC (f) MBC (g) As-loaded MBC (h) As-loaded MBC, focused on a magnetite aggregate. Gray and black particles are BC and MBC composites lying on the copper grid. As-loaded MBC samples were prepared using pH 7, 12 mg/L [As(III)] solutions (25 mL) equilibrated with 50 mg of MBC for 1h at 25 °C (2 g/L dose).](image)

Figure 2.1 also displays STEM-EDX elemental maps of As(III) adsorbed on MBC illustrating the presence of As (~0.5 wt %). The As was preferentially adsorbed onto the Fe$_3$O$_4$ rich areas on the MBC and absent on the carbonaceous surface (Figure 2.1 g and h). Almost no As(III) adsorption occurred on BC over the pH range from 2 to 12 (Figure 2.2). STEM-EDX is a
The calculated As capacity from STEM-EDX mapping is ~5.0 mg/g, corresponding to ~8.3 mg/g of arsenite (AsO$_3^{3-}$) adsorption on MBC based on the wt. fraction of Fe$_3$O$_4$ in MBC and negligible adsorption on biochar surface. Elemental STEM-EDX composition analyses are presented in the Appendix, Figure A.2.

The XRD of MBC confirmed the precipitated iron oxide was primarily magnetite (Fe$_3$O$_4$) (Appendix, Figure A.3). The major peak at 2θ=35.45° is for the crystalline plane with Miller indices of (311). Other low intensity peaks were observed at 30.10° (220), 43.08° (400), 53.45° (422), 56.98° (511), 62.57° (440), and 74.02° (444), matching the standard diffraction patterns of Fe$_3$O$_4$ [47].

### 2.4.2 Point of zero charge and As(III) adsorption pH dependence

The point of zero charge (PZC) of a biochar depends on its surface organic and ash functionality [48]. Arsenic speciation varies with solution pH (Figure 2.2) [49]. The points of zero charge of MBC and BC, are ~6.50 and ~9.20 respectively. BC’s PZC reflects its high pyrolysis temperature (~ 900 °C), where basic carbonates and oxides of Ca$^{2+}$, Mg$^{2+}$, Na$^{+}$ and K$^{+}$ formed. MBC’s PZC reflects the influence of the surface Fe-OH groups of the deposited magnetite. As(III) adsorption’s pH dependence was established using 2 g/L doses of BC or MBC at pH 7 using 10 mg/L As(III) solutions at 25 °C. As(III) removal is approximately constant from pH 2 to 6 for MBC at ~40 % and then increased to 65 % at pH 8 (Figure 2.2). Then from pH 8 to 12 removal fell steadily to 58 %. Conversely, BC failed to remove significant amounts of As (III).

Arsenite speciation vs. pH is also displayed on Figure 2.2. H$_3$AsO$_3$ predominates in solution through pH 9. H$_2$AsO$_3$ begins to form at ~pH 8 and predominates from ~pH 9.2-12 (Figure 2.2). HAsO$_3^{2-}$ is first formed at ~pH 10 and is the dominant species from ~pH 12.2-13.
H$_3$AsO$_3$ can protonate (H$_4$AsO$_3^+$) but only in strongly acidic solutions [50]. Furthermore, H$_4$AsO$_3^+$ has less affinity to the positively charged BC and MBC surfaces that would be generated by protonation at such acidic pH values. Thus, from pH 2-7, H$_3$AsO$_3$ was the only As(III) species being adsorbed. The rise in As(III) removal from pH ~6.5 to 8 might be due to H$_2$AsO$_3^-$ adsorption at Fe-OH sites on magnetite before these surfaces became more negatively charged. Also, H$_3$AsO$_3$ could hydrogen-bond to deprotonated Fe-O$^-$ surface sites at pH~ 8 to 10 prior to chemisorption. Further increase in pH from 10 to 12 lead to more HAsO$_3^{2-}$ and H$_2$AsO$_3^-$ interacting with the increasingly negative magnetite and carbonaceous surfaces of MBC. Electrostatic repulsion may reduce As(III) uptake in this range somewhat, but adsorption remained robust. Over the entire pH 2-10 range MBC remains an effective As(III) adsorbent. The adsorption mechanism will be discussed in section 2.4.9.
Figure 2.2  pH dependence of As(III) (10 mg/L) adsorption onto BC and MBC (at 25 °C and 1 h equilibration) and fractional composition curves for As(III) speciation. (Error bars represent the standard deviation of 3 replicates). Note that the H$_4$AsO$_4^{4-}$ speciation is not shown in the graph due to the unavailability of equilibrium constants for H$_4$AsO$_4^{4-}$ formation.

2.4.3 Adsorption kinetics

As(III) removal on MBC was plotted versus the equilibrium time (Figure 2.3a) at initial concentrations of 5, 10 and 20 mg/L. All experiments (at pH 7, 25 °C with 2 g/L dose) exhibited high initial As(III) adsorption rates on MBC and due to a lack of data in the initial equilibrium region, kinetics models were not fitted. Equilibrium was rapidly attained in 1-2 h time range. Maximum removal percentages at initial As(III) concentration of 5, 10, and 20 mg/L were 57.8, 51.0 and 68.4 %, respectively at equilibrium (Figure 2.3a). When the initial adsorbate concentration increased from 5 mg/L to 10 mg/L, the removal percentage decreased. When the initial concentration rose to 20 mg/L, adsorption went up. This increases the concentration to 20 mg/L may have led to multilayer arsenite adsorption onto magnetite or a higher monolayer site density of arsenite. Either situation (multilayer adsorption or higher monolayer site density)
would lead to higher removal percentages [51]. Higher As(III) concentrations may also have triggered some iron dissolution from magnetite and formation of arsenic-iron stoichiometric compounds that lead to higher removal percentages.

2.4.4 Adsorption isotherms

As(III) adsorption on the Fe$_3$O$_4$ on MBC involves the formation of complexes at the magnetite surface (section 2.4.9). The adsorption isotherm data obtained at 20 °C, 25 °C and 40 °C were fitted to Langmuir, Freundlich and Sips models (Figure A.4 and Table A.2). The best fit isotherm was selected by its goodness of fit, correlation coefficient ($R^2$) and Chi-square ($\chi^2$) value. The best correlation coefficient fits and Chi-square values of fitting to experimental data (Figure 2.3b) were given by the three parameter Sips model, a hybrid form of the Langmuir and Freundlich expressions for heterogeneous adsorption systems. This circumvented the limitation of the rising adsorbate concentration associated with Freundlich isotherm model [52]. Three-parameter models generally better fit the data versus two-parameter isotherm models. At low adsorbate concentrations, the Sips model reduces to the Freundlich isotherm; at high concentrations, it predicts a monolayer adsorption capacity characteristic of the Langmuir isotherm. The Sips parameters are governed mainly by the operating conditions (eg: pH, temperature, and concentration) [52].

The Sips model adsorption intensity value ($n = 0.87$) at 25 °C (2 g/L MBC dose) suggested that the Sips model can be reduced to the Langmuir isotherm (eg. when $n \sim 1$). This corresponds to a monolayer adsorption. The essential characteristic of Langmuir isotherm can be characterized with separation factor, $R_L = (q_0 - q_e)/q_0$, where $q_0$ is the maximum adsorption capacity and $q_e$ is the capacity at equilibrium (Appendix A.3.1, equation scheme A.1-4) [53, 54]. $R_L$ was calculated (equation A.4) for the Langmuir isotherm data at 20, 25 and 40 °C.
respectively. R_L values were in ~0.07 to 1 range. This indicated a favorable adsorption (Figure A.5). The R_L values for the temperatures 20, 25 and 40 °C were in the 0.95-0.39, 0.96-0.22 and 0.95-0.07 ranges, respectively. Several favorable subgroups [favorable (R_L=0.364), very favorable (R_L=0.054)] have been demonstrated in previous studies [55]. Adsorption became very favorable with increasing temperatures as the R_L reached 0.07. R_L values close to ~1 indicate a favorable linear adsorption [54]. For linear adsorption, the shape of isotherm curve or the breakthrough curve in fixed-bed column sorption was nearly independent of the rate-determining mechanism for the adsorption. This concept is based on either pore diffusion or solid diffusion in series with a mass-transfer resistance outside the particle [53].

2.4.5 Thermodynamics of adsorption

Temperature influenced As(III) sorption equilibrium and capacities. The Sips isotherm capacity (q_0) increased going from 20 to 25 °C (5.03 to 5.46 mg/g) but then decreased going to 40 °C (4.79 mg/g) (Table 2.1). At higher temperatures the adsorption does not fit to the Sips isotherm as well. However, the enhanced Sips n value of 1.63 indicated that multilayer adsorption increasingly occurred at 40 °C (Table A.2). The Langmuir model capacity of 5.35 mg/g at 40 °C, also indicated increasing capacity as temperature rises.
Figure 2.3  a) Normalized adsorption vs time for initial As(III) concentrations of 5, 10, 20 mg/L (at 25 °C and pH 7), b) Fits to the Sips isotherm of As(III) adsorption on MBC at 20, 25 and 40 °C (pH = 7, 1 h equilibration time) (Error bars represent the standard deviation of 3 replicates) and c) van’t Hoff plot of lnKs vs 1/T for the As(III) adsorption on MBC from 20-40 °C.
Table 2.1 Thermodynamic parameters for the adsorption of As(III) by MBC from 20–40 °C.\(^a\)

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>(q_0) (Sips) (mg/g)</th>
<th>(R^2)</th>
<th>(K_S) (L/mg)</th>
<th>(K_S/10^4)</th>
<th>(\ln K_S)</th>
<th>(\Delta G) (kJ/mol)</th>
<th>(\Delta H) (kJ/mol)</th>
<th>(\Delta S) (kJ/mol.K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>5.03</td>
<td>0.99</td>
<td>0.48</td>
<td>48</td>
<td>13.08</td>
<td>-32</td>
<td></td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>5.49</td>
<td>0.98</td>
<td>1.14</td>
<td>114</td>
<td>13.94</td>
<td>-35</td>
<td></td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>4.79</td>
<td>0.97</td>
<td>5.23</td>
<td>523</td>
<td>15.46</td>
<td>-40</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^a\)Isotherm capacity data were generated by local refinement of empirical isotherm equations via the Levenberg–Marquardt distant nonlinear regression algorithm in Origin2018 using the average value of 3 replicates for each data point. Significant figures on isotherm specific capacities and regression coefficients are based on the model fittings and may not reflect the actual uncertainties of experimental data.

The Gibbs free energy (\(\Delta G\)), enthalpy (\(\Delta H\)) and entropy (\(\Delta S\)) were calculated using van’t Hoff’s equations. First, the Sips isotherm constant (\(K_S\)) for each temperature was converted to dimensionless constants (\(K_S\)) via multiplying by the density of the liquid phase (~10E06 mg/L) [56]. The negative \(\Delta G\) values indicated a spontaneous adsorption, and its magnitude increased with temperature. The positive \(\Delta H\) confirmed an endothermic adsorption. Physisorptions occur when \(\Delta H<20\) kJ/mol and chemisorptions occur when \(\Delta H>40\) kJ/mol [57]. \(\Delta H = 70\) kJ/mol indicated clearly that arsesnic(III) adsorption on MBC is a chemisorption process. The positive value of \(\Delta S^0\) showed randomness slightly increased during arsenite chemisorption from solution onto the MBC Fe\(_3\)O\(_4\) particles.

2.4.6 Adsorption from wastewater and simulated water samples

Competitive adsorption of other species effected As(III) uptake. Competition with uptake of As(III) present at 4 ppm onto MBC was assessed by batch experiments (outlined in section 2.3.5) on 4-nitroaniline (4NA), salicylic acid (SA), CrO\(_4^{2-}\)/Cr\(_2\)O\(_7^{2-}\), SeO\(_4^{2-}\), MoO\(_4^{2-}\), PO\(_4^{3-}\), NO\(_3^{-}\), F\(^-\), Cd\(^{2+}\) and Pb\(^{2+}\), where 1 ppm each added to industrial zinc waste water (IWW). We had previously studied on 4NA and SA [35, 36], as well as these same oxyanions [41], anions [41]
and heavy metal cations [34] on MBC. These contaminants were considered excellent competing adsorbates for As(III) because they previously had exhibited high adsorption capacities on magnetite-decorated Douglas fir biochar.

Three solution samples were studied with MBC as shown in Figure A.6. Sample A was industrial zinc (~0.4 mg/L) waste water (IWW) containing As(III) (4 ppm). Sample B had 1 ppm each of the organics, oxyanions, anions, and metal cations as noted above in the IWW. Sample C was heavy metal waste water from the Mississippi State Chemical Laboratory (HMW) with 4 ppm of added As(III). After these samples were equilibrated with MBC, all As(III) concentrations dropped below the WHO safe limit of 0.2 mg/L (2 ppm) for these wastewater discharges (Figure A.6) [7]. The neat IWW sample (A) had the lowest concentration after equilibrium (0.05 mg/L) while the IWW sample spiked with competitive contaminants (B) contained 0.09 mg/L of As(III). The higher As(III) concentration in B is probably due to competitive sorption of the spiked oxyanion (CrO$_4^{2-}$, PO$_4^{3-}$, NO$_3^-$ etc.) contaminants, decreasing the availability of magnetite surface for As(III) adsorption. Water sample HMW (C) retained the most As(III) (0.14 mg/L). Chemical laboratory heavy metal waste usually have high concentrations of competing contaminants (mainly CrO$_4^{2-}$) that decrease the availability of magnetite surface sites. Since all the As(III) levels dropped below the WHO safe limits, magnetite/biochar composites qualify as potential adsorbents for removing As(III) from industrial wastewater samples.

2.4.7 Column sorption, breakthrough studies and regeneration

Fixed-bed continuous flow tests are necessary to obtain design models for predicting how much effluent a column bed can treat and how long the bed will last before regeneration is necessary. Packed bed performance was described using a breakthrough curve [58, 59]. The
break-point time was reached when the concentration ratio ($C/C_0$, where $C$ is the concentration of As(III) at time $t$, and $C_0$ is the initial concentration of As(III)) that rises rapidly to 1.0. At the end of the breakthrough curve, the bed was judged ineffective. The mass transfer zone width and shape depends on the adsorption isotherm, flow rate, mass-transfer rate to the particles and pore diffusion [58]. A fixed-bed continuous flow MBC column sorption experiment was performed as described in section 2.3.6. The results are described below and in figure 2.4.

Figure 2.4  a) Breakthrough curve for As(III) adsorption onto MBC and b) desorption curve for As(III) (particle size, 300-500 µm range)

The ratio ($t_u/t_t = H_b/H_t$) is the fraction of the total bed capacity or length utilized up to the breakpoint. Hence, the bed length of $H_t$, $H_b$ is the bed length used upon reaching the break point [58]. The usable and unusable bed lengths were 3.1 cm and 1.9 cm, respectively, in the 5.0 cm long, 1.5 cm dia. bed used. The fraction of total capacity used at the break point was 0.285. The capacity at saturation was 2.85 mg/g, which is ~60 % of the Sips isotherm batch sorption capacity, corresponding to the ratio between the usable and total column lengths.
Upon stripping with KH$_2$PO$_4$, the concentration of As in the column effluent reached 0.725 mg/L after 150 min. Mass balance calculations showed that 1.01 mg of As(III) were removed versus 1.16 mg of As initially retained on the column (87 %) (Figure 2.4b). Three cycles restored 85%, 81% and 79% of the column’s initial capacity, respectively. The desorption efficiency dropped from 87% to 80% and 76%, respectively. This was attributed to unreleased arsenic remaining on the column. Other alkaline stripping reagents (Na$_2$CO$_3$, NaHCO$_3$ and NaOH) can be used and complete desorption may be achieved at higher stripping agent concentrations [46]. As(III)-laden columns can be recycled when scaled up.

2.4.8 Comparison of capacities

Table 2.2 summarizes previous reports of As(III) or As(V) uptake on different adsorbents. As(III) capacities ranged 0.02-7.0 mg/g while the As(V) capacities spanned 0.27-5.85 mg/g. Most of these high capacities reported are for the acidic pH (4-5) solutions. MBC compares favorably with fast (~1-1.5 h) As(III) removal kinetics, a satisfactory capacity at pH 7 (close to natural waters) and 25 °C and exhibits regeneration abilities.
Table 2.2 Comparative evaluation of various adsorbents for As(III) and As(V) removal at room temperature (22-25 °C)\(^a\)

<table>
<thead>
<tr>
<th>Adsorbents</th>
<th>Temp / °C</th>
<th>Kinetics</th>
<th>pH</th>
<th>Surfac e Area (m(^2)/g)</th>
<th>Adsorption Capacity, Q(^0) (mg/g)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maghemite nanoparticles (As(V))</td>
<td>25</td>
<td>2 h, Pseudo 1(^{st}) and 2(^{nd}) order</td>
<td>NA</td>
<td>NA</td>
<td>4.64, Langmuir and Freundlich</td>
<td>[60]</td>
</tr>
<tr>
<td>Magnetite-maghemite (As(III) and (V))</td>
<td>25</td>
<td>3 h, two steps</td>
<td>6.5</td>
<td>NA</td>
<td>0.01, Langmuir</td>
<td>[61]</td>
</tr>
<tr>
<td>Pine wood char (As(V))</td>
<td>25</td>
<td>24 h, Pseudo 2(^{nd}) order</td>
<td>5</td>
<td>2.73</td>
<td>1.20, Langmuir and Freundlich</td>
<td>[54]</td>
</tr>
<tr>
<td>Oak bark char (As(V))</td>
<td>25</td>
<td>24 h, Pseudo 2(^{nd}) order</td>
<td>5</td>
<td>25.4</td>
<td>5.85, Langmuir and Freundlich</td>
<td></td>
</tr>
<tr>
<td>Pine wood biochar (As(V))</td>
<td>25</td>
<td>24 h, Elovich</td>
<td>7</td>
<td>209.6</td>
<td>0.27, Langmuir</td>
<td></td>
</tr>
<tr>
<td>Hematite modified biochar (As(V))</td>
<td>22</td>
<td>24 h, Elovich</td>
<td>7</td>
<td>193.1</td>
<td>0.43, Langmuir</td>
<td>[62]</td>
</tr>
<tr>
<td>Biochar / γ - Fe(_2)O(_3) composite (As(V))</td>
<td>22</td>
<td>24 h, Pseudo 2(^{nd}) order</td>
<td>NA</td>
<td>NA</td>
<td>3.147, Langmuir</td>
<td>[25]</td>
</tr>
<tr>
<td>Pinewood MnO(_x)-modified biochar (As(V))</td>
<td>22</td>
<td>24 h, Elovich</td>
<td>7</td>
<td>67.4</td>
<td>0.91, Langmuir</td>
<td>[62]</td>
</tr>
<tr>
<td>Zn-loaded raw pine cone biochar (As (III))</td>
<td>25</td>
<td>1 h, Pseudo 2(^{nd}) order (intra-particle diffusion)</td>
<td>4</td>
<td>11.54</td>
<td>7.0, Langmuir</td>
<td>[63]</td>
</tr>
<tr>
<td><strong>Biochar-magnetite composite (As(III))</strong></td>
<td><strong>25</strong></td>
<td><strong>(1-1.5) h</strong></td>
<td><strong>7</strong></td>
<td><strong>320.1</strong></td>
<td><strong>5.06, Langmuir</strong></td>
<td><strong>This study</strong></td>
</tr>
</tbody>
</table>

\(^a\)Regeneration studies were not reported for any of the entries to this tables except for those used in this study (~3h using 0.5 M Na\(_2\)HPO\(_4\)). As(III) sorptive removal is not widely reported.

2.4.9 Mechanism of adsorption

2.4.9.1 X-ray photoelectron spectroscopy (XPS)

XPS probed the MBC surface region elemental composition and oxidation states, both before and after As(III) adsorption at pH 7. Low resolution survey spectra of fresh MBC and
MBC after As(III) sorption are illustrated in Figure A.7a and b, respectively. New peaks at 44.9 and 1326.9 eV binding energies are, due to electron ejection from arsenite As3p and As3d levels from As(III)-laden MBC [64]. A 0.4 atomic percent of As was determined in the XPS-probe of the surface regions.

High Resolution (HR) XPS of MBC probed the states of C and O before and after As(III) uptake. The C1s and O1s spectra were each resolved into four peaks, assigned and shown in Figure 2.5. The broad C1s 289.0 eV binding energy peak contains both CO$_3^{2-}$ and −COOH(R) oxidation states, which typically occur in 288-291 eV and 287-295 eV binding energy regions, respectively (see Table A.3). The 286.4 eV peak belongs to keto (C=O) carbons but overlaps both −COOH(R) and C-OH and C-O-C regions, making these evaluations approximate. Example C1s and O1s binding energies are given for inorganic, organic and polymeric model carbonates, aldehydes, ketones, carboxylic acids (Table A.3). Figure 2.5 also depicts the corresponding O1s spectra of fresh MBC and arsenite-laden MBC, where arsenite was adsorbed at pH 7. The amount of As(III) adsorbed is small, so the amount of oxygen present as As-O-Fe was small. Thus, the O1s binding energy (531.1 eV) for As-O-Fe cannot be differentiated from that of C-O within the large broadened 530.7 eV peak [61].

The O1s peak centered at 531.9 belongs to the magnetite Fe-OH (octahedral 111 plane) and C-O [65]. The 530.1 eV BE peak is due to Fe-O-Fe (Fe$^{2+}$-O-Fe$^{2+}$, Fe$^{2+}$-O-Fe$^{3+}$ or Fe$^{3+}$-O-Fe$^{3+}$) [66]. This Fe-O-Fe 530.1 eV peak atomic percentage on MBC after As(III) adsorption decreased from 17.9% to 12.5% in MBC. When this occurred, the O1s C-O peak at 530.7 eV, which would also contain any As-O-Fe contribution, increased from 3.8% to 9.8%. This increase in O1s contribution is consistent with the formation of FeOAsO$_2$H$_2$ functions chemisorbed at
surface Fe-OH groups [64, 67]. While the integrations reported are very curve-resolution dependent, the overall increase seems real. CO$_3^{2-}$ salts, -COOH, -COOR functions can span a wide O1s binding energy range (~531-538 eV) making resolution difficult and also possibly broadening the O1s C=O region.

Next, the As2p and 3d XPS spectra (Figure 2.5e and f) were de-convoluted into individual component peaks arising from the different arsenic (III) and (V) oxidation states which partially overlap [65]. The As2p peak for As(III) and As(V) have binding energies of 1327.2 eV and 1326.0 eV, respectively [68]. The As3d peaks appear at binding energies of 46.7 eV for As(III), 45.4 eV for As(V) and 44.2 eV for As(III) (Figure 2.5) [61, 65]. Thus, both As2p and As3p spectra confirmed that oxidation of a portion of As(III) to As(V) has occurred, either in the solution or at the Fe$_3$O$_4$ surfaces or during the XPS sample preparation.

The Fe2p high resolution XPS spectra of MBC, before and after As(III) adsorption, were deconvoluted into its peak components (Figure 2.5g and h). The theoretical multiplet peaks for both magnetite (Fe$_3$O$_4$) and some maghemite (Fe$_2$O$_3$) appeared in both spectra. The peaks full widths at half maximum (FWHM) were generally held to be between 1.4 and 3.5 eV (Table A.4). Fe$_3$O$_4$ has a Fe$^{2+}$:Fe$^{3+}$ ratio of 1:2. The spectral deconvolution (Figure 2.5) using these parameters gave Fe$^{2+}$:Fe$^{3+}$ = 0.3 : 0.7 (3:7) for MBC. This stoichiometric ratio exceeded somewhat the 1:2 ratio in magnetite because the excess balance of Fe$^{3+}$ is due to presence of some maghemite (Fe$_2$O$_3$) that also precipitated on MBC [69]. The atomic percent of arsenic detected by XPS after adsorption was in the surface region only (~1.27%) versus ~14.51 - 15.16% for iron. Thus, any contribution to the Fe2p XPs spectrum by Fe-O-As(III)/As(V)
complexes or changes in oxide atomic percentages due to arsenite oxidation to As(V) via iron reduction would be obscured by the large Fe-O-Fe magnetite and maghemite signals [61].

Figure 2.5 HR-XPS deconvolutions of MBC’s C1s, O1s and Fe2p (a), (c) and (g) spectra, respectively, before As(III) adsorption and also As(III)-laden MBC’s C1s, O1s and Fe2p (b), (d) and (h) spectra, respectively. Deconvolution of As2p (e) and As3d (f) spectra for arsenic-laden MBC, initially prepared by As(III) adsorption are also given. (CPS – counts per second). Note that the As3p third peak was not identified due to its low signal to noise ratio. Experimental data is not distinguishable from curve fittings in C1s, O1s and Fe2p HR-XPS due to their high signal to noise ratio.
The O1s binding energy and intensity changes depend on the specific MBC surface species present and their amounts. A relationship between atomic charge and O1s binding energy was derived from *ab initio* Hartee-Fock frontier molecular orbital theory (equation 2.2) [70].

\[
Q^* = -4.372 + \frac{\sqrt{385.023-8.976\times(545.509-BE_{O1s})}}{4.488}
\]

Here, \(Q^*\) values are the actual oxygen atomic charges (esu) in the sorbent’s oxygen atoms and \(BE_{O1s}\) are the XPS O1s binding energies obtained from XPS. The Fe2p binding energies and intensities of the iron atomic charges are correlated and can be calculated by equation 2.3 [65].

\[
Q^* = 0.3233BE_{Fe2p} - 228.51
\]

Here, \(BE_{Fe2p}\) is the Fe2p binding energy from XPS. The calculated O1s and Fe2p atomic charges and their variations on surface complexation are summarized in Table A.5.

After adsorbing As(III) at pH 7, the magnitude of oxygen and iron atomic charge in MBC has changed. Oxygen became more negative and iron less positive, respectively. Arsenite oxygen atoms act like a Lewis base and are chemisorbed by forming covalent (inner-sphere) Fe-O-As complexes in the place of some Fe-OH surface sites [65]. The mechanism for chemisorption of As(III) onto magnetite is summarized in Scheme 2.1. Arsenite adsorbs on magnetite’s 111 outer planes as monodentate links to a single iron or as a bidentate species, which can be to a single iron atom or to two adjacent surface iron atoms (see Scheme 2.1 and A.9). Also, tridentate adsorption of As(III) might occur at a tetrahedral vacancy (Scheme 2.1). EXAFS and XANES studies by Monárrez-Cordero et al. and Liu et al. demonstrated predominant formation of bidentate binuclear corner-sharing complexes (\(^2\)C) for As(V) (arsenate) adsorption on magnetite.
Tridentate trinuclear corner-sharing (3C) complexes were favored for As(III) on magnetite (Figure 2.8) [72]. A similar mechanism for As(III) adsorption on the MBC’s magnetite surface is in agreement with all our results. MBC’s PZC and arsenic speciation versus solution pH, discussed in section 2.4.2, also confirm with scheme 2.1.

The reported pKₐ of magnetite surface hydroxyl groups is 5.6 [73] and magnetite’s PZC is ~6.5 [74]. In ~pH 5.6 solutions, -FeOH or -Fe₂O (O between iron atoms) species are the dominant forms of magnetite surface [73] and As(III) exists as H₃AsO₃ in water. No electrostatic attraction exists between As(III) and magnetite surface hydroxyls. Magnetite protonation at more acidic pH values generated positively charged surface (-Fe-OH⁺) sites which could induce or assist chemisorption by activating loss of H₂O from iron (Scheme A.1), but not by electrostatic attraction. Adsorption is higher in the pH 7-12 region, maximizing at pH 8. At pH 7, MBC is slightly negatively charged. Negative surface charge density increases as pH rises and deprotonation of surface Fe-OH groups proceeds to produce more Fe-O⁻ sites. Most reasonably, H₃AsO₃ adsorbs at neutral Fe-OH and negative Fe-O⁻ surface sites from pH 6-9. H₂AsO₃⁻ adsorption at Fe-OH sites could pick up going above pH 8 to pH 10 since the [H₂AsO₃⁻] is growing (Figure 2.2). At very high pH values the negative charge surface concentration rises, but adsorption still remained robust at pH 12, where Fe-O⁻ sites dominate on the magnetite’s surface and. At pH 12, H₂AsO₃⁻ and HAsO₃²⁻ almost exclusively are present in solution. Here, chemisorption proceeds despite electrostatic repulsion.

At acidic pH values of 2 and 3, far below magnetite’s pKa (5.6), the dominant protonated surface magnetite species are –FeOH₂⁺ and –Fe-O⁺(H)-Fe, while As(III) exists as H₃AsO₃ and possibly small amounts of H₄AsO₃⁺. H₃AsO₃ could hydrogen-bond to the Fe₃O₄ neutral surface
or to the already protonated surface site (see Scheme A.1). Accompanied by requisite proton transfers, arsenite oxygen displaces water from iron via an association process. The overall view of the As(III) adsorption mechanism on magnetite is presented in Scheme 2.1, showing the stepwise formation of both monodentate (2, 3, and 4) and bidentate complexes (5 and 6 at one Fe and 7 and 8 at two Fe sites). Also, a tridentate complex, 9 that can form at a tetrahedral vacancy is shown [72].
Scheme 2.1  Mechanism of As(III) sorption. Structure 9 ([72])
2.4.10 Redox transformation of arsenic

Redox reactions can occur, either at the magnetite surface or in solution, that oxidize As(III) to As(V). Air oxidation might occur in the original solution or during sample drying for XPS studies. Such oxidations could account for the presence of both As(III) and As(V) in the HR-XPS spectra of MBC after adsorbing As(III) (Figures 2.5 and A.9). If As(V) forms, it would bind more strongly to magnetite and become less mobile [72]. Arsenic redox in solution could be triggered by dissolved oxygen or dissolved iron ions available from the slight dissolution of magnetite. Furthermore, dissolved Fe$^{2+}$ could catalyze the formation of reactive oxygen species (O$_2^-$ and `OH), promoting As(III) to As(V) oxidation [72, 75]. Surface magnetite to maghemite transformation [72], iron-oxy-hydroxide mediation [76] and X-ray beam-induced reactions during XPS analysis [76, 77] might cause As(III) oxidation. As(III) redox during adsorption on magnetite/maghemite was also observed in XPS spectra by Liu [72], but no mechanistic evidence was provided.

As(III) and (V) were originally both observed by XPS, when As(III)-laden MBC had been exposed previously to air. Thus, samples were prepared anoxically for XPS analysis. However, they also exhibited As(V) on the Fe$_3$O$_4$ surface, suggesting surface Fe(III) had oxidized As(III) to As(V). The As2p peak of samples prepared by both oxic and anoxic adsorption were deconvoluted into two peaks, As(III) and As(V). Both shift to lower binding energies when the adsorption was performed at increasing pH. This was expected for surface Fe-O-AsO$_2$H$_2$ chemisorbed groups because they deprotonate to Fe-O-AsO$_2$H$^-$ and to Fe-O-AsO$_2^{2-}$ (and their bidentate analogues) as pH increases (represented in Scheme 2.1). Similar trends in pH-dependent As(V) XPS BE shifts were observed on magnetite-doped carbon fiber [65].
third peak tail (~1324.5 eV) was observed in As2p HR-XPS for As(III) sorbed to MBC under oxic conditions, but the signal noise ratio was too small to assign (Figure A.9). Anoxic samples did not display this peak. As(V)/As(III) atomic ratios were, higher for samples made under oxic conditions (~1.4) (at pH 7) versus anoxic conditions (~0.85) (Table A.6). Thus, a portion of the As(III) oxidation to As(V) must be facilitated by atmospheric O2.

Under both oxic and anoxic conditions the adsorbed As(III) was oxidized to As(V). Oxidation under anoxic conditions is accompanied by magnetite to maghemite redox (net Fe2+ to Fe3+) transformation of the magnetite surface, identified by the observation of a reduction of magnetite’s Fe2p3/2 (Fe3+) peak atomic percentage of 2.7 % at ~710 eV to 1.9 % upon As(III) uptake (Figure 2.6 and Table A.4). As(III) is converted to less toxic As(V) when regenerating MBC or during the drying in air of As(III)-laden adsorbents [72].

2.5 Conclusion

A biochar/iron oxide composite, MBC, was prepared with magnetite primary nanoparticles (~18.1±3.9 nm dia.) and their aggregates (~2-7 µm) with an Fe3O4 loading of 29.2 % wt. MBC remediated with relatively fast kinetics (~1-1.5 hrs) As(III) contaminated water and waste waters containing several coexisting contaminants. Dispensing magnetite provides a high Fe3O4 surface area but on larger char particles that allow column flow. The adsorbent is magnetic, allowing its use in stirred tank batch treatments with facile magnetic removal and regeneration. During and after As(III) adsorption on Fe3O4, portions of As(III) is converted to less toxic As(V) via redox reactions. MBC exhibited a 5.49 mg/g As(III) Sips isotherm capacity (5.06 mg/g for Langmuir). Fixed-bed column continuous flow adsorption with regeneration was demonstrated. As(III) concentrations in several treated wastewater samples containing a variety of other contaminants
were remediated to below the WHO tolerance limit of 0.2 mg/L. Robust adsorption of arsenite was achieved over a large pH range from 2-10, maximizing at pH 8. The pH-dependent adsorption mechanism was discussed with evidence supplied by C$_{1s}$, O$_{1s}$, As$_{2p}$, As$_{3d}$ and Fe$_{2p}$ XPS spectroscopy and previous surface structural studies from literature.
2.6 REFERENCES


76. Tian, Z., et al., Opposite effects of dissolved oxygen on the removal of As (III) and As (V) by carbonate structural Fe (II). Scientific Reports, 2017. 7(1): p. 17015.

CHAPTER III
RHODAMINE B ADSORPTIVE REMOVAL AND PHOTOCATALYTIC DEGRADATION
ON MIL-53-FE MOF/MAGNETIC MAGNETITE/BIOCHAR COMPOSITES


3.1 Abstract

MIL-53-Fe Metal-Organic Framework (MOF) was grown using terephthalic acid linker and FeCl$_3$ into an already prepared, high surface area, magnetic, Douglas fir biochar/Fe$_3$O$_4$ (MBC) adsorbent hybrid. This resulting triphase hybrid, multifunctional, magnetically recoverable, sorptive, photocatalytic and degradative, adsorbent (MOF-MBC) was used both to remove and catalyze the photodegradation of rhodamine B (Rh B) with or without Cr$^{6+}$ present. Rh B is a widely used colorant in textile, printing and tanning industries that is also associated with deleterious health effects. Batch aqueous sorption studies were performed at various pHs, Rh B concentrations and temperatures in-order to determine the optimum adsorption pH, kinetics, thermodynamics, and sorption capacity. Rh B adsorption exhibited a Langmuir adsorption capacity of $\sim$55 mg/g at pH 6, 200 rpm agitation and 25 °C. This MOF-MBC hybrid was characterized by SEM, TEM, EDS, XRD, FT-IR, TGA, BET, Elemental Analysis and XPS. Deethylated and carboxylic compounds were identified as photodegradation intermediates. Electrostatic and $\pi$-$\pi$ stacking interactions are thought to play a significant role in Rh B sorption. Hexavalent chromium (Cr$^{6+}$) and Rh B often co-exist in tannery and printing wastewater. Cr$^{6+}$ can trigger the photo-degradation of Rh B into CO$_2$ and H$_2$O in the presence of both MIL-53-Fe
MOF and MOF-MBC. Hence, adsorbent stripping regeneration can be minimized in real world applications. Additionally, the biochar phase, aids on MOF dispersion to prevent particle aggregation and provide extra stability to MOF, with a secondary adsorption site for heavy metal, oxy anion and organic contaminants.

3.2 Introduction

Water remediation has become a huge problem worldwide, due to rising contamination levels [1]. Efficient contaminant removal from wastewater is a crucial environmental need. Colorant dyes contaminate waters from various textile industry effluents [2] and should be addressed.

Metal-organic frameworks (MOFs) are crystalline structures consisting of metal center units connected by organic framework linker units which spontaneously assemble by forming strong bonds into three-dimensional regular crystalline structures [3, 4]. They have highly porous characteristics that are beneficial for molecular separations based on their range of pore sizes, pore volumes, large surface areas, ease of assembly and wide variability of interactions that are possible for guests to undergo within the host cavities of their inorganic and organic structural components [4]. Many MOFs also possess semiconductor properties that allow them to reduce contaminants and degrade dyes in the presence of light [5-7]. These properties suggest that some MOFs might be used for simultaneous or in-series adsorption/degradation of contaminants. Ideally, such MOFs might adsorb and catalyze destruction of a pollutant in either batch or continuous flow processes and never require regeneration [8]. MOFs have already been used in acid catalysis, esterification, hydrolysis of esters, coupling reactions, reduction reactions etc [9]. A major drawback of many MOFs for use in aqueous adsorption is poor stability in water [10].
The MOF’s framework structure could be destroyed by displacement of bound ligands [10]. Competitive blockage of internal binding sites by water might prevent adsorption of targeted adsorbents [10]. Many MOFs have been compared to such semiconductors as n-doped TiO$_2$ due to their remarkable photocatalytic degradation properties [11]. Some MOFs [11, 12] possess high chemical stabilities similar to TiO$_2$ [13, 14] and have proved efficient for use in degradation. These example MOFs were easy to use [11, 12].

Biochar is a readily available byproduct from both fast biomass pyrolysis during bio-oil production or slow pyrolysis processes at a variety of temperatures [15, 16]. The H/C and O/C ratios drop as the pyrolysis time and temperatures are increased, leading to a plethora of biochar compositions, morphologies, surface areas, pore volumes etc. Biochars are being widely studied as low cost adsorbents [17-19], soil modifiers [20], carbon sequestrants [21], and nanoparticle dispersants [22-27]. We envisioned biochar serving as a surface dispersant for MOFs to reduce particle agglomeration, to increase mechanical strength, and to form larger particle size biochar-MOF hybrids which allow rapid water flow through fixed beds, while dispersing tiny attached MOF particle sizes. Beds of tiny MOF particles alone would result in large pressure drops and slow flows in columns. For many years we have also made magnetically manipulatable adsorbents by decorating Douglas fir biochar (BC) with small magnetic Fe$_3$O$_4$ nanoparticles [22, 24, 28] to produce MBC. These Fe$_3$O$_4$-containing biochar surfaces exhibit Fe-OH functions which enhance the adsorption of oxyanion contaminants (AsO$_4^{3-}$, AsO$_3^{2-}$, PO$_4^{3-}$ and others) [29]. At lower pH, these surface Fe-OH hydroxyl groups are protonated, attracting and binding oxyanions while also allowing the adsorbent to be magnetically manipulated [30]. In this study, the initial Douglas fir, high surface area biochar (BC) was produced as a biproduct of wood gasification, (Biochar Supreme, Inc). Then BC was first decorated with magnetite (Fe$_3$O$_4$)
magnetic nanoparticles and then was further decorated with MIL-53-Fe MOF (Figure 3.1) to form a dual hybrid (Figure 3.1). This sorbent was employed to adsorb and catalytically photodegrade the dye rhodamine B (Rh B) (Figure 3.1).

Rh B is a dye and often used as a tracer to determine flow direction and transport rates [31]. Rhodamine dyes have many fluorescence applications [31]. Studies of contaminant dye separations and aqueous adsorption motivate this current study [32], including rhodamine B effluents from textile, printing, and tannery industries.

*Figure 3.1* Structure of MIL-53-Fe MOF
Figure 3.2  Schematic representation of a) MOF-MBC and b) the chemical structure of rhodamine B

3.3  Materials and methods

All the chemicals and reagents used were analytical grade (Sigma-Aldrich), unless otherwise noted.

3.3.1  Synthesis of MIL-53 Fe MOF and MOF-MBC composite

A mixture of terephthalic acid ($p$-$C_6H_4(CO_2H)_2$) (~1.6 g), iron(III) chloride hexahydrate (FeCl$_3$·6H$_2$O) (~2 g) and $N,N$-dimethylformamide (DMF) (~20 mL) was sonicated for 1 h at 25 °C and transferred to a Teflon-lined stainless-steel bomb (~23 mL). This mixture was heated at 150 °C for 15 h [33]. Once cooled, the resulting MIL-53-Fe MOF suspension was filtered, thoroughly washed with methanol (3 x 50 mL), and dried under vacuum at 100 °C for 12 h. MIL-53-Fe MOF occurs as a poorly crystalline light orange powder. Washing with excess methanol exchanges the DMF solvent trapped in the MOF. The crystallinity can be enhanced by using HF acid for the synthesis mixture [34], but HF can dissolve the Fe$_3$O$_4$ in MBC, so it was not used in either the MIL-53-Fe MOF or MOF-MBC preparation.

MBC was prepared first as a substrate for MIL-53-Fe MOF according to our previously describe procedure [24]. Then, ~50 g of Douglas fir biochar (Black Owl, Biochar Supreme Inc.) (particle size was sieved to 1-2 mm, surface area 687 m$^2$/g, and porosity 0.251 cm$^3$/g) was added
to water and homogenized (~1950 mL water in total) with a mixed iron (III) chloride (~18 g) and iron (II) sulfate (~36.6 g) solution. Then magnetite precipitation onto the “Black Owl” biochar was triggered by the drop-wise addition of 10 M NaOH, maintaining the pH at 10 for ~24 hrs. The resulting Fe₃O₄-magnetized biochar (MBC) was filtered, then repeatedly washed with distilled water, followed by three ethanol washes. The MBC was then vacuum-filtered and dried overnight at 50 °C in a hot air oven. The MBC was used as a substrate onto which MIL-53-Fe MOF was both deposited and nucleated during synthesis of this MOF. The same amounts of MOF precursor reagents and identical procedures as stated above were employed for the preparation of MOF-MBC, except that 8 g of dried MBC was added into the MOF synthesis mixture in a DMF slurry that was prepared as described above. Similar to the independent MOF preparation, the resulting MOF-MBC composite was washed with 3 x 50 mL of methanol and dried under vacuum at 100 °C for 12 h. The weight gain of MIL-53-Fe onto MBC after the MOF formation and deposition was ~3.8 g. This corresponds to ~89 % yield of MIL-53-Fe MOF out of the total amount formed that became deposited or grew from nucleation onto MBC carrier. Since complete DMF exchange with methanol is difficult, MOF-MBC may contain some DMF that contributes to this measured weight gain despite thorough MeOH extractive washings. Traces of MeOH from washings may also remain. It is possible that some traces of terephthalic acid and iron chloride may also have deposited on MOF-MBC.

3.3.2 Adsorption kinetics and isotherm experiments

Aqueous solutions of 50 mg/L Rh B (20.0 mL) at 25°C were made to study the effects of pH on Rh B adsorption on MOF-MBC (50.0 mg). The solution pH values were adjusted to values ranging from pH 1 to pH 13 in pH intervals of 2 by using different molarities of HCl and NaOH. The optimal pH for adsorption was found to be 8, but a pH of 6 was chosen for kinetic
and isotherm experiments because it is closer to the natural pH of water. Moreover, the percentage Rh B removal values between pH 6 and pH 8 were similar, so this adsorption difference was negligible. The adsorption of Rh B dependence on pH is discussed in section 3.4.3.1.

Rh B adsorption kinetics on MOF-MBC were determined using 50.0 mg MOF-MBC doses with 20.0 mL of Rh B at separate concentrations of 25, 50 and 75 mg/L, placed into 50 mL polypropylene containers at pH 6 and 25°C. The filled containers were shaken in an orbital shaker at 200 rpm for specific times and then removed, filtered through a 0.22 μm filter, and the remaining Rh B concentrations, were determined using UV-Vis at 554 nm versus a predetermined, calibration curve. The limit of the detection (LOD) for the method was 0.01 mg/L. The matrix effect was assessed by tests performed using matrix matched calibration curves. Briefly, standard Rh B solutions were spiked into water pre-equilibrated with biochar and the calibration curve slopes were compared with the calibration curves prepared in ultra-pure water. Slope differences were \( \sim \pm 6\% \) and hence, an external calibration curve was used in the analysis. Kinetics study results are discussed in section 3.4.3.2.

Isotherm experiments employed 5 to 1000 mg/L Rh B solutions (25.0 mL) which were equilibrated with MOF-MBC (50.0 mg) and then adjusted to pH 6 using aqueous HCl and NaOH. Rh B adsorption values per unit of adsorbent \( (q_e) \) were each calculated using equation 3.1

\[
q_e = \frac{V(C_0 - C_e)}{M}
\]

3.1

This equation is discussed on page 65. If you have any questions, please contact the author.
Here, $C_0$ and $C_e$ are the initial and equilibrium concentrations of Rh B in units of mg/g, $V$ is the volume of the solution in L, and $M$ is the total mass in g of adsorbent added. Each experiment was performed three times in Figures 3.9-3.13. Isotherm results appear in section 3.4.3.4.

### 3.3.3 Characterization of BC, MBC, MIL-53-Fe MOF and MOF-MBC

BC, MBC, MIL-53-Fe MOF, MOF-MBC and Rh B-MOF-MBC were each individually characterized. A batch equilibrium adsorption experiment consisting of 50.0 mg of MOF-MBC that was equilibrated in 20 mL of solution composed of 1000 mg/L Rh B at pH = 6 was the source of Rh B samples sorbed on MOF-MBC. The N$_2$ Brunauer-Emmet-Teller (BET) specific surface area, pore volume, and pore sizes were determined using a N$_2$ adsorption isotherm at ~77 K (Micromeritics Tristar II Plus). MIL-53-Fe MOF surface area was also determined by CO$_2$ adsorption at ~273 K. C, H, O, N and S contents of the adsorbents and Rh B-laden-MOF-MBC were measured by combustion analysis using a CHN elemental analyzer (CE-440). Ash content was determined through heating in air at 650 °C for 15 hrs in an open-top porcelain crucible in the muffle furnace. The content of organic oxygen was calculated using the equation ($O\% = 100 - (C + H + N + S + ash)$). The weight percentages of iron in BC, MBC, MIL-53-Fe, MOF, and MOF-MBC were determined using atomic absorption spectroscopy (AAS) (Shimadzu AA-7000). Complete acid digestions were performed on 0.1 g of biochar using 50.0 mL of 1:1 95% H$_2$SO$_4$/70% HNO$_3$. Iron dissolved from both the oxidizing biochar and MOF samples into the acid for 24 h (70 °C) with stirring. These solutions were then diluted 10-fold with deionized water prior to AAS analysis. A recovery test was performed with Fe$_2$O$_3$ and produced ~94 % recovery.

A JEOL JSM-6500F FE instrument run at 5 kV generated the scanning electron microscopy (SEM) images of the MBC and MOF-MBC surface morphologies. A Zeiss, EVO 40
SEM containing a BRUKER EDX system was used to obtain SEM/EDS surface region elemental compositions and their distributions. A JEOL model 2100 TEM electron microscope operated at 200 kV produced transmission electron microscopy (TEM) micrographs of MBC and MOF-MBC. An Oxford X-max-80 detector was used to perform TEM/Energy-dispersive X-ray spectroscopy (EDX) analysis (elemental mapping) of MBC, MIL-53-Fe MOF, MOF-MBC, and Rh B-laden MOF-MBC. A Rigaku ultima III (using Cu-K(λ =1.54 Å X-rays) was used to conduct X-ray diffraction (XRD) analysis and determine the crystallographic structures.

X-ray photoelectron spectroscopy (XPS) analyses were run on a Thermo Scientific K-Alpha XPS system equipped with a monochromatic X-ray source at 1486.6 eV, corresponding to the Al Kα line, with a spot size of 400 µm². Photoelectrons were collected from a takeoff angle of 90° relative to the overall sample’s fractal particle surface. Measurements were done in the constant analyzer energy mode. The survey spectra were taken at a pass energy of 200 eV, while the high resolution (HR) core level spectra were taken at a 40 eV pass energy. Fourier Transformed Infrared spectroscopic (FT-IR) analysis (ATR mode) was carried out using a Thermoscientific iD-5 (Nicolet) instrument. Adsorbent thermogravimetric analysis (TA instruments, TGA Q 50) was performed under a 100 mL/min nitrogen flow over 30-800 °C. An Agilent 1200 series LC-MS equipped with a UV-vis diode array and mass spectrometric (Agilent 6120 Quadrupole) detector separated (C18 reverse phase 150 mm * 4.6 i.d, column) and then analyzed intermediate products. Methanol and 5 mM ammonium acetate were used in the mobile phase. The programmed gradient was 55% methanol flow was held for 10 min, linearly increased to 65% within 0.5 min, and then maintained for 12.5 min before returning to 55 % in the last 1 min. The flow rate was 50 µL and mass scan was conducted in 10-500 m/Z range at positive ion mode.
3.4 Results and discussion

3.4.1 Characterization of MIL-53-Fe MOF, MBC, and MOF-MBC

3.4.1.1 Surface morphology

MIL-53-Fe MOF grew in octahedral rod-like shapes in ~0.5 µm to ~1.1 µm diameters and ~0.7-1.5 µm lengths (Figure 3.3a) which are aggregated as in Figure 3.3b. The MBC surface exhibited magnetite primary nanoparticles (~16-19 nm) and their aggregates (Figure 3.3c) [30]. The MOF-MBC surface exhibited octahedral rod-like MOF structures after the MIL-53-Fe MOF synthesis/deposition step onto the MBC present (Figure 3.3d). Extensive coverage of the original MBC surface by MIL-53-Fe MOF rods was observed on MOF-MBC. Many of these were observed to be fractured in this dual hybrid. MIL 53-Fe MOF crystals or deposits that begin to grow within some biochar pore sizes may be not be able to complete growth due to wall boundaries or lack of component diffusion. The MBC surfaces (both Fe₃O₄ and biochar regions) also may initiate MOF nucleation differently than nucleation in the solutions, giving the MOF-MBC hybrid surface a different mixture of MIL-53-Fe MOF textures. Other possible causes of MOF defects generated during MOF-MBC formation are cation substitution, mixed valence and cation vacancies, ligand defects and anion or ligand substitution as implicated in other systems [35].
Successful MIL-53-Fe MOF formation onto MBC surfaces was further confirmed using TEM-EDX and elemental mapping (Figures B.1 and B.2) and EDX (~1-2 µm penetration depth) patterns can sample MOF-MBC below the surface. TEM elemental mapping images were produced (Figure B1) to show surface-near surface region elemental composition in the MBC, MIL-53-Fe MOF, MOF-MBC, and the Rh B-laden MOF-MBC samples. MBC contains Fe and O on the biochar surface phase due to the Fe₃O₄ deposition. The MIL-53-Fe MOF sample exhibits its regular elemental composition, with some residual Cl present from FeCl₃ that was not reacted and had not been washed away in the preparation. The nitrogen likely originated from DMF that had not been exchanged with methanol during purification. In MOF-MBC, the C content was larger than in MBC. This large C contribution is from the terephthalic acid linker within the MOF which covers much of the surface. Rh B has ~70 % carbon and upon Rh B
adsorption, the C content of MOF-MBC has further been increased from 44 % to 68.5 % (Figure B.2).

3.4.1.2 X-ray diffraction analysis

The XRD peak pattern for MBC corresponds to that of the precipitated magnetite particles on BC, (Figure 3.4). Locations (2θ) and intensities of the diffraction peaks in MBC are consistent with the standard pattern for magnetite, JCPDS Card No. (79-0417). The major peak at 35.45° is for the crystalline plane of Fe₃O₄ with Miller indices of (311). Other peaks were observed at 30.10° (220), 43.08° (400), 53.45° (422), 56.98° (511), 62.57° (440), and 74.02° (622). The characteristic XRD peaks (Figure 3.4) for MIL-53-Fe MOF alone in the 8 to 27 degree 2θ range (9.36°, 12.50°, 17.34°, 18.74°, 21.94°, 25.21° and 27.98°) were observed. The XRD pattern for MOF-MBC exhibited all the key peaks for both magnetite and MIL-Fe-53 MOF [36]. Since the MOF-MBC sample’s XRD pattern contains peaks characteristic of both MIL-53-Fe MOF and the magnetite peaks for MBC, the production of the dual hybrid MOF-MBC is confirmed. Some weaker peaks were difficult to resolve from substantial broad amorphous peaks from biochar [37] and the peaks from magnetite. Several peaks (12.50°, 18.74° and 27.98°) originally observed on MIL-53-Fe MOF were not seen in the XRD spectrum of MOF-MBC composite, and this is possibly due to the formation of amorphous phases of MIL-53-Fe MOF during the MOF-MBC synthesis.
3.4.2 FTIR analysis

The FTIR spectra of MBC, MIL-53-Fe MOF, Rh B, MOF-MBC, and Rh B-laden MOF-MBC are displayed in Figure 3.5. The FTIR spectrum of MBC (Figure 3.5a) like that of other biochars does not give sharp bands. This is due to the unavailability of significant amounts of functionality to produce strong, sharp vibrational or bending bands in IR absorption. During the pyrolysis at 400 °C and above decarboxylation, deamination etc. occur [38]. The Douglas fir biochar, precursor of MBC, was originally pyrolyzed at 900 °C, although for a short residence time of a few seconds. The FTIR spectrum of the Douglas fir biochar (BC) is almost identical to that of MBC. Figure 3.5b shows the IR spectrum of MIL-53-Fe MOF with a broad peak centered at ~3300 cm\(^{-1}\) which can be attributed mostly to the stretching vibrations of the O-H from
adsorbed and surface-bonded water or residual methanol. Bands at \(\sim 1600 \text{ cm}^{-1}\) and \(\sim 1300 \text{ cm}^{-1}\) are due to the asymmetric stretching vibrations of Fe(III)-coordinated carboxylate groups and stretching vibrations of -O-C-O- framework, respectively [39]. The peak at \(\sim 400 \text{ cm}^{-1}\) corresponds to C–H bending vibrations on the aromatic rings of the terephthalic acid linker [39]. Figure 3.5c shows the FTIR spectrum of Rh B with broad, H-bonded carboxyl OH vibrations centered at \(\sim 3300 \text{ cm}^{-1}\), symmetric carboxylic carbonyl stretching at \(\sim 1600 \text{ cm}^{-1}\) regions and sp\(^2\)-hybridized C–H in plane bending on aromatic rings at \(\sim 400 \text{ cm}^{-1}\). The MOF-MBC surface (Figure 3.5d) contains functional groups corresponding to those from MIL-53-Fe MOF, which further confirms the MOF has been successfully attached to MBC. The RhB-laden MOF-MBC spectrum (Figure 3.5e) shows the peak intensity enhancements in many locations associated with Rh B (especially in -C–H stretching, bending and carboxylic -C=O). However, distinguishing these from MIL-53-Fe MOF is difficult. However, in the “finger print” region from 1200-900 cm\(^{-1}\) peaks of Rh B are observed in the spectra (Figure 3.5e) of Rh B-MOF-MBC, confirming the successful adsorption of Rh B on MOF-MBC.
Figure 3.5  FT-IR characterization of MBC, MIL-53-Fe MOF, Rh B, MOF-MBC and Rh-laden MOF-MBC
3.4.2.1 Elemental, proximate and surface area analysis

The combustion elemental analyses of MBC (Table 3.1) found less C and H than in BC due to the added Fe$_3$O$_4$ weight fraction (~29 %) that MBC contains. The high C/H (45.6) ratio and observed O/C (0.14) ratio of BC is attributed loss of oxygenated and hydrogenated functionalities during the high temperature pyrolysis of the precursor Douglas fir wood. Precipitating iron oxide onto BC to form MBC leads to partial surface coverage and partial pore blockage of the BC portion of MBC. This causes a loss of ~48 % of its original surface area (687 to 327 m$^2$/g) and almost half of its pore volume (0.251 to 0.129 cm$^3$/g), despite adding the new surface generated by the small magnetite particles [28, 30]. The ash content in BC (2.65 %) is primarily composed of stable oxides and carbonates formed from sodium, potassium, magnesium, calcium and iron salts in the wood feed [30, 40]. Magnetic biochar had a high ash content (~31.6 %) mostly due to added magnetite deposits are illustrated by the amount of iron (27.8 %) in MBC.

Elemental composition for the MIL-53-Fe MOF corresponds well with the empirical formula, Fe$^{(III)}$(OH)(O$_2$C-C$_6$H$_4$-CO$_2$).H$_2$O (Fe = 21.9%, C = 37.7%, H = 2.77% and O = 37.6%) [34]. Trace DMF in this MOF may have contributed to the slightly higher C, H and N content versus its empirical formula. The IR spectra further confirmed the presence of a hydrated MOF structure, with a broad -OH peak centered at 3300 cm$^{-1}$ regions. The N$_2$ BET surface area of MIL-53-Fe MOF is very low (2.1 m$^2$/g) compared to the values reported in previous studies (7.3-38.2 m$^2$/g) [39]. This could be due to N$_2$ not being able to access the MOF pores because of its low pore diameter. However, the CO$_2$ BET surface area (42.2 m$^2$/g) was very close to the higher reported values in literature. CO$_2$ isotherms were conducted at 273 K providing sufficient energy for CO$_2$ to move from initial pore adsorption locations near the surface to occupy surfaces deep...
within ultramicro-pores. This is an alternative option for materials containing very small pores in which nitrogen and argon molecules cannot access at cryogenic temperatures, since they condense in the pores near the surface, thereby blocking access to surface area deeper within the pores [41]. Poorly crystalline MOF structures may also lead to the low surface area [39].

MOF-MBC’s elemental composition reflect that the MOF has been successfully incorporated onto MBC. The iron percentage decreased when MIL-53-Fe MOF was added to MBC as expected because the %Fe in the MBC is greater than that the MIL-53-Fe MOF being added. MOF crystalline growth on MBC during MOF-MBC synthesis may further block biochar pore access on MOF-MBC. The dual hybrid’s biochar surface region is now covered with both magnetite and MIL-53-Fe MOF particles, which result in further N₂-BET surface area loss from 326.9 m²/g to 7.8 m²/g. Rh B-laden MOF-MBC has a greater C content (61%) than MOF-MBC (46%) as expected because Rh B has ~70% C in its structure. This further confirms the successful adsorption of Rh B, but it does not define how much Rh B is adsorbed on each of the three surface phases of MOF-MBC.
Table 3.1 Elemental, proximate analysis and surface area data for BC, MBC, MOF, MOF-MBC and Rh-laden MOF-MBC

<table>
<thead>
<tr>
<th>Sample</th>
<th>% C</th>
<th>% H</th>
<th>% N</th>
<th>% O</th>
<th>% Ash</th>
<th>% Fe</th>
<th>Surface area (m²/g)</th>
<th>Pore volume (cm³/g)</th>
<th>Pore diameter (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BC</td>
<td>82.98</td>
<td>1.84</td>
<td>1.28</td>
<td>11.26</td>
<td>2.65</td>
<td>0.08</td>
<td>687.1</td>
<td>0.251</td>
<td>14.47</td>
</tr>
<tr>
<td>MBC</td>
<td>54.66</td>
<td>1.42</td>
<td>1.03</td>
<td>11.34</td>
<td>31.56</td>
<td>28.71</td>
<td>326.9</td>
<td>0.129</td>
<td>13.56</td>
</tr>
<tr>
<td>MOF</td>
<td>44.87</td>
<td>3.95</td>
<td>3.52</td>
<td>29.66</td>
<td>18.01</td>
<td>20.90</td>
<td>2.1b</td>
<td>0.000053</td>
<td>1.01</td>
</tr>
<tr>
<td>MOF-MBC</td>
<td>46.18</td>
<td>5.23</td>
<td>6.78</td>
<td>25.83</td>
<td>16.00</td>
<td>27.49</td>
<td>7.8</td>
<td>0.007797</td>
<td>7.39</td>
</tr>
<tr>
<td>Rh B-laden MOF-MBCa</td>
<td>62.35</td>
<td>2.34</td>
<td>2.28</td>
<td>33.05</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

a Ash and Fe analysis were not carried out for Rh B-laden MOF-MBC
b From N₂ BET adsorption isotherm at 77 K
c From CO₂ BET adsorption isotherm at 273 K

3.4.2.2 Thermogravimetric analysis (TGA)

TGA weight loss versus temperature plots (10 °C/min under 100 mL/min N₂) for BC, MBC, MOF and MOF-MBC are reproduced in Figure 3.6. BC and MBC show little mass loss up to 800 °C, because BC was originally pyrolyzed at ~900 °C for a short time. Also, the Fe₃O₄ deposited, when making MBC from BC, is stable to 800 °C in TGA [42]. MIL-53-Fe MOF undergoes a small mass loss in 100-290 °C temperature range, attributed mostly to adsorbed water and residual DMF removal. Drastic losses occur between 350 – 450 °C and 520 - 620 °C from a two stage decomposition of terephthalic linkers and their carbonization, collapse of the MOF and partial iron oxide formation [43]. MOF-MBC shows the expected lower mass drop versus MIL-53-Fe MOF since ~32 % wt of this specific MIL-53-Fe MOF was deposited onto the
more thermally robust MBC to form MOF-MBC. Similar results were observed on carbon nanotubes functionalized with MIL-53 Fe MOF [36].

Figure 3.6  Thermogravimetric analysis profiles of BC, MBC, MIL-53-Fe MOF and MOF-MBC (10 °C/min heating rate under 100 mL/min N₂)

3.4.2.3  X-ray photoelectron Spectroscopy (XPS)

Low resolution XPS scan spectra for BC, MBC, MOF, MOF-MBC and Rh-laden MOF-MBC are given in Figure 3.7. All show Fe2p peaks except BC, where the original iron content in the biochar is low. These survey spectra exhibit changes in the elemental composition upon deposition of magnetite onto BC to give MBC and MIL-53-Fe MOF formation on MBC during conversion to MOF-MBC. The surface region’s Fe atomic percentage (4.2 %) in MIL-53-Fe MOF is lower than MBC (9.3 %). Upon deposition/growth of the MIL-53 Fe MOF on MBC, the Fe atomic percentage has reduced to 7.6 %. This is because MOF-MBC only contains
approximately ~68% by wt. of MBC. Residual N and Cl peaks appear in MIL-53-Fe MOF and MOF-MBC from small amounts of DMF and chloride that was not exchanged or not washed away, respectively, during the MOF preparation. The formation of fluorinated MIL-53 MOF, Fe$^{III}$(OH)$_{0.8}$F$_{0.2}$(O$_2$C-C$_6$H$_4$-CO$_2$)$\cdot$H$_2$O has previously been reported [34], so some chlorinated MIL-53-Fe might have formed during MOF-MBC synthesis. TEM-EDX elemental mapping also supports this (Figure B.1).

![Image of XPS spectra](image.png)

**Figure 3.7** Low resolution (LS) survey scan XPS spectra for BC, MBC, MIL-53-Fe MOF, MOF-MBC and Rh B-laden MOF-MBC (CPS – counts per second).

The C1s, O1s and Fe2p High Resolution (HR) spectra of BC, MBC, MIL-53-Fe MOF, MOF-MBC and Rh B-laden MOF-MBC were each resolved and displayed in Figure 3.8. The expanded labelled version of C1s, O1s and Fe2p of these HR-XPS are shown in the supporting material (Figures B.3-B.7). The C1s and O1s spectra were each resolved into four peaks and these are assigned in Table 3.2. The Roman numerals in Figure 3.8 and Table 3.2 designate the resolved peaks and coordinate the resolved peaks in Figure 3.8 with their binding energies (BE)
and atomic percentages in Table 3.2. Binding energies for C1s at 289.7-288.4 eV, 287.7-286.4 eV, 285.8-285.3 eV and 284.7-284.2 eV range correspond to -CO2R(H) and CO3\textsuperscript{2-}, C=O, C-O and (C-H, C-C). However, C-C and -CH\textsubscript{3}, -CH\textsubscript{2}, -C\textsubscript{4}- (quaternary) and aromatic C in rings (the sp\textsuperscript{2} versus sp\textsuperscript{3} are all found in the 284.7-284.2 eV peak, but this peak for C-H and C-C vs those for C-O, C=O, -CO\textsubscript{2}R, CO\textsubscript{3}\textsuperscript{2-} are different carbon oxidation states and are resolved. MIL 53-Fe MOF has a higher C=O and C-O atomic percentage compared to BC and MBC. The C=O and C-O atomic percentages (from peak intensities) increased going from MBC to MOF-MBC and this further confirms successful deposition of MOF onto MBC.

Peaks were resolved in the O1s high resolution XPS binding energy (BE) ranges of (534.4-533.3) eV, (533.1-532.0) eV, (532.2-530.7) eV and (531.7-529.9) eV. These regions are assigned to (CO\textsubscript{3}\textsuperscript{2-}, O-C=O), O-C, C=O and Fe-O, respectively [30]. The atomic percentage of Fe-O drops as MIL-53-Fe MOF is generated and deposited on MBC. It covers a large fraction of the surface including some of the surface magnetite. XPS does not detect elements that are 100 Å below the surface and is quite surface specific to the top 15-20 Å. Likewise, the high resolution C1s spectra show that the atomic percent of C=O drops after MIL-53-Fe MOF deposited on MBC (Table 3.2).

The Fe2p curve-resolved envelop was not interpreted due to its complexity. The Fe2p\textsubscript{1/2} (724.7 eV) and Fe2p\textsubscript{3/2} (711.3 eV) doublet BEs found for MBC match the standard BEs reported for magnetite [44]. Also, the Fe2p\textsubscript{1/2} 725.5 eV and Fe2p\textsubscript{3/2} 711.7 eV BEs for MIL-53-Fe MOF match its literature values [36]. After this MOF is generated on MBC, the Fe2p\textsubscript{1/2} and Fe2p\textsubscript{3/2} BEs exhibit peaks 725.5 eV and 711.8 eV, respectively. The maximum intensities of these two
iron envelops in MOF-MBC are close to those of MIL-53-Fe MOF because such a large amount of the MOF was deposited and also it covers over much of the magnetite nanoparticles.
Table 3.2 High resolution (HR) C1s, O1s and Fe2p XPS data for BC, MBC, MIL-53-Fe MOF, MOF-MBC and Rh B-laden MOF-MBC

<table>
<thead>
<tr>
<th>Peak&lt;sup&gt;a&lt;/sup&gt;</th>
<th>BC</th>
<th>MBC</th>
<th>MIL-53-Fe MOF</th>
<th>MOF-MBC</th>
<th>Rh-laden MOF-MBC</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>C1s</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>I</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO&lt;sub&gt;3&lt;/sub&gt;&lt;sup&gt;2-&lt;/sup&gt;, O-C=O</td>
<td>BE (eV)</td>
<td>289.7</td>
<td>289.0</td>
<td>289.0</td>
<td>289.1</td>
</tr>
<tr>
<td></td>
<td>Atomic %</td>
<td>2.4</td>
<td>3.9</td>
<td>7.7</td>
<td>4.1</td>
</tr>
<tr>
<td></td>
<td>FWHM (eV)</td>
<td>1.8</td>
<td>2.0</td>
<td>1.3</td>
<td>1.5</td>
</tr>
<tr>
<td><strong>II</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C=O</td>
<td>BE (eV)</td>
<td>287.7</td>
<td>286.7</td>
<td>286.4</td>
<td>286.6</td>
</tr>
<tr>
<td></td>
<td>Atomic %</td>
<td>3.8</td>
<td>4.7</td>
<td>12.9</td>
<td>10.7</td>
</tr>
<tr>
<td></td>
<td>FWHM (eV)</td>
<td>1.8</td>
<td>2.0</td>
<td>1.5</td>
<td>1.9</td>
</tr>
<tr>
<td><strong>III</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C-O</td>
<td>BE (eV)</td>
<td>285.8</td>
<td>285.3</td>
<td>285.1</td>
<td>285.5</td>
</tr>
<tr>
<td></td>
<td>Atomic %</td>
<td>13.9</td>
<td>14.9</td>
<td>45.9</td>
<td>12.2</td>
</tr>
<tr>
<td></td>
<td>FWHM (eV)</td>
<td>1.8</td>
<td>1.7</td>
<td>1.2</td>
<td>1.3</td>
</tr>
<tr>
<td><strong>IV</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C=C, C=C, C=H</td>
<td>BE (eV)</td>
<td>284.5</td>
<td>284.6</td>
<td>-</td>
<td>284.7</td>
</tr>
<tr>
<td></td>
<td>Atomic %</td>
<td>72.2</td>
<td>42.7</td>
<td>-</td>
<td>32.1</td>
</tr>
<tr>
<td></td>
<td>FWHM (eV)</td>
<td>1.0</td>
<td>1.1</td>
<td>-</td>
<td>1.3</td>
</tr>
<tr>
<td><strong>O1s</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>I</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO&lt;sub&gt;3&lt;/sub&gt;&lt;sup&gt;2-&lt;/sup&gt;</td>
<td>BE (eV)</td>
<td>533.8</td>
<td>533.3</td>
<td>533.7</td>
<td>534.4</td>
</tr>
<tr>
<td></td>
<td>Atomic %</td>
<td>1.1</td>
<td>1.3</td>
<td>2.5</td>
<td>1.2</td>
</tr>
<tr>
<td></td>
<td>FWHM (eV)</td>
<td>1.5</td>
<td>1.4</td>
<td>1.4</td>
<td>1.5</td>
</tr>
<tr>
<td><strong>II</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O-C=O</td>
<td>BE (eV)</td>
<td>532.8</td>
<td>531.9</td>
<td>532.8</td>
<td>533.1</td>
</tr>
<tr>
<td></td>
<td>Atomic %</td>
<td>2.2</td>
<td>4.4</td>
<td>3.2</td>
<td>4.1</td>
</tr>
<tr>
<td></td>
<td>FWHM (eV)</td>
<td>1.5</td>
<td>1.5</td>
<td>1.1</td>
<td>1.5</td>
</tr>
<tr>
<td><strong>III</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O-C, C=O</td>
<td>BE (eV)</td>
<td>531.7</td>
<td>530.7</td>
<td>532.2</td>
<td>532.0</td>
</tr>
<tr>
<td></td>
<td>Atomic %</td>
<td>2.9</td>
<td>5.4</td>
<td>7.5</td>
<td>11.5</td>
</tr>
<tr>
<td></td>
<td>FWHM (eV)</td>
<td>1.5</td>
<td>1.5</td>
<td>1.0</td>
<td>1.5</td>
</tr>
<tr>
<td><strong>IV</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe-O</td>
<td>BE (eV)</td>
<td>530.5</td>
<td>530.3</td>
<td>531.7</td>
<td>530.4</td>
</tr>
<tr>
<td></td>
<td>Atomic %</td>
<td>1.2</td>
<td>12.2</td>
<td>5.4</td>
<td>6.5</td>
</tr>
<tr>
<td></td>
<td>FWHM (eV)</td>
<td>1.5</td>
<td>1.9</td>
<td>1.5</td>
<td>1.4</td>
</tr>
</tbody>
</table>

<sup>a</sup>The Roman numeral represent the peaks showing in figure 3.8 designated by these same numerals.
Figure 3.8  High resolution (HR) C1s, O1s and Fe2p XPS spectra for a) BC, b) MBC, c) MIL-53-Fe MOF, d) MOF-MBC and e) Rh B-laden MOF-MBC (CPS – counts per second). The Roman numerals given on the C1s and O1s HR XPS spectra correspond to those assigned in Table 2. *Due to the complex nature of Fe2p, the curve-resolved peaks are not labeled here. These HR-XPS figs are given in expanded form in the supporting materials (Figures B.3, B.4, B.5, B.6 and B.7) with the assignments shown.
3.4.3 Adsorption kinetics and isotherms on MOF-MBC

3.4.3.1 pH dependence of Rh B adsorption

The maximum Rh B uptake on MOF-MBC occurred at pH = 8 with a removal percent of ~75% (Figure 3.9). However, uptake was 70% or more over the pH range 4-10, illustrating the excellent pH window offered by this adsorbent. The pKₐ value of Rh B is 3.7. So below pH 3.7 it is predominantly a positive ion (Rh B⁺). A pH value above 3.7 the carboxylic acid function increasingly deprotonates to produce its zwitterionic form (Rh B±) [45]. The points of zero charge (PZC) determined in this work for MIL-53-Fe MOF and MOF-MBC are 7.1 and 6.7, respectively. PZC of this MIL-53-Fe MOF is consistent with reported values in literature [46]. MOF-MBC is slightly more acidic because Fe₃O₄ is available on the surface (which is not covered by the MOF). The PZCs of BC and MBC, reported in our previous work [23], are ~9.3 and ~6.3, respectively. Analysis of Rh B adsorption versus pH is a complex task, because three different phases on MOF-MBC can adsorb Rh B (MIL-53-Fe MOF, the biochar surface after adding magnetite, and the magnetite nanoparticles) and each phase has a different PZC value and different chemical functionality. Lower Rh B removal percentages at pH 2 most likely occur due to electrostatic repulsions between the positive MOF-MBC surface, where all three surface phases carry net positive charge, and cationic Rh B⁺ which is present at pH 2. Since pH = 6 gives a removal percentage almost as large as pH = 8 and is closer to the natural pH of water, pH = 6 was selected for kinetics and isotherm experiments instead of pH = 8. At pH = 14 the removal is ~100 %, but the Rh B color in solution disappears prior to the adsorption at pH = 14, perhaps due to its degradation or tautomerization to UV inactive spirolactam form [47].
MOF-MBC’s three phases each might contribute to the Rh B\(^+\) cation or zwitterion adsorption. These include biochar (BC) regions, Fe\(_3\)O\(_4\) nanoparticles and MIL-53-Fe MOF particles, all of which are positively charged below pH 6.7. The distribution of adsorbed Rh B among these phases are not known. Above pH 7.1 both Fe\(_3\)O\(_4\) and MIL-53-Fe particle surfaces become negative. The biochar phase’s PZC after loading with magnetite at pH 10 followed by extensive washing is unknown and will not be the same as the original PZC of BC (9.3). The zwitterionic form of Rh B, increasingly predominant above pH 4, will adsorb at neutral surface locations and some changed sites. At pH ~7 and above, the overall MOF-MBC will be net negatively charged. The ability of Rh B’s -NE\(_2\), ether and -CO\(_2^-\) groups to be H-bond acceptors, its -CO\(_2\)H and -N\(^+\)HE\(_2\) to be H-bond donors, and its aromatic regions to be π-donors and π-acceptors provides this sorbate with a wide pH window (4-10) to be highly adsorbed on MOF-MBC.

![Figure 3.9](image)

**Figure 3.9** pH dependence of aqueous Rh B adsorption onto MOF-MBC (50.0 mg MOF-MBC dose, 20 mL of 50 ppm Rh B, 1 h equilibration, 200 rpm agitation at 25 °C)
3.4.3.2 Kinetics

Figure 3.10 plots Rh B removal versus time at initial concentrations of 25, 50 and 75 mg/L at 25 °C, illustrating a similar adsorption behavior in each case. Equilibrium was attained within 120-180 min. Kinetic model fittings were not performed due to a lack of data during the initial period of the sorption step [48].

![Figure 3.10 Effect of contact time on Rh B adsorption at 25 °C onto MOF-MBC (50.0 mg dose MOF-MBC, 50 ppm Rh B (20 mL), pH = 6, and 200 rpm agitation)](image)

3.4.3.3 Isotherms and thermodynamics of adsorption

Isotherm studies were performed at 10°, 25°, and 40°C (Figure 3.11) to determine the temperature dependence of Rh B adsorption per unit weight of adsorbent (q_e). The data fit well to the Langmuir isotherm model with correlation coefficients >0.99 for all three temperatures [49]. The Langmuir plot shows that capacity (q_e) increased significantly with temperature 40°C (73 mg/g) > 25°C (48 mg/g) > 10°C (40 mg/g).
The Gibbs free energy ($\Delta G$), enthalpy ($\Delta H$) and entropy ($\Delta S$), calculated using the van’t Hoff equation 3.2, were -25.05 kJ/mol, 5.62 kJ/mol and 0.10 kJ/mol.K, respectively.

$$\ln K = -\frac{\Delta H}{R} \left(\frac{1}{T}\right) + \frac{\Delta S}{R}$$  \hspace{1cm} 3.2

Adsorption is spontaneous and the positive $\Delta H$ confirms the adsorption is endothermic, but its magnitude suggests physisorption is occurring [50].

### 3.4.3.4 Comparison of adsorbents for simultaneous removal of Rh B and Cr(VI)

Rh B only (~104 µM) and simultaneous Rh B (~104 µM) and Cr(VI) (~231 µM) (1:2 concentration ratio) adsorptive removal were studied at 25 °C and pH 6 (Figure 3.12) on BC, MBC, MIL-53-Fe MOF and MOF-MBC. Equal weights of BC, MBC and MOF-MBC showed similar removal percentages (~66-71 %) of Rh B. MIL-53-Fe MOF adsorbed less Rh B, ~36%,
possibly related to its lower surface area or difficulty of the large Rh B molecule to penetrate the MIL-53-Fe MOF porous crystalline structure.

The amount of Rh B adsorption from a solution containing both RhB and Cr(VI) mixture dropped from ~66% to ~41% on BC, suggesting competition from Cr(VI) adsorption. In contrast, MBC and MOF-MBC did not exhibit a significant change in Rh B removal when Cr(VI) was present. Cr(VI) exists as both Cr$_2$O$_7^{2-}$ and HCrO$_4^{-}$ oxyanions in experiments at pH 6. The magnetite particles adsorb Cr(VI) at neutral or protonated surface sites (-Fe-OH and Fe-OH$_2^{+}$). Magnetite is reported to be a good adsorbent for Cr(VI) under slightly acidic conditions [51]. The MIL-53-Fe MOF is a poorer Cr(VI) adsorbent. However, Cr(VI) adsorption increases on both MIL-53-Fe MOF and MOF-MBC when Rh B is also present and being adsorbed.

All four adsorbents generally adsorb more Rh B than Cr(VI) from a neat solution or a mixture of Cr(VI) and Rh B. The biochar (BC) used to make MBC, MOF-MBC lacks functionality that can drive large amounts of Cr(VI) oxyanion adsorption. MIL-53-MOF is not a very good Cr(VI) sorbent. However, MOF-MBC removes ~26% of the Cr(VI) and ~62% of Rh B simultaneously showing it can function to remove both.
3.2.5 Rh B degradation

Photo-induced Rh B degradation was conducted on pure aqueous Rh B (50 mg/L) and simulated tannery waste solutions (50 mg/L Rh B and 50 mg/L Cr(VI)) \[52\] by placing samples in front (3 cm distance) of a long range UV wavelength (365 nm) TLC UV-light (placed inside a box) for their respective times. The vials used (borosilicate) can transmit light down to 180 nm \[53\]. BC, MBC, MIL-53-Fe MOF, and MOF-MBC were added as heterogenous adsorbents/photocatalysts to each of these two types of solutions. Vials were covered with Al foil and pre-equilibrated in the dark with each adsorbent/catalyst in a shaker (at 200 rpm) for 3h to establish the adsorptive removal equilibrium before UV exposure. The foil was removed to
permit exposure to irradiation from the UV light, while magnetic stirring (50 rpm) was carried out during the catalytic photodegradation experiments. Figure 3.13 (a, b) shows the pseudo first order degradation kinetics for Rh B in these experiments. Degradation of Rh B is relatively insignificant (both with (a) and without (b) Cr(VI) present) in the absence of any adsorbent/catalyst.

BC modestly accelerated Rh B photo-degradation, both with or without Cr(VI) present. Photocatalytic activity has been reported previously for activated carbons via the formation of hydroxyl radicals from hydroxide ions at carbon surfaces or by capturing water molecules [54]. Thus, similar behavior might be expected with BC and MBC. However, MBC shows much higher photocatalytic activity than BC due to some role played by the dispersed magnetite nanoparticles. *In situ* formation of reactive oxygen species (ROS); superoxide (O$_2^-$), hydroxyl (OH) radicals and hydrogen peroxide (H$_2$O$_2$) might be possible. These radicals are known to be produced by the photocatalytic reduction of oxygen and oxidation of water on the surface of magnetite by electron (e$_{CB}^-$)/hole (h$_{VB}^+$) pair generation [54]. Some further degradation effect could be expected from the biochar phase in MBC. Adsorptive removal by the biochar phase also occurs during the photodegradation experiments. The sorbed Rh B may continuously degrade and less strongly sorbed products go into the solution reversibly, making available more surface to adsorb Rh B.

Rh B degradation on MBC was slightly slower in the model tannery waste (Figure 3.13). Perhaps surface adsorption of Cr(VI) onto magnetite particles decreased the availability of free hydroxyl functional groups to generate ROS. Rh B alone exhibited high photodegradation rates on MIL-53-Fe MOF and MOF-MBC. However, both their performances are further accelerated by the presence of Cr(VI) (simulated tannery waste). This enhancement can be attributed to the
more complete oxidation of intermediate degradation products to CO₂ and H₂O by Cr(VI) [43, 55, 56]. MIL-53-Fe MOF acts as a heterogenous photocatalyst to degrade Rh B (Figure 3.13) and it can also adsorb some Rh B (Figure 3.12). Thus, both magnetite nanoparticles and MIL-53-Fe MOF are the active catalysts, but the relative importance of the roles they play using MOF-MBC is unknown. The MOF was deposited after magnetite. Thus, much of the magnetite surface has been covered and this portion may not play a role in adsorption or photodegradation. Differences in surface areas of the active phases, their availability to light, their porosity, and other factors currently complicated straight forward explanations and understanding.

![Figure 3.13](image-url)  
*Figure 3.13* Pseudo first order plots for photodegradation of Rh B (50.0 mg catalytic adsorbent, pH = 6, 25 °C and 20 mL of the solution) and (b) Rh B in the presence of Cr(VI) during adsorption on BC, MBC, MIL-53-Fe MOF and MOF-MBC (Initial Rh B and Cr(VI) concentrations were each 50 mg/L before sorptive equilibrium).

### 3.4.3.5 Degradation product identification

The photodegradation product solutions from the simulated tannery waste of all four adsorbents (BC, MBC, MIL-53-Fe, MOF and MOF-MBC) were analyzed by LC-MS (Figures B.8 and B.9) using Electro Spray Ionization (ESI) in the positive ion mode, where most
compounds provide their (M+H)^+ fragments. N-Deethylated intermediates such as N,N-diethyl-
N'-ethyl-rhodamine (C_{26}H_{26}N_{2}O_{3}, m/z 415) were identified [57]. In addition, 2-(2,5-
dihydroxypheny)acetic acid (C_{8}H_{8}O_{4}, m/z 168), malonic acid (C_{3}H_{4}O_{4}, m/z 104), oxalic acid
(C_{2}H_{2}O_{4} m/z, 90), acetic acid (C_{2}H_{4}O_{2}, m/z 60) and formic acid (CH_{2}O_{2}, m/z 46) were identified
[58]. These products originate from chromophore cleavage from deethylated Rh B intermediates
and ring-opening [57, 59]. Some intermediates reported in previous Rh B degradation studies
over MIL-53-Fe MOF were not observed [58, 60]. This could be due to the rapid further
oxidation of these unstable intermediates by Cr(VI). Importantly, when the remaining solution
was analyzed after adsorptive photodegeneration of Rh B in tannery waste [Cr(VI) present] over
MOF-MBC no, organic degradation products could be detected. This suggests conversion to
water and CO_{2} might be close to quantitatively achieved.

3.4.3.6 Iron leaching experiments

Some iron leaching was expected at acidic pH based on our previous studies with MBC
during Arsenite and phosphate adsorption on MBC [30]. Thus, iron leaching was studied at pH
1-13 at a pH interval of 2 from all four adsorbents (BC, MBC, MIL-53-Fe MOF and MOF-
MBC). BC did not leach iron in significant amount, which was expected since BC contained
only 0.08 wt.% Fe. In the leaching experiments (Figures B.10a and b), 50 mg of each adsorbents
was immersed in 20.0 mL of water at each pH and stirred at 200 rpm in a shaker for 3 hrs. In
Figure B.10a, only Rh-B 50 mg/L was present, which in Fig b) 50 mg/L of both Rh-B and
Cr(VI) 50 mg/L were present.

In all cases the amount of iron leached into solution increased as the pH becomes more
acidic. In both the presence and absence of Cr(VI), the amount of iron leached increased in the
order MBC < MOF-MBC < MIL-53-Fe MOF. More iron leaches when Cr(VI) is present at all equivalent pH values. The pH dependence of iron leaching was higher for MIL-53-Fe MOF and MOF-MBC. Clearly MBC (with Fe₃O₄ nanoparticles) resists acidic leaching better than the MIL-53-Fe MOF. These studies teach us that MBC will be a more desirable adsorbent and can be used over a wide pH range (Figure B.10) and that MIL-53-Fe MOF and MOF-MBC may erode faster in following acidic solutions.

3.4.3.7 Comparison of adsorbents for Rh B sorption and photocatalytic degradation

Table 3.3 summarizes previous reports Rh B uptake and photocatalytic degradation on different adsorbents/catalysts.

Table 3.3 Comparative evaluation of various adsorbents/catalysts for Rh B sorption and degradation

<table>
<thead>
<tr>
<th>Adsorbents</th>
<th>Temp. / °C</th>
<th>Conc.</th>
<th>Kinetics and pH</th>
<th>Surface Area (m²/g)</th>
<th>Adsorption Capacity, Q₀ (mg/g)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>MIL-100(Fe)</td>
<td>30</td>
<td>400 mg/L</td>
<td>2 hrs, 7</td>
<td>-</td>
<td>35.77</td>
<td>[61]</td>
</tr>
<tr>
<td>Fe₃O₄</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.52</td>
<td></td>
</tr>
<tr>
<td>Fe₃O₄/MIL-100 (Fe)</td>
<td>20</td>
<td>206.14</td>
<td></td>
<td>28.36</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Activated carbon</td>
<td>40</td>
<td>2 hrs, 2.1</td>
<td>-</td>
<td>-</td>
<td>5.33</td>
<td>[62]</td>
</tr>
<tr>
<td>Rice husk</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>5.87</td>
<td></td>
</tr>
<tr>
<td>MOF-MBC</td>
<td>10</td>
<td>5-1000 mg/L</td>
<td>3 hrs, 6</td>
<td>42.2</td>
<td>40.24</td>
<td>This study</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td></td>
<td></td>
<td></td>
<td>47.69</td>
<td></td>
</tr>
<tr>
<td></td>
<td>40</td>
<td></td>
<td></td>
<td></td>
<td>73.05</td>
<td></td>
</tr>
</tbody>
</table>
Table 3.3 (continued)

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>WL (nm)</th>
<th>Temp / °C</th>
<th>Conc.</th>
<th>Kinetics and pH</th>
<th>Surface Area (m²/g)</th>
<th>Degradation percentage</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO₂</td>
<td>254</td>
<td>30</td>
<td>-</td>
<td>-</td>
<td>14.4</td>
<td>[62]</td>
<td></td>
</tr>
<tr>
<td>MIL-53-Fe MOF (1:2:190)</td>
<td>420</td>
<td>25</td>
<td>10 mg/L</td>
<td>3 hrs, 7</td>
<td>38.17</td>
<td>80</td>
<td>[39]</td>
</tr>
<tr>
<td>Fe₃O₄/H₂O₂</td>
<td>420</td>
<td>25</td>
<td>10 mg/L</td>
<td>70 min</td>
<td>-</td>
<td>20</td>
<td>[63]</td>
</tr>
<tr>
<td>MIL-53(Fe) hybrid magnetic composites</td>
<td>420</td>
<td>25</td>
<td>10 µM</td>
<td>30 mins, 7</td>
<td>-</td>
<td>7</td>
<td>[64]</td>
</tr>
<tr>
<td>H₂O₂/UV</td>
<td>254</td>
<td>25</td>
<td>10 µM</td>
<td>30 mins, 7</td>
<td>-</td>
<td>7</td>
<td>[64]</td>
</tr>
<tr>
<td>MOF-MBC</td>
<td>365</td>
<td>25</td>
<td>50 mg/L</td>
<td>20 hrs, 6</td>
<td>42.2</td>
<td>70</td>
<td>This study</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>50 mg/L with + 50 mg/L Cr</td>
<td>20 hrs, 6</td>
<td>42.2</td>
<td>70</td>
<td>This study</td>
</tr>
</tbody>
</table>

*aTo best of our knowledge reports on Rh B sorption onto MIL-53-Fe MOF were not reported in the literature.

### 3.5 Conclusions

For the first time an MOF has been successfully immobilized on a high surface area biochar carrier surface to serve as both an adsorbent and UV photodegradation catalyst to degrade the pollutant (Rh B) being adsorbed. A second dispersed Fe₃O₄ nanoparticle component on the biochar surface serves to allow magnetic adsorbent manipulation, allowing facile adsorbent removal from batch solutions for regeneration. The presence of three different adsorbing surface phases permits a wider application of this single sorbent. High surface area biochar allows dispersion of other small co-adsorbent particle phases (Fe₃O₄ and MIL-53-Fe MOF) on biochar adsorbent particles. These biochar carriers are large enough to allow column flow. In contrast, use of the tiny Fe₃O₄ and MOF particles alone would create larger pressure drops and slow flow. Many MOF properties can be improved by functionalization followed by
immobilizing derivatized MOF on biochar or other carriers. In this work, toxic Rh B was photodegraded and its toxicity neutralized in the same adsorption remediation step, chromium (VI), is reduced to Cr(III). This is a preliminary study of a very complex catalytically active adsorbent. It is very far from being optimized and well understood. Iron is leached into the Rh B and Rh B/ Cr(VI) solutions. Thus, it and Cr(VI) may absorb impinged UV-Vis light along with Rh B in the solvent phase. Adsorbed Rh-B can be absorbing light or a variety of radical intermediate species may be generated at the surface. We see no advantage in currently speculating about mechanisms. Future studies which decrease the amount MIL-53-Fe MIF deposition should permit greater Cr(VI) adsorption capacity by uncovering and exposing Fe₃O₄ surface. Improved MIL-53-Fe MOF crystallization generating smaller well formed crystals should increase its surface area. The independent photocatalytic behavior of the Fe₃O₄ nanoparticle adsorbent was initially unforeseen, as it was prepared for magnetic manipulation. However, the simultaneous high surface area exposure of both Fe₃O₄ and MIL-53-Fe MOF needs to be explored. Also layering MOF adsorption columns to promote Rh B photodegradations followed by MBC or MBC-MOF for adsorption will be explored.
3.6 REFERENCES


34. Guillou, N., R.I. Walton, and F. Millange, *MIL-53 (Fe): a good example to illustrate the power of powder diffraction in the field of MOFs.* Zeitschrift für Kristallographie Crystalline Materials, 2010. **225:** p. 552-556.


100


CHAPTER IV

BIOCHAR ADSORBENTS WITH ENHANCED HYDROPHOBICITY FOR OIL SPILL REMOVAL

(Published in ACS Appl. Mater. Interfaces 2020, 12, 8, 9248-9260)

4.1 Abstract

Oil spills cause a massive loss of aquatic life. Oil spill cleanup can be very expensive, have secondary environmental impacts, or be difficult to implement. This study employed five different adsorbents. Commercially available byproduct Douglas fir biochar (BC), S.A ~695 m²/g, pore volume ~ 0.26 cm³/g and pore diameter ~13-19.5 Å), 2. BC modified with lauric acid (LBC), 3. iron oxide-modified biochar (MBC), 4. LBC-modified with iron oxide (LMBC) and 5. MBC modified with lauric acid (MLBC) for oil recovery. Transmission, engine, machine and crude oils were used to simulate oil spills and perform adsorption experiments. All five adsorbents adsorbed large quantities of each oil in fresh and simulated sea water with only a slight pH dependence and fast kinetics (sorptive equilibrium reached before 15 mins). The Sips isotherm model oil sorption capacities for these sorbents were in the range ~3-11 g oil/1 g adsorbent. Lauric acid-decorated (60 to 2 wt%) biochars gave a higher oil adsorption capacity than the undecorated biochar. Lauric acid enhances biochar hydrophobicity, its water contact angle and reduces water influx into biochar’s porosity preventing it from sinking in water for 3 weeks. These features were observed even at 2% wt. of lauric acid (sinks only after 2 weeks). Magnetization by magnetite nano particle deposition onto BC and LBC allows the recovery of
the exhausted adsorbent by a magnetic field as an alternative to filtration. Oil sorption was endothermic. Recycling was demonstrated after toluene stripping. The oil-laden adsorbents’ heating values were obtained, suggesting alternative use of these spent adsorbents as a low-cost fuel after recovery avoiding waste disposal costs. The initial and oil-laden adsorbents were characterized by SEM, TEM, EDX, FT-IR, XRD, BET, CA, TGA, DSC, VSM magnetometry, elemental analysis and XPS.

4.2 Introduction

The Exxon Valdez oil spill in Alaska (1989) [1] and the Deepwater Horizon oil spill in the Gulf of Mexico (2010) [2] have fueled interest in developing ways to clean oil from aquatic environments. Accidental oil spills into rivers, bays, and the ocean often occur from tankers, barges, pipelines, refineries, drilling rigs, and storage facilities. Oil spills can kill marine bird populations, whales, dolphins, seals, sea otters [3] and often take a deadly toll on fish, shellfish, and other marine life, particularly when fish eggs or larvae are exposed to oil [4]. Aquatic macrophytes are harmed by interfering with gas exchange, and decreases occur in the diversity of benthic organisms [5-7].

In addition to spills, crude oil-producing operations generate brine, which must be extracted from the oil and disposed of in accord with environmental standards [8]. Furthermore, the treatment and disposal of oily wastewater from palm oil mill effluent is a serious and increasing concern [9].

Methods for removing oil include dissolved air floatation, mechanical separation (booms, skims, etc), chemical (surfactants, dispersants), physicochemical, and biological methods [10].
Such strategies are partially successful for various situations, but also exhibit drawbacks, like secondary environmental pollution, high cost, and complicated operations.

One oil cleanup method for spills employs adsorbents [11, 12]. Anthropomorphic adsorbents including polypropylene webs, polyurethane foams, and superhydrophobic sponges have been tested [13-15]. Many are expensive and require complicated synthetic routes, generating waste. Bio-mass-derived adsorbents, such as activated carbon [16], rice husk [17-19], and bagasse [13, 18, 20], have also been tested as oil adsorbents. Ideal adsorbents should be cheap, available in commercial scale, cheap, easily recoverable, and safely disposed of. Adsorbents with high surface area and high oil sorption, derived from available agricultural by-products or wastes might contribute oil recovery options.

Biochar, produced via pyrolysis of biomass at high temperatures in a low oxygen environment, produce high porosities and surface areas [21]. Biomass derived adsorbents have a fuel value and might be used for heat or steam generation after oil uptake. Biochar can adsorb heavy metals [22, 23], oxy-anions [24-26], organic dyes [27], hormones, and pharmaceutical residues [28-30]. The main drawback of biochar for oil-spill treatment is that it absorbs water quickly and can sink when applied on bodies of water. Decoration with lauric acid can increase biochar hydrophobicity as indicated by an increase in water contact angle [31]. This should make biochar a better oil adsorbent and might help it float in order to stay in contact with the surface oil. Also, magnetization with iron oxides will allow the exhausted oil-covered adsorbent to be recovered magnetically from water instead of needing to filter a sticky goo [24, 25].

Very few studies discussed the use of biochar or bio-mass for oil spill treatment, and only specific oils or oil models, such as toluene or diesel fuels have been studied [32, 33].
Commercial biochars have not been reported for crude oil spill remediation in simulated seawater and environmental conditions. This study focused on evaluating a commercially available biochar tailored as an oil adsorbent. Herein, we now report the following results.

1) Preparation and characterization lauric acid-decorated biochars and their analogues containing deposited magnetite, which don’t sink in water.

2) These adsorbents rapidly take up significant amounts (up to ~11 oil/g of adsorbent) of four oils (engine, transmission, machine, and crude oils) from fresh and simulated sea water at various pH values with only minor differences.

3) The adsorbent can be stripped and recycled.

4) The exhausted adsorbent with adsorbed oil can be directly destroyed by combustion at good heating values to produce useful heat, while avoiding disposal of a toxic or undesirable waste.

This data can be used to evaluate if biochar can be used in oil spill cleanups alone or combined with mechanical techniques such as booms and skims.

4.3 Methods and Materials

4.3.1 Preparation of magnetite-bearing magnetic biochar, lauric acid-decorated biochar and two types of lauric acid-decorated and magnetite-bearing magnetic biochar analogues

Biochar (BC) (average pore size range = 13 to 19.5 Å and particle density ~ 0.4 cm³/g, determined using water displacement) originated from Douglas fir and was purchased from Biochar Supreme INC. The BC was produced by a proprietary process in an updraft wood gasifier at ~900 °C for short (1-30 s) residence times from wet Douglas fir chips [24]. Lauric
acid decoration was first conducted by making a BC slurry (~100 g) in 1 M lauric acid (~100 g) 10 % warm (70 °C) methanol solution (500 mL) to generate LBC-30 which contained ~30 wt% lauric acid loading [31]. The solution was vacuum filtered to remove the lauric acid-coated biochar. Crude LBC-30 was washed with hexane (3 × 50 mL) to remove excess lauric acid and vacuum dried at 100 °C and 34 KPa for 24 h (Scheme 4.1). LBC-30 contained ~30 % by wt. Lauric acid and ~70 % by wt. BC. LBC-2 was prepared using a similar approach, but in a scaled down process. Briefly, a 2.5 g portion of BC was slurried with 1.25 g lauric acid dissolved in 10 % (v/v) warm aqueous methanol (50 mL) followed by filtering, washing with hexane and drying (at 100 °C, 34 kPa for 24 h) process. However, only 50 mL of hexane was used in the washings. Other carboxylic acids (saturated and unsaturated) could replace lauric acid, including tallow-derived mixtures, fatty acids form plant oils, etc. The chain-length dependence of oil sorption is being studied.

Magnetite-bearing magnetic biochar (MBC) and their two lauric acid analogues (LMBC and MLBC) were prepared as we previously described [24, 28]. Briefly, ~50 g of BC was slurried in 1950 mL of water containing ~18 g dissolved iron (III) chloride and ~36.6 g iron (II) sulfate (total iron = ~20.8 g) [34]. Magnetite (Fe₃O₄) precipitation onto BC was triggered by drop-wise addition of 10 M NaOH until pH 10 was reached and maintained for ~24 h (Scheme 4.1). The resulting Fe₃O₄-magnetized biochar (MBC) was filtered, repeatedly washed with distilled water, three ethanol washes, and dried under 5 psig vacuum at 100 °C for 24 h. MBC contained 26.3 % iron oxide (Fe₃O₄ with Fe₂O₃ as a possible minor product). Magnetic biochar (MBC) coated with lauric acid (MLBC) was made by mixing 50 g MBC with 50 g lauric acid in 10 % warm (70 °C) aqueous methanol (250 mL) followed by three hexane (3 × 50 mL) washes.
Lauric acid-coated magnetic biochar (LMBC) was prepared by adding 50 g LBC into a 1950 mL aqueous solution of ~36.6 g iron(III) chloride and ~18 g iron(II) sulfate. Then the pH was raised to 10 by NaOH and held at pH 10 for 24 h. LMBC was repeatedly washed with distilled water, followed by three ethanol washes. MBC and LMBC were vacuum-filtered and dried overnight at 70 °C in a hot air oven at atmospheric pressure. MLBC was vacuum dried at 100 °C and 5 psi for 24 h. All five adsorbents were ground and sieved into 150-300 µm particles, ensuring the same particle size range was used in all experiments, and stored in polythene bags until further use.

Scheme 4.1 Preparation of magnetite-coated magnetic biochar char (MBC), lauric acid-coated biochar (LBC), lauric acid-coated magnetite-bearing biochar (LMBC) and magnetite-bearing magnetic biochar coated with lauric acid (MLBC).

4.3.2 Characterization methods

BC, LBC, MBC, LMBC, MLBC and their oil-laden analogues were each individually characterized. Batch equilibrium adsorption experiments consisting of 0.25 g of adsorbent were equilibrated with 8 g of each oil.
The N₂ Brunauer-Emmet-Teller (BET) determinations of BC and MBC specific surface areas, pore volumes [from the Dubinin-Astakhov equation \( log \, a = \log \, a_0 - D \log^n \left( \frac{P_0}{P} \right) \)], where \( a \) denotes amount of gas adsorbed per unit mass of adsorbent (mol/g), \( a_0 \) is the micropore capacity (mol/g), \( D \) is a constant, \( P \) is the equilibrium pressure and \( P_0 \) is the saturation vapor pressure of adsorbate at temperature \( T \) (K), and pore sizes [density functional theory (DFT) was used to calculate micropore volume \( W_0 = \frac{\frac{44000 \, a_0}{\rho}}{\rho} \), where \( W_0 \) is the limiting micropore volume (cm³/g), \( a_0 \) is the micropore capacity (mol/g), and \( \rho \) is the density of adsorbed gas (g/cm³)] were conducted using a N₂ adsorption isotherm at ~77 K (Micromeritics Tristar II Plus). Alternatively, surface areas of LBC, LMBC and MLBC were determined by CO₂ adsorption at 273 K (see Section 4.4.1.3).

C, H, O and N elemental contents of both neat and oil-laden adsorbents were measured by combustion analysis using a CHN elemental analyzer (CE-440). Ash content was determined after heating in air at 650 °C for 15 h in an open-top porcelain crucible in the muffle furnace. The oxygen content of organic portion of the char was calculated using \( O \% = 100 - (C + H + N + ash) \)). The weight percentages of iron in all adsorbents were determined using atomic absorption spectroscopy (AAS) (Shimadzu AA-7000). Complete acid digestions were performed on 0.1 g of each adsorbent using 50.0 mL of 1:1 95% H₂SO₄ /70% HNO₃ [35]. Iron dissolved from the oxidizing adsorbent samples goes into the acid over 24 h (70 °C) with stirring. These solutions were then diluted 10-fold with deionized water prior to AAS analysis. A recovery test performed with Fe₂O₃ gave a ~96 % recovery.
A JEOL JSM-6500F FE instrument run at 5 kV generated the scanning electron microscopy (SEM) images of the neat and oil-laden adsorbent morphologies. A Rigaku Ultima III (using Cu-K\(\lambda=1.54\) Å X-rays) was used for X-ray diffraction analysis (XRD) [(5-90°) 2θ range was scanned]. X-ray photoelectron spectroscopy (XPS) analyses were run on a Thermo Scientific K-Alpha XPS system with a monochromatic X-ray source at 1486.6 eV, corresponding to the Al K\(_{\alpha}\) line, with a spot size of 400 µm\(^2\). Photoelectrons were collected at a takeoff angle of 90° relative to the overall sample’s fractal particle surface. Measurements were made in the constant analyzer energy mode. The survey spectra were taken at a pass energy of 200 eV. High resolution (HR) core level spectra were taken at a 40 eV pass energy. The XPS data acquisition were performed using the Avantage v5.932 software provided with the instrument.

The water contact angle (CA) of BC and modified BCs were determined by the sessile drop method [36]. Briefly, a double-sided adhesive tape was fixed to a flat woodblock and then ground and sieved samples were adhered to obtain a homogeneous layer covering on the tape surface. After placing a 10 μL water drop on the surface of adhered samples, a picture was taken using an iPhone-X camera. The CA values were then measured using Image J software. Six measurements were conducted for each sample.

Fourier transformed infrared spectroscopic (FT-IR) analysis (ATR mode) was carried out using a Thermoscientific iD-5 (Nicolet) instrument. Adsorbent thermogravimetric analyses (TA instruments, TGA Q 50) were performed under a 100 mL/min nitrogen flow from 30 to1000 °C. Differential scanning calorimetric (DSC) analyses (TA instruments, DSC Q 20) were performed under 50 mL/min nitrogen flow over the 40-550 °C range. Magnetic hysteresis measurements were carried out on a Lake Shore 7304 vibrating sample magnetometer (VSM). The magnetic properties of adsorbents are represented by plots of magnetization (\(M\)) against the field strengths.
(H) giving the hysteresis loop. The saturation magnetization was measured from the hysteresis curve. Bomb calorimeter experiments of adsorbents, oils and oil-laden adsorbents were performed using a Parr bomb calorimeter using ~0.5 g of each sample.

4.3.3 The lauric acid wt % effect on BC sinking and oil uptake

The lauric acid doses on LBC to prevent it from sinking and their respective oil uptakes were assessed using LBC samples prepared from seven different lauric acid molarity impregnating solutions (0.125, 0.25, 0.5, 0.75, 1, 1.25, and 1.5 M) following the method described in section 4.3.1, which was scaled down to 2.5 g of BC. Each different oil uptake capacity on 0.25 g of LBC was then studied by simulating 2 g crude oil spills in sea water (25 mL) and equilibrating for 1 h at 25 °C.

4.3.4 Oil recovery and adsorbent recycling

Oil adsorption-desorption recycling was assessed for LBC (LBC-2, LBC-30 and LBC-60) and MLBC. LBC (0.5 g) was sprinkled onto 4 g of crude oil dispersed in 50 mL of simulated sea water for 1 h (pH 7, 25 °C). The contents in the beaker were then filtered through a Whatman filter paper. Filter paper was washed with toluene for four times (4 × 50 mL) until the color of toluene (bpt. ~ 110.6 °C) wash become very pale. During washing, glass rod stirring was performed to aid oil dissolution. This method will remove some oil from the sorbent surfaces, so the measured oil uptake will be a lower value than the intrinsic amount associated with each particle.

MLBC was regenerated by separating from the sea-water/oil matrix with the aid of a horse-shoe magnet with a handle. The magnet was held over the top of the mixture to recover the
oil-laden MLBC. Then oil was stripped by dipping and rotating the magnet with its adsorbent load inside 50 mL (4-5 times) of toluene until the color of toluene wash becomes pale.

These washing solutions were combined and heated on a hot plate at 120 °C to distill away toluene. Subsequently, the LBC in the filter paper was dried in an oven at 120 °C to remove adsorbed toluene and reused in sorption experiments. MLBC was physically removed from magnet to a watch glass and dried at 120 °C. This process was repeated through 3 adsorption-desorption cycles. Weight gains were recorded after each sorption cycle and the recovered oil weights were recorded.

4.3.5 Sorption experiments

Artificial oil spills were simulated by adding 25 mL of distilled water or simulated seawater and 2 g of oil to a 50 mL glass beaker. Each adsorbent (0.25 g) was sprinkled onto the surface oil layer, allowed to equilibrate for 1 h (no agitation or swirling), and then collected by filtration onto filter paper. Alternatively, magnetic separation of MBC, LMBC and MLBC were also carried out using magnets. Blanks were run as controls to determine the weight of the filter paper only when oil with no biochar was filtered. The filter paper was dried in an oven at 100 °C to remove adsorbed water. Mass balancing determined each oil’s adsorption capacity. In order to determine the optimum oil adsorption pH, the pH of the water added to the beakers was varied (1, 3, 5, 7, 9, 11, and 13) using either HCl or NaOH. The sorption kinetics of the biochar’s equilibration with oil was determined by varying contact times from 0 to 360 min for each adsorbent. Adsorbent uptake capacities were determined by varying the amount of each oil added to the beakers from 0.25 to 8 g/0.25 g of adsorbent, while holding other factors constant. This allowed determination of the ideal pH, equilibration times and uptake capacities of the five
adsorbents for all four oil types. Sea water samples were simulated using aqueous solutions containing NaCl (23.5 g/L), MgCl₂ (5.0 g/L), Na₂SO₄ (3.9 g/L), CaCl₂ (1.1 g/L), KCl (0.66 g/L), NaHCO₃ (0.2 g/L), KBr (0.10 g/L), H₃BO₃ (0.026 g/L), SrCl₂ (0.024 g/L) and NaF (0.003 g/L) [37]. The influence of temperature during sorption was studied using 8 g of oil and 0.25 g of each adsorbent under the above-mentioned optimized conditions at 10, 25 and 40 °C temperatures in the sea water matrix.

4.4 Results

4.4.1 Characterization results

The extensive characterizations of BC, MBC, LBC, LMBC and MLBC are described first in section 4.4.1. Readers can go directly to section 4.4.2 to see the adsorption results for all adsorbents, pH-dependence, fresh vs sea water, kinetics, heating values, sinking behavior, recycling etc.

4.4.1.1 Effect of lauric acid (LA) and LA wt % on BC for sinking

Lauric acid-decorated biochar (LBC) and its magnetite variants LMBC and MLBC, floated on water, showing water was prevented from occupying much of the adsorbents’ open pore volume (Figure 4.1a). Lauric acid addition to BC enhances hydrophobicity. The esterification of its carboxylic acid groups to oxygenated functions anchors lauric acid on the biochar surface. This could result in hydrocarbon chains of lauric acid protruding from the surface where it would prevent water from moving to the surface and into biochar pore networks. By reducing water penetration and preventing the filling of substantial fractions of the pore volume with water, the biochar remains buoyant and does not sink. In contrast, BC imbibes water into its pore networks, filling large fractions of the pore volume with water, reducing buoyancy. Since the carbonaceous
char and inorganic mineral regions have densities far greater than water, as pores take up water, the overall particle densities exceed that of water and BC particles sink (Figure 4.1a). Adsorbent particles that sink cannot be used for oil spill remediation unless they can preferentially fill with oil rapidly enough and remain lighter than water.

All three lauric acid-containing biochar types (LBC-30, LMBC and MLBC) continued floating (0.25 g in 25 mL under non-stirred conditions) in a saltwater solution for 3 weeks before some of the adsorbent particles started sinking. All LBC-2 (2 % wt. LA) floated on water for only 2 weeks and then progressively started sinking. Increasing the lauric acid amounts (LBC-30) increased the time to ~3 weeks before any sinking occurred and to 1 month for LBC(60) with 60 % lauric acid (Figure 4.1C3). Since LBC-30 had a performance similar to LBC-60, LBC-30 was used for the majority of experiments. Stirring the water reduces the time until sinking begins. Lauric acid prevents water penetration into biochar macropores, micropores and ultra-micro pores. It stopped water from filling much of the biochar internal porosity, preventing the particle densities from exceeding that of the aqueous phase. Thus, the adsorbents can be recovered from water surfaces either before or after oil uptake. Also, the fraction of LBC 30 that sunk after three weeks (<0.1) was small. The lauric acid weight content in LBC-30, LMBC and MLBC are 30 %, 26.8% and 34.5 %, respectively, corresponding to a thick lauric acid coating on the biochar.
Figure 4.1  a) Lauric acid surface uptake on BC, where outer surface and large pores are made hydrophobic, blocking water access to substantial pore volume further below the surface where lauric acid cannot penetrate; b) oil molecules adhering to lauric acid adsorbed at the biochar surfaces. More oil adsorbs to lauric acid, to already adsorbed oil and to hydrophobic biochar surface regions. Finally, oil takes up more oil building a thick coating; c1) Neat biochar sinks in water; c2) biochar after decoration with lauric acid floats and c3) effect of lauric acid dose on BC sinking (Lauric acid weight % (wt/wt %); 0.125 M = 2.0 %, 0.5 M = 1.2 % and 0.5 M = 3.9 %).

4.4.1.2  Surface morphology

At a ~30 % (wt/wt %) weight loading of lauric acid (LBC-30), the surface morphology observed by SEM changed versus that of BC. LBC-30 visually appears less highly porous and somewhat smoother than BC (Figure 4.2). MBC, LMBC and MLBC surfaces exhibited primary magnetite nanoparticles (~7-20 nm) and their aggregates (2-7 µm) [24, 25]. The oil-laden LBC’s surface was completely covered with oil.
4.4.1.3 Surface area and elemental analysis

The combustion elemental analyses of the neat adsorbents (Table 4.1) found less C % and H % than in their oil-laden variants due to large C and H contributions from adsorbed crude oil. The lower C wt% in MBC, LMBC and MLBC (46.7, 50.5 and 60.0 %, respectively) results from the added Fe₃O₄ weight fraction (~26.9-29.2 %). The high C/H (~39) weight ratio and observed O/C (~0.2) weight ratio of the unmodified BC illustrates significant loss of oxygen and hydrogen during the high temperature (900-1000 °C) fast pyrolysis (10-30 seconds) of the precursor Douglas fir wood. Precipitating iron oxide onto BC to form MBC gives partial char surface coverage and partial BC pore blockage, causing a loss of over half the original BC surface area (from 695.1 to 312.6 m²/g) and almost half of its BET-measured pore volume (0.264 to 0.135 cm³/g), despite adding the new surface generated by the small magnetite particles [24].

When lauric acid was added (LBC, LMBC and MLBC), CO₂ adsorption isotherms were used for surface area determinations, since N₂ BET adsorption at cryogenic temperatures
produced very low surface areas. Multiple lauric acid layers present caused pore blockage. High temperature (273 K) provided more energy for CO$_2$ to detect surface. However, both low temperature N$_2$ BET and the CO$_2$ isotherms both indicate huge drops in BC’s and MBC’s surface area after adding lauric acid to the 30-40 m$^2$/g range for LBC, MLBC and LMBC (Table 4.1). Lauric acid coatings also greatly reduced the measured LBC, LMBC and MLBC pore volumes to the 0.014 to 0.018 cm$^3$/g range. This agrees with the previous interpretation that much of the still existing pore volume is unable to be reached by water and remains filled with air, providing buoyancy. Thus, N$_2$ and CO$_2$, like water, are denied access to most pore surfaces and significant internal void volume after lauric acid treatment. Nevertheless, large oil uptakes occurred as oil was incorporated into the lauric acid and also as oil adhered to itself, occupying and filling surface fractural crevices and depressions.

The ash content in BC (2.3 %) and LBC (1.4 %) is composed of oxides and carbonates formed from sodium, potassium, magnesium, calcium and iron salts and some silica in the wood feed (Table 4.1). Magnetite-laden magnetic biochars had a high ash content (MBC = 30.5 %, LMBC = 29.1 % and MLBC = 25.3 %) because magnetite (Fe$_3$O$_4$) particles had been deposited, as illustrated by their iron contents (26.9-29.2 %). The calculated iron is more than that calculated from Fe$_3$O$_4$ deposited together with original BC ash iron (even if some was Fe$_2$O$_3$). This excess was due to some Fe$^{2+}$ and or Fe$^{3+}$ salt deposition occurring before Fe$_3$O$_4$ nucleates and deposits during the Fe$_3$O$_4$ nanoparticle deposition process. Additionally, some (RCOO)$_2$Fe or (RCOO)$_3$Fe formation from lauric acid complexing with soluble Fe$^{3+}$ or Fe$^{2+}$ can take place when Fe$_3$O$_4$ is deposited on LBC.
Table 4.1  Elemental, proximate analysis and surface area data for adsorbents and oil-laden adsorbents.\textsuperscript{a,b,c}

<table>
<thead>
<tr>
<th>Sample</th>
<th>Lauric acid wt%</th>
<th>Iron Oxide wt%</th>
<th>Oil wt %</th>
<th>Ash (wt %)</th>
<th>C (wt %)</th>
<th>H (wt %)</th>
<th>N (wt %)</th>
<th>Organic O (wt %)</th>
<th>Fe (wt %)</th>
<th>Surface area (m(^2)/g)</th>
<th>Pore Volume (cm(^3)/g)</th>
<th>Average pore diameter (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BC</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>2.3</td>
<td>81.5</td>
<td>2.1</td>
<td>1.2</td>
<td>13.0</td>
<td>0.07</td>
<td>695.1\textsuperscript{b}</td>
<td>0.264</td>
<td>14.47</td>
</tr>
<tr>
<td>LBC</td>
<td>30.0</td>
<td>-</td>
<td>-</td>
<td>1.4</td>
<td>84.6</td>
<td>4.1</td>
<td>1.1</td>
<td>9.2</td>
<td>0.02</td>
<td>35.9\textsuperscript{b}</td>
<td>0.018</td>
<td>4.11</td>
</tr>
<tr>
<td>MBC</td>
<td>-</td>
<td>26.3</td>
<td>-</td>
<td>30.5</td>
<td>46.7</td>
<td>1.5</td>
<td>0.9</td>
<td>20.4</td>
<td>29.2</td>
<td>312.6\textsuperscript{b}</td>
<td>0.135</td>
<td>13.56</td>
</tr>
<tr>
<td>LMBC</td>
<td>26.8</td>
<td>23.4</td>
<td>-</td>
<td>29.1</td>
<td>50.5</td>
<td>2.9</td>
<td>0.9</td>
<td>16.7</td>
<td>28.3</td>
<td>37.3\textsuperscript{c}</td>
<td>0.014</td>
<td>14.52</td>
</tr>
<tr>
<td>MLBC</td>
<td>34.5</td>
<td>21.5</td>
<td>-</td>
<td>25.3</td>
<td>60.0</td>
<td>4.0</td>
<td>1.0</td>
<td>10.3</td>
<td>26.9</td>
<td>30.6\textsuperscript{c}</td>
<td>0.016</td>
<td>4.30</td>
</tr>
<tr>
<td>Crude oil\textsuperscript{a}</td>
<td>-</td>
<td>-</td>
<td>100</td>
<td>-</td>
<td>85.0</td>
<td>12.7</td>
<td>1.8</td>
<td>0.6</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Crude oil-laden BC</td>
<td>-</td>
<td>-</td>
<td></td>
<td>87.3\textsuperscript{d}</td>
<td>0.3</td>
<td>84.0</td>
<td>9.6</td>
<td>0.7</td>
<td>5.6</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Crude oil-laden LBC</td>
<td>-</td>
<td>-</td>
<td></td>
<td>90.4\textsuperscript{d}</td>
<td>0.4</td>
<td>81.4</td>
<td>11.6</td>
<td>0.8</td>
<td>5.8</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Crude oil-laden MBC</td>
<td>-</td>
<td>-</td>
<td></td>
<td>76.8\textsuperscript{d}</td>
<td>7.1</td>
<td>71.0</td>
<td>7.3</td>
<td>1.2</td>
<td>13.8</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Crude oil-laden LMBC</td>
<td>-</td>
<td>-</td>
<td></td>
<td>85.1\textsuperscript{d}</td>
<td>4.3</td>
<td>84.0</td>
<td>11.0</td>
<td>1.1</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Crude oil-laden MLBC</td>
<td>-</td>
<td>-</td>
<td></td>
<td>86.1\textsuperscript{d}</td>
<td>4.1</td>
<td>76.3</td>
<td>9.7</td>
<td>1.2</td>
<td>8.8</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\textsuperscript{a}Ash and Fe analyses were not carried out for crude oil or crude oil-laden adsorbents

\textsuperscript{b}From N\(_2\) BET adsorption isotherms at 77 K

\textsuperscript{c}From CO\(_2\) BET adsorption isotherms at 273

\textsuperscript{d}These data are based on the Sips isotherm fitting capacities
4.4.1.4 FTIR analysis

Adsorbent and lauric acid FTIR (ATR) spectra are displayed in Figure 4.3a. The spectra of BC and MBC do not exhibit sharp bands, since the total amount of organic functional groups on the outer surfaces is low. Temperatures above 400 °C cause dehydration, decarbonylation, decarboxylation, deamination, carbonization etc. Douglas fir was converted to BC at 900-1000 °C for short periods leaving low surface oxygen functionalization. MBC is formed by magnetite precipitation onto BC surfaces. Its spectrum is almost identical to that of BC, because the Fe$_3$O$_4$ IR bands are largely obscured by BC [27]. Lauric acid, LBC, LMBC and MLBC spectra display some sp$^3$ C-H stretching for -CH$_2$ (~2900-2850 cm$^{-1}$) while LBC shows carbonyl stretching bands (carboxylic, carboxylate) from lauric acid and MLBC exhibits carboxylic, carboxylate and iron-carboxylate carbonyl stretching bands (~1700-1550 cm$^{-1}$) [38] from lauric acid uptake and laurate complexation of Fe$^{2+}$/Fe$^{3+}$ during Fe$_3$O$_4$ deposition at pH 10 described in section 4.4.1.3.

LMBC did not exhibit this carbonyl band because lauric acid was added first, before being partially covered by magnetite precipitation during a 24 h process in water at pH 10. Also, laurate carboxylate anions from lauric acid already deposited, formed during the subsequent pH 10 exposure to precipitate Fe$_3$O$_4$ while making MLBC, will coordinate with the Fe$^{2+}$ and Fe$^{3+}$ ions present in this aqueous pH 10 solution. This generates (C$_{11}$H$_{23}$CO$_2$)$_2$Fe and (C$_{11}$H$_{23}$CO$_2$)$_3$Fe carboxylate/iron complexes, which then deposit on the LMBC surface. These complexes are known to exhibit carbonyl stretching bands in range ~1590-1450 cm$^{-1}$ [38]. Additionally, laurate available in solution can react on the surface of growing magnetite nano-particles, coating their surface and limiting their growth (Scheme 4.2) [39]. This raises the possibility that the deposited
Fe₃O₄ nanoparticles formed, when making LMBC, will be smaller than those formed and deposited on MBC and MLBC. This possibility was confirmed by XRD (see section 4.4.1.5).

4.4.1.5 XRD analysis and explanation of particle sizes of precipitated Fe₃O₄

The XRD peak patterns for MBC, LMBC and MLBC confirm that precipitated magnetite particles formed (Figure 4.3b). Diffraction locations (2θ) and intensities are consistent with the standard magnetite pattern, JCPDS Card No. (79-0417). The major peak at 35.45° is for the crystalline plane of Fe₃O₄ with Miller indices of (311) [24]. Other peaks were observed at 30.10° (220), 43.08° (400), 53.45° (422), 56.98° (511), 62.57° (440), and 74.02° (622) [24]. Weaker peaks were seen, resolved from the broad amorphous peak from biochar (~15-30°). This broad peak disappeared after magnetite precipitated due to magnetite’s highly intense crystalline peaks. Biochar surface oxidation can occur with the large amount of aqueous Fe³⁺ present in solution during the magnetite deposition step. A sharp peak was observed for LBC at 7.42° due to lauric acid [40]. LBC, LMBC and MLBC have a broad peak ~10-30° from the amorphous biochar peak and lauric acid -CH₂ chain alignments [24, 40].

The magnetite crystallite sizes deposited on MBC, LMBC and MLBC were analyzed using the Debye–Scherrer equation, \[D_{hkl} = \frac{0.9\lambda}{(\beta \cos \theta)}\], where \(\lambda\) is the XRD analysis wavelength (nm), \(\beta\) is the full-width at half-maximum value (rad) for XRD lines, and \(\theta\) is half of the diffraction angle of 2θ [34]. The magnetite crystallite size was determined from the D311 peak for MBC, LMBC and MLBC. These crystallite sizes were ~16.5 nm (MBC), ~7.7 nm (LMBC) and ~12.3 nm (MLBC). This agrees directly with formation of surface laurate iron complexes (Scheme 4.2) on the growing magnetite nanoparticles, which caps their continued growth during LMBC synthesis.
The 16.5 nm crystallite particle size calculated from XRD for MBC is in excellent agreement with SEM/TEM size analyses of Fe$_3$O$_4$ nano-particles that we prepared previously by the same method (~16.7 nm) [34]. In the current and previous work, aqueous precipitation of Fe$_3$O$_4$ took place directly on BC from pH 10 solutions. Why should smaller Fe$_3$O$_4$ nanoparticles be produced on LMBC and MLBC? Fe$_3$O$_4$ particles form on LMBC where lauric acid is already present (Scheme 4.1). Deprotonation of some deposited lauric acid to laurate occurs in the pH 10 deposition step (Scheme 4.2). Thus, this laurate terminates the growth of nano-magnetite particles being precipitated on LMBC by capping Fe-OH surface sites on growing particles. This limits the average size to ~7.7 nm versus that for MBC (~16.5 nm). MLBC’s Fe$_3$O$_4$ nanoparticle have ~12.3 nm average sizes. The Fe$_3$O$_4$ particles were deposited first at pH 10 in the absence of lauric acid when preparing MLBC. Subsequent addition of lauric acid to the initially formed MBC in de-ionized water/in 10% CH$_3$OH will cause the pH at the developing MLBC surface to be acidic, since lauric acid’s pKa ~ 4 in water. Under these conditions some iron ions can leach from Fe$_3$O$_4$ particles decreasing their original size [41]. The leached iron will also tend to form laurate iron complexes which can redeposit on the surface but do not reconvert to magnetite-nano particles (Scheme 4.2). This explains the ~16.5 to ~12.3 nm drop in particle size comparing MBC with MLBC.
Scheme 4.2  Capping growth of nano Fe$_3$O$_4$ particles during their formation during LMBC synthesis in pH 10 solution. This capping does not occur during MBC synthesis and would be less likely in MLBC synthesis.

4.4.1.6  Contact angle (CA) measurements

The water contact angle (CA) values for BC, LBC, MBC, MLBC, LMBC and model samples are shown in Table 4.2. Surfaces with water contact angle below 90° are considered to be hydrophilic and vice versa. Biochar CAs have been reported in the 91-132° range. Consistent with that, BC had a hydrophobic CA value of 122.3°. The water droplet size (2.67 mm) is 20-50 times larger than the BC particle size (150-300 μm) used for these determinations. The influence of BC fractal surface geometry, particle porosity and water droplet size for the CA measurement versus other studies are unknown [44]. Despite its 122.3° CA, BC imbibes water and begins to
sink fairly rapidly. Upon magnetization with Fe$_3$O$_4$ (MBC), the CA value (61.8°) was shifted to the strongly hydrophilic domain. This is expected [45] since magnetite is a hydrophilic material, containing surface hydroxyl groups (Scheme 4.2). Lauric acid decoration of both BC and MBC (to LBC and LMBC) significantly increased their hydrophobicity consistent with literature reported values [46-47]. The CA values for LBC-30 and MLBC were 138.2° and 135.9°, respectively. Moreover, increasing the lauric acid (LA) dose (2-41.5 %) increased the CA values from 127.9° (LBC-2) to 140.9° (LBC-40). With the higher LA dose (to 60% w/w), the CA remained almost the same (139.4°). The increased hydrophobic LMBC has a large contact of 141.3° versus its MBC (61.8°) precursor. The highest CA of LMBC 141.3° can be attributed to (1) the lauric acid capping effect (Scheme 4.2 and Table 4.2), where the surface Fe-OH hydroxyl groups of magnetite were capped by lauric acid complexation and (2) the effect of lauric acid on the biochar surface similar to that in LBC.

The regenerated LBCs (designated LBCRs) show higher CA values than the neat LBC (Table 4.2). This might signify trapped residue oil (or toluene) remained in the LBCs after regeneration. In addition, there was no significant difference in CA between regenerated LBCs with different initial lauric loadings, i.e., LBC2-R, LBC30-R, and LBC60-R. All regenerated samples might have a similar amount of trapped oil (1.5-2.1 g, see Figure 4.6b). The regenerated MLBC (MLBC-R) also has an increased CA value compared to regenerated LBCs.
Table 4.2: Contact angle data for BC, LBC, MBC, MLBC and LMBC

<table>
<thead>
<tr>
<th>Sample</th>
<th>Lauric acid wt/%</th>
<th>Contact angle (CA)a</th>
</tr>
</thead>
<tbody>
<tr>
<td>BC</td>
<td>-</td>
<td>122.3±4.2</td>
</tr>
<tr>
<td>LBC-0.125</td>
<td>2.0</td>
<td>127.9±3.3</td>
</tr>
<tr>
<td>LBC-0.25</td>
<td>1.2</td>
<td>134.4±4.9</td>
</tr>
<tr>
<td>LBC-0.5</td>
<td>3.9</td>
<td>138.8±4.4</td>
</tr>
<tr>
<td>LBC-0.75</td>
<td>15.7</td>
<td>138.2±2.8</td>
</tr>
<tr>
<td>LBC-1.0</td>
<td>33.2</td>
<td>139.3±5.1</td>
</tr>
<tr>
<td>LBC-1.25</td>
<td>41.5</td>
<td>140.9±4.6</td>
</tr>
<tr>
<td>LBC-1.5</td>
<td>61.3</td>
<td>139.4±4.6</td>
</tr>
<tr>
<td>LBC-0.125R</td>
<td>~2.0</td>
<td>142.7±3.4</td>
</tr>
<tr>
<td>LBC-1.0R</td>
<td>~33.2</td>
<td>144.1±6.5</td>
</tr>
<tr>
<td>LBC-1.5R</td>
<td>~61.3</td>
<td>141.3±3.1</td>
</tr>
<tr>
<td>MBC</td>
<td>-</td>
<td>61.8±2.2</td>
</tr>
<tr>
<td>MLBC</td>
<td>34.5</td>
<td>135.9±5.5</td>
</tr>
<tr>
<td>MLBCR</td>
<td>~34.5</td>
<td>147.8±2.0</td>
</tr>
<tr>
<td>LMBC</td>
<td>26.8</td>
<td>141.3±5.5</td>
</tr>
</tbody>
</table>

aStandard deviation for the average of 6 measurements
bThese samples were obtained after 3 adsorption-desorption cycles (stripped with toluene)

4.4.1.7 Thermal analysis

TGA weight loss versus temperature plots (10 °C/min under 100 mL/min N₂) for all adsorbents and lauric acid are presented in Figure 4.3c. BC and MBC show little mass loss up to 800 °C, because BC was originally pyrolyzed at ~900 °C and the deposited magnetite on MBC is stable at 800 °C during TGA. Neat lauric acid undergoes a drastic mass loss from 150 to 250 °C from decomposition and volatilization. LBC and MLBC exhibit similar lauric acid mass losses in this temperature range. However, the TGA of LMBC indicates the lauric acid component’s mass loss begins at 240 °C and extends to 400 °C. This difference from LBC and MLBC is pronounced. This suggests that the originally added lauric acid in LMBC, which was partially converted to iron carboxylate complexes during exposure to aqueous pH 10 during magnetite deposition, decomposes differently than neat lauric acid.
DSC profiles of lauric acid, BC, LBC, MBC, LMBC and MLBC are given in supporting material (Figure C1). Lauric acid gives an exotherm upon crystallization at ~50 °C [40]. This exotherm was also present in MLBC, where lauric acid was loaded on top magnetite. LBC or LMBC, where lauric acid chains can have extensive contact with the carbonaceous BC surfaces don’t exhibit this exotherm. Iron oxide nano particles may increase the ease and degree of deposited lauric acid orientation allowing more crystallinity. The exothermic peaks at 120-160 °C for BC, MBC and LMBC arise due to the loss of tightly held water and volatile compound losses. LBC is and MLBC with overlying lauric acid coatings do not show any strong peaks in this region. Their hydrophobicity may prevent water from adsorbing. Interestingly, LMBC peaks in the region 120-160 °C could be arising from water adsorbed to the magnetite. The exothermic lauric acid peak at ~325-350 °C is consistent with its decarboxylation. LBC decarboxylation/decomposition occurs around ~290-340 °C. MLBC, where laureate salts formed during magnetite deposition at pH 10, exhibits lower temperature (250 °C) decarboxylation, probably catalyzed by iron complexes present.
Figure 4.3  a) FT-IR characterization, b) XRD data and c) thermogravimetric analysis profiles (10 °C/min heating rate under 100 mL/min N₂) of lauric acid, BC, LBC, MBC, LMBC and MLBC.*The amorphous biochar peak is due to aromatic plane region separations.

4.4.1.8 Magnetic moment (M) experiments

The magnetic moment properties of BC and MBC were reported in our previous studies [34]. BC has a tiny saturation magnetization (0.02 emu/g) at 10 K induced by traces of iron oxide present, but no detectable magnetic moment (M) was found at 300 K. The reported saturation magnetizations of MBC at 10 and 300 K were 23.85 and 20.41 emu/g, respectively [24]. The
LBC, made in this current study, as expected, has only tiny M values of 0.12 emu/g and 0.05 emu/g at 5 K and 300 K respectively (Figure C.2). LMBC’s M values are quite low at 1.49 emu/g and 0.76 emu/g at 5 K and 300 K respectively. In sharp contrast, MLBC has much larger values of M, occurring at 8.73 and 17.07 at 5 K and 300 K, respectively (Figure C.2). These are much closer to those of MBC.

The magnetic moment magnitudes (M) are directly proportional to the size of the superparamagnetic nanoparticles [48]. Synthetic methods to tune superparamagnetic iron oxide nanoparticles by size are desirable [48]. The low values of LMBC’s magnetism resulted from its tiny magnetite particle size (~7.7 nm). A higher fraction of LMBC’s magnetite mass is present in its more amorphous surface region due to its tiny particle size. Also, LMBC’s magnetite XRD peak with Miller indices of 311 is less intense that of MLBC. MLBC’s stronger XRD peak is expected since it also has a far stronger saturation magnetite moment and a larger particle size (~12.3 nm). This correlation is summarized in Table 4.3.
Table 4.3 Saturation magnetization (or Magnetic moments) (M) values vs Fe₃O₄ crystallite particle sizes from XRD and Debye-Scherrer equation

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>M (emu)</th>
<th>Crystallite size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>5/10 K</td>
<td>300 K</td>
</tr>
<tr>
<td>MBCᵃ</td>
<td>23.85</td>
<td>20.41</td>
</tr>
<tr>
<td>MLBCᵇ</td>
<td>8.73</td>
<td>17.07</td>
</tr>
<tr>
<td>LMBCᵇ</td>
<td>1.49</td>
<td>0.05</td>
</tr>
</tbody>
</table>

ᵃ10 K
ᵇ5K

4.4.2 Adsorption results

4.4.2.1 pH dependence of sorption

Effect of the aqueous pH on oil sorption was negligible, because oil sorption occurs predominantly via hydrophobic interactions with the adsorbent biochar’s surface or lauric acid coating and with oil that is initially sorbed. MBC had the lowest uptake performance per gram, keeping in mind that Fe₃O₄ adsorption increases the sorbent’s weight per unit volume and its surface is the most hydrophilic of all the adsorbents. No hydrophobic lauric acid was present on MBC, and substantial pore volume was blocked with deposited iron oxide particles. Sorption capacities are summarized for pH 1-13 in Table 4.4.

The sorption capacities for transmission, machine and engine oils onto MBC were (4.2-5.1), (1.5-1.9) and (0.4-1.2) g/g, respectively. BC gave capacities of (3.0-4.1) g/g for transmission oil, (2.3-3.2) g/g for machine oil, and (3.6-4.7) g/g for engine oil. LBC showed similar sorption capacities for these three oils; (3.3-3.6) g/g (transmission), (2.8-3.2) g/g (machine) and (3.1-4.2) g/g (engine). Both LMBC and MLBC showed similar sorption trends and their capacities were ~(3.0-3.9), ~(3.5-5.0) and ~(0.5-2.7) g/g for transmission, machine and engine oils, respectively.
Table 4.4  Summary of oil uptake (transmission, machine and engine oils) for BC, LBC, MBC, LMBC and MLBC over the pH 1-13 range (25 °C, 1 h equilibration)

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Oil uptake (g/g)</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Transmission</td>
<td>Machine</td>
<td>Engine</td>
</tr>
<tr>
<td>BC</td>
<td>3.0-4.1</td>
<td>2.3-3.2</td>
<td>3.6-4.7</td>
</tr>
<tr>
<td>LBC&lt;sup&gt;a&lt;/sup&gt;</td>
<td>3.3-3.6</td>
<td>2.8-3.2</td>
<td>3.1-4.2</td>
</tr>
<tr>
<td>MBC</td>
<td>4.2-5.1</td>
<td>1.5-1.9</td>
<td>0.4-1.2</td>
</tr>
<tr>
<td>LMBC</td>
<td>3.2-4.9</td>
<td>3.5-4.8</td>
<td>0.5-2.7</td>
</tr>
<tr>
<td>MLBC</td>
<td>3.0-3.9</td>
<td>3.8-5.0</td>
<td>1.6-2.1</td>
</tr>
</tbody>
</table>

<sup>a</sup>LBC has 30% (w/w) LA

4.4.2.2  Sorption kinetics

Sorption uptake was fast for all five adsorbents with all three (transmission, machine, and engine) oils. Oil uptake reached equilibrium within less than 15 mins. Due to a lack of data in the initial sorption regime, kinetic model fittings were not used.

4.4.2.3  Sorption isotherms

Langmuir [49] and Freundlich [50] models failed to give satisfactory fits to isotherm data. The best correlation coefficient fits and $\chi^2$ fitting values to experimental data were given by the three parameter Sips [51] model (equation 4.1 and Figure 4.4c), a hybrid form of the Langmuir and Freundlich expressions for heterogeneous adsorption systems. This circumvented the limitation of the rising adsorbate concentration associated with the Freundlich isotherm model. At low adsorbate concentrations, the Sips model reduces to the Freundlich isotherm; at high concentrations, it predicts a monolayer adsorption capacity characteristic of the Langmuir isotherm. The Sips parameters [51] are governed mainly by the operating conditions (eg: pH, temperature and concentration).
Here, $q_e$ is the amount of adsorbate in the adsorbent at equilibrium (g/g), $q_o$ is the theoretical isotherm saturation capacity (g/g), $C_e$ is equilibrium concentration (g/g), $n$ is adsorption intensity and $K_s$ is Sips isotherm constant (L/g).

All five adsorbents adsorbed large amounts of oil (Table 4.5). The capacities listed are based on the Sips-fitting and should be considered only approximations. Lauric acid decorated biochar (LBC) had the highest capacities for both transmission (11.0 g/g) and engine (8.2 g/g) oils, while MBC showed the highest capacity for machine oil (8.1 g/g). Both LMBC and MLBC gave almost the same capacities for transmission and engine oils, but LMBC capacity for machine oil was greater.

Given the large amounts of oil uptake that occurs, and the thickness of the oil layers formed, the use of isotherm models may be misleading. If smaller numbers of oil molecular layers were adsorbed, the use of isotherms would be on firmer grounds, but oil uptake rapidly becomes oil associating with oil many adsorbate layers above the adsorbent surfaces. Thus, the adsorbent surface is no longer playing a chemical role in adsorbing more oil. However, these fittings gave good estimations of the experimental sorption capacities reaching a ~ 5-15 % plateau deviation.
Table 4.5  Sips isotherm model data for transmission, machine and engine oils at 25 °C (pH = 7 and 1 hour equilibration).\textsuperscript{a, b}

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Isotherm derived parameter</th>
<th>Oil uptake (g/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Transmission</td>
</tr>
<tr>
<td>BC\textsuperscript{b}</td>
<td>$q_0$ (g/g)</td>
<td>4.2 ± 0.2</td>
</tr>
<tr>
<td></td>
<td>$K_s$ (L/g)</td>
<td>2.6 ± 1.1</td>
</tr>
<tr>
<td></td>
<td>$n$</td>
<td>3.0 ± 2.2</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.98</td>
</tr>
<tr>
<td>LBC</td>
<td>$q_0$ (g/g)</td>
<td>11.0 ± 1.2</td>
</tr>
<tr>
<td></td>
<td>$K_s$ (L/g)</td>
<td>9.8 ± 0.7</td>
</tr>
<tr>
<td></td>
<td>$n$</td>
<td>0.03 ± 1.2</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.99</td>
</tr>
<tr>
<td>MBC</td>
<td>$q_0$ (g/g)</td>
<td>7.2 ± 0.2</td>
</tr>
<tr>
<td></td>
<td>$K_s$ (L/g)</td>
<td>4.5 ± 0.3</td>
</tr>
<tr>
<td></td>
<td>$n$</td>
<td>2.3 ± 0.4</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.95</td>
</tr>
<tr>
<td>LMBC</td>
<td>$q_0$ (g/g)</td>
<td>5.3 ± 0.1</td>
</tr>
<tr>
<td></td>
<td>$K_s$ (L/g)</td>
<td>3.6 ± 2.3</td>
</tr>
<tr>
<td></td>
<td>$n$</td>
<td>19.3 ± 1.2</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.98</td>
</tr>
<tr>
<td>MLBC</td>
<td>$q_0$ (g/g)</td>
<td>5.4 ± 0.3</td>
</tr>
<tr>
<td></td>
<td>$K_s$ (L/g)</td>
<td>5.0 ± 1.0</td>
</tr>
<tr>
<td></td>
<td>$n$</td>
<td>1.4 ± 0.4</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.88</td>
</tr>
</tbody>
</table>

\textsuperscript{a}The capacities, $q_0$, based on the Sips isotherm fittings are considered approximations.

\textsuperscript{b}BC has an excellent ability to uptake all three oils, especially when considering the BC phase only represents a fraction of the total weight of LBC (~0.7), MBC (~0.7), LMBC (~0.4) and MLBC (~0.4). However, BC will sink when it contacts water, so some BC will be lost even when oil is taken up in competition with sinking, which changes the amount of BC that is lost.
Figure 4.4  
a) pH dependences of oil uptake (at 25 °C and 1 h of equilibration), b) Normalized uptake vs time plots (at 25 °C and pH 7) and c) Sips isotherm fits of oil sorption (25 °C, pH = 7, 1 h of equilibration) for BC, LBC, MBC, LMBC and MLBC
4.4.2.4 Effect of sea water and temperature on crude oil uptake.

The crude oil uptake of each adsorbent was determined using both distilled water and synthetic sea water matrices. Crude oil consists of light ends (C1-C4), gasoline (C5-C6), light naptha (C6-C8), heavy naptha (C9-C10), kerosene (C10-C14), heavy gas oil (C16, C18), vacuum gas oil (C20-C28), pitch, VOC, resins, asphaltenes and waxes) [52]. The amounts of crude oil uptake from deionized water followed the order LBC-30 (10.6 g/g) > BC (7.5 g/g) > MLBC (6.7 g/g) > LMBC (6.3 g/g) > MBC (3.6 g/g) (Figure 4.5a). LBC-30 has a greater lauric acid content than MLBC or LMBC’s possibly assisting its exceptionally high capacity. MBC has the lowest capacity since no lauric acid was present, and magnetite deposition enhanced this adsorbent’s density. Both MLBC and LMBC provided similar crude oil uptakes. This same uptake trend was observed from the sea water matrix (Figure 4.5a). A small drop in oil uptake capacity was observed in sea water versus distilled water. Similar results were reported for toluene sorption onto pine wood biochar [32]. Crude oil uptake rose slightly for all sorbents as temperature rose from 10 to 40 °C (Figure 4.5b). This robust crude oil uptake from simulated sea water encourages further studies of this adsorbent class to remove oil spills.

Oil-laden adsorbents were characterized by SEM (See Figures 4.2b and f) and FT-IR (Figure 4.5c). SEM clearly depicts the presence of surface crude oil (Figure 4.2f). The IR spectrum of neat crude oil was almost identical to that of the crude oil-laden LBC.
Figure 4.5  Crude oil uptake by BC, LBC, MBC, LMBC and MLBC, b) temperature dependence of crude oil uptake and c) FT-IR of LBC before and after crude oil uptake vs neat crude oil (In each experiment 0.25 g of each adsorbent and 8.0 g of crude oil were equilibrated for 1 h at 25 °C water layer and pH = 7).
*Characterization results are only presented for LBC and crude-oil laden LBC as the results for other adsorbents and crude-oil laden adsorbents were similar.

4.4.3  Adsorbent sustainability

4.4.3.1  Effect of Lauric acid dose

At a lauric acid dose of only 2 wt%, the biochar did not sink for 2 weeks. Dose increments increased the lauric acid wt % on the adsorbents, but the influence on oil uptake was modest (Figure 4.6a). These experiments teach us that even only small amounts of lauric acid are required to form coatings which block water access into substantial pore volume creating a buoyant adsorbent. This will lower adsorbent cost.
4.4.3.2 Oil recovery and adsorbent recycling

Oil recovery from the sorbents must be considered after uptake and removal from water. LBC-30 oil uptakes for three cycles were 5.4, 4.9 and 4.5 g/g, respectively, and the oil recoveries were 3.6, 3.2 and 3.5 g/g with toluene stripping (Figure 4.6b). MLBC had uptakes of 4.3, 4.0 and 3.9 g/g respectively and recoveries of 3.4, 3.3 and 3.4 g/g respectively. LBC-20 and LBC-60 showed a similar cyclic uptake-recovery performance versus LBC-30 despite the slight drop in uptake capacity. Small drops in oil sorption capacity with recycling might be due to partial loss of lauric acid during toluene stripping and/or some unstripped oil or toluene trapped on biochar surfaces. Also, a small experimental weight loss of biochar occurs due to difficulty in recovering it from filter paper or magnet, although the capacities are reported after accounting for this weight loss. MLBC exhibited more robust performance versus LBC, which could be due to high quantity of oil stripped in each cycle. These experiments suggest that these adsorbents can be reused for oil recovery and recovered oil could be refined.

4.4.3.3 Heating values

Recovery by distillation or extraction is only one option. Since biochar itself has value as a fuel, the retrieved oil-laden adsorbent can be directly burned as a fuel without the need for an oil separation step. Bomb calorimeter combustion data for the neat oils, the adsorbents as and oil-laden adsorbents were obtained (Figure 4.6c). These heating values were compared with those of ethanol, kerosene, gasoline and diesel [53]. Biochar (BC) has a heating value (28.9 MJ/kg) close to that of ethanol (29.7 MJ/kg). Upon lauric acid decoration (~30 % wt), LBC-30’s heating value increased to 33.1 MJ/kg (~29. 2 MJ/kg for LBC-2) from BC’s 28.9 MJ/kg. MBC has the lowest heating value (16.7 MJ/kg) because of the high ash (30.5 % wt) contribution from iron oxides. LMBC (19.8 MJ/kg) and MLBC (24 MJ/kg) have slightly higher heating values than MBC.
because of their added lauric acid contents. The oil-laden adsorbents gave high heating values. The samples from the highest oil/adsorbent wt/wt experimental data in isotherm experiments (8 g oil/0.25g of sorbent) were tested. This range of values for BC, MBC, LBC, LMBC and MLBC spanned following ranges for transmission (33.7-41.8 MJ/kg), machine (32.5-43.2 MJ/kg), engine (34.0-42.5 MJ/kg) and crude (32.6-41.2 MJ/kg) oils. Adsorbing crude oil from salt versus de-ionized water did not significantly influence the heating value of oil-laden adsorbents. Thus, these recovered oil-laden adsorbents can used as fuels where biochar particles can be tolerated. A big advantage of this route is that it avoids the waste disposal of a potentially toxic waste.
Figure 4.6  
a) Effect of lauric acid dose on BC sinking and and crude oil uptake (Lauric acid weight %; 0.125 M = 2.0 %, 0.5 M = 1.2 % and 0.5 M = 3.9 %), 
b) crude oil uptake-recovery data for LBC and MLBC (25 °C, 1 hour in simulated sea water) 
and c) bomb calorimeter heating values for oils, adsorbents and oil-laden adsorbents.
4.4.3.4 Comparison of adsorbents

Table 4.6 summarizes previous oil adsorbent uptake reported in the literature. Previous capacities are compared to our five sorbents using uptake from crude oil in simulated in salt water. BC, LBC, MBC, LMBC and LMBC exhibited fast equilibrium uptake (<15 mins), low pH dependence, promising unsinkability (except for BC and MBC), and reasonable fuel values. Furthermore, MBC, LMBC and MLBC could be collected from the oil spills using magnets, thus avoiding the requirement to perform difficult filtration of oil-laden sorbents. Magnetic collection may also improve oil separation yields vs centrifugal cyclone separations, because, with the large oil uptake weight ratios where oil greatly exceeds the weight of the initial sorbent, centrifugal forces separating the water and oil/sorbent might spin off significant oil back into the separating water.
Table 4.6  Comparison to oil absorbents in the literature.

<table>
<thead>
<tr>
<th>Type of adsorbent</th>
<th>Type of oil</th>
<th>Matrix</th>
<th>Adsorption Capacity (g/g)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maple biochar</td>
<td>Crude oil</td>
<td>Sea water</td>
<td>(3.8 – 6.2)</td>
<td>[54]</td>
</tr>
<tr>
<td>Coconut shell based activated carbon–iron oxide magnetic nanocomposite</td>
<td>Premium motor oil</td>
<td>Sea water</td>
<td>(3.01 – 12.93)</td>
<td>[55]</td>
</tr>
<tr>
<td></td>
<td>Used oil</td>
<td>Sea water</td>
<td>(7.59 – 7.65)</td>
<td></td>
</tr>
<tr>
<td>Lauric acid modified-palm leaves</td>
<td>Crude oil</td>
<td>Sea water</td>
<td>1.18</td>
<td>[31]</td>
</tr>
<tr>
<td>Activated carbon-PDMS coated sponge</td>
<td>Octane</td>
<td>De-ionized water</td>
<td>(26.95 – 85.86)</td>
<td>[56]</td>
</tr>
<tr>
<td>Pine wood biochar</td>
<td>Toluene</td>
<td>De-ionized water</td>
<td>0.70</td>
<td>[32]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Sea water</td>
<td>0.18</td>
<td></td>
</tr>
<tr>
<td>BC</td>
<td>Crude oil</td>
<td>Sea water</td>
<td>6.87</td>
<td>This study</td>
</tr>
<tr>
<td>LBC</td>
<td></td>
<td></td>
<td>9.40</td>
<td></td>
</tr>
<tr>
<td>MBC</td>
<td></td>
<td></td>
<td>3.31</td>
<td></td>
</tr>
<tr>
<td>LMBC</td>
<td></td>
<td></td>
<td>5.70</td>
<td></td>
</tr>
<tr>
<td>MLBC</td>
<td></td>
<td></td>
<td>6.18</td>
<td></td>
</tr>
</tbody>
</table>

### 4.5 Conclusion

All adsorbents (BC, LBC, MBC, LMBC and MLBC) were found to be effective oil adsorbents with fast uptake rates (≤15 min). The Sips oil sorption capacities spanned the range ~3-11 g oil/g adsorbent, and oil uptake rose with temperature. Lauric acid decoration (2 % wt) made the biochar resistant to sinking in water and increased oil uptake capacity. In fact 2 % wt lauric acid uptake gave LBC-2 that had >90 % of the uptake of LBC-30 (see Figure 4.6a). Little
uptake dependence on water, pH or salt content was found, suggesting freshwater, sea water or process effluent applications are possible. The sequence of magnetite versus lauric acid decoration greatly did not influence the sorption performance, but it affected both the chemical makeup and magnetic properties of the adsorbents. Oil recovery and cyclic adsorption-desorption was also demonstrated using toluene for stripping. Oil-laden adsorbents had fuel value close to some commercial fuels. These factors and magnetic separation options should allow undecorated and lauric acid decorated/magnetic biochar composites to be applied in future oil spill clean-ups.
4.6 REFERENCES


APPENDIX A

REMOVAL OF ARSENIC(III) FROM WATER USING MAGNETITE PRECIPITATED ONTO DOUGLAS FIR BIOCHAR
A.1 Characterization of BC, MBC and As-laden MBC

A.1.1 Point of zero charge (PZC) measurements

The points of zero charge (PZC) of MBC (~6.50) and BC (~9.20) were determined using the pH drift method holding the ionic strength constant with 0.01 M NaCl. Briefly, the solution pH was adjusted from 2 to 12, in intervals of 2, using either NaOH or HCl solutions. The solutions (25 mL) were equilibrated with 50 mg of adsorbent in a shaking water bath (200 rpm) for 1 h at 25 °C. After equilibration, the pH of the supernatant was measured using a pH meter (SPER SCIENTIFIC, 860031 Benchtop). The PZC was obtained by plotting pH of the initial solution against pH of the final solution.

A.1.2 Surface Morphological characterization

MBC and BC surface architectures were examined using a JEOL JSM-6500F FE-Scanning electron microscopy (SEM) at 5 kV, and SEM/energy dispersive analysis by X-ray (EDX) analysis. EDX analyses employed a Zeiss, EVO 40 scanning electron microscope with a BRUKER EDX system. Transmission electron microscopy (TEM) studies of MBC and BC were undertaken using a JEOL model 2100 TEM electron microscope operated at 200 kV. STEM/EDX analyses were carried out using an Oxford X-max-80 detector.
A.1.3 X-ray powder diffraction (XRD) and X-ray photoelectron spectroscopy (XPS)

XRD patterns for both MBC and BC were obtained using a Rigaku ultima III instrument (using Cu-K\(_\alpha\) (\(\lambda =1.54\) Å). XPS analyses were performed using a Thermo Scientific K-Alpha XPS system equipped with a monochromatic X-ray source at 1486.6 eV, corresponding to the Al K\(_\alpha\) line, with a spot size of 400 \(\mu\)m\(^2\). Photoelectrons were collected from a takeoff angle of 90\(^\circ\) relative to the overall sample’s fractal particle surface. Measurements were done in the constant analyzer energy mode. The survey spectra were taken at a pass energy of 200 eV, while the high resolution (HR) core level spectra were taken at a 40 eV pass energy.

A.1.4 Surface area measurements and elemental analysis

The surface areas of MBC and BC were examined using a TriStar II Plus 3030 surface area analyzer using BET N\(_2\) adsorption isotherms (~273 K). The Dubinin-Astakhov equation was employed to calculate the pore diameter and density functional theory (DFT) was used to calculate micropore volume. Ash analysis was done by weighing the mass of ash produced after incinerating 1 g of each MBC and BC in a muffle furnace at 650 °C for 15 h. Once cooled, microwave-induced acid digestion (CEM MARS 6 EXPRESS) was separately employed on 0.25 g of the ash from MBC and BC using HNO\(_3\) and HCl (3:1 v/v) (12 mL). The liquid samples were filtered into 250 mL volumetric flasks and the flasks were filled to the mark with de-ionized water. Fe contents in BC and MBC were determined using AAS under the flame mode.
A.1.5 Quantification of arsenic(III)

Arsenic amounts on MBC and BC after sorption experiments were determined by atomic absorption (AAS) [Hitachi Zeeman Polarized, ZA3000 equipped with a hydride generator (HF-4) (HGAAS)]. All arsenic species were reduced to As$^{3+}$ using 10% ascorbic acid and 20% potassium iodide, and then to AsH$_3$ by subsequent treatment with 5% HCl and 1% sodium borohydride (NaBH$_4$) (equation 1). AsH$_3$ was then aspirated into the quartz tube mounted to the AAS burner head and absorbance was measured at 193.7 nm. Recovery tests were performed by spiking As(III) standard solutions into water (pH = 7) equilibrated for 1 h with both BC or MBC samples, to assess the matrix effect. The recoveries were in 94% - 96% range, hence the external calibration curve was used for the As(III) determination. The limit of quantification (LOQ) of As(III) in the AAS is 15 µg/L.

$$6\text{NaBH}_4(\text{aq}) + 3\text{H}^+(\text{aq}) + \text{As}^{3+}(\text{aq}) \rightarrow 3\text{B}_2\text{H}_6(\text{aq}) + 3\text{H}_2(\text{g}) + \text{AsH}_3(\text{g}) + 6\text{Na}^+(\text{aq}) \quad (1)$$

Competitive adsorption on wastewater samples and the breakthrough column analysis experiments required lower detection limits. Hence, they were conducted using an inductively coupled plasma mass spectrophotometer (ICP-MS) (PerkinElmer SCIEX, ELAN DRC II) which has a LOQ of 0.1 µg/L.

A.1.6 Ash content of BC and MBC

The BC wt. fraction of MBC is ~0.67, which corresponds to a 448.0 m$^2$/g surface area versus the 320.1 m$^2$/g measured for MBC. This further confirms that biochar pore blockage leads to low surface area.

MBC had a high ash content (31.33%) while BC contained 2.12% ash. Iron content in the MBC ash detected in AAS is 20.91% which corresponds to ~64 % yield of iron oxide ($\text{Fe}_3\text{O}_4$) deposited on synthesis (Table A.1). This is consistent with the SEM-EDX elemental percentages
obtained for MBC (Figure A.1). The Fe content of the starting BC was below the FAAS detection limits. High ash content in MBC is due to the sum of precipitated iron oxide and the original ash present in BC resulting from the oxides and carbonates of sodium (Na\(^+\)), potassium (K\(^+\)), calcium (Ca\(^{2+}\)) and magnesium (Mg\(^{2+}\)) formed at high temperatures [2].
### A.2 Tables

#### A.2.1 Calculation for iron oxide yield

<table>
<thead>
<tr>
<th>Description</th>
<th>Calculation</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron weight percentage in MBC (quantification from AAS)</td>
<td>~20.9 %</td>
<td></td>
</tr>
<tr>
<td>Mass of iron in 50 g MBC (g)</td>
<td>20.91 % x 50 g</td>
<td>~10.5 g</td>
</tr>
<tr>
<td>Mass of BC in 50 g MBC (g)</td>
<td>50 g – 10.5 g</td>
<td>~39.5 g</td>
</tr>
<tr>
<td>Mass of FeCl₃ added to 50 g of BC (g) for Fe₃O₄ precipitation</td>
<td>18 g</td>
<td></td>
</tr>
<tr>
<td>Mass of iron (Fe³⁺) in FeCl₃ (g)</td>
<td>(18 g/162.2 g/mol) x 55.5 g/mol</td>
<td>~6.2 g</td>
</tr>
<tr>
<td>Mass of Fe₂(SO₄)₃·7H₂O added to 50 g of BC Fe₃O₄ precipitation</td>
<td>36.6 g</td>
<td></td>
</tr>
<tr>
<td>Mass of iron (Fe²⁺) in Fe₂(SO₄)₃·7H₂O</td>
<td>2 x (36.6 g/278.02 g/mol) x 55.5 g/mol</td>
<td>~14.6 g</td>
</tr>
<tr>
<td>Total mass of iron (Fe²⁺ + Fe³⁺) added to 50 g of BC (g) Fe₃O₄ precipitation</td>
<td>~20.8 g</td>
<td></td>
</tr>
<tr>
<td>Total mass of iron (Fe²⁺ + Fe³⁺) required for 39.5 g of BC</td>
<td>(39.5 g/50 g) x 20.8 g</td>
<td>~16.4 g</td>
</tr>
<tr>
<td>Percentage Fe (or Fe₃O₄) yield</td>
<td>(10.5 g/16.4 g) x 100</td>
<td>64 %</td>
</tr>
</tbody>
</table>
### A.2.2 Isotherm data fits for adsorption of As(III)

Table A.2 Isotherm data fits for adsorption of As(III) on MBC at 20, 25 and 40 °C, pH = 7, 1 h equilibration time.\(^b\)

<table>
<thead>
<tr>
<th>Isotherm</th>
<th>Equation (Non-linear form)</th>
<th>(R^2)</th>
<th>(\chi^2)</th>
<th>(K)</th>
<th>(q_0)</th>
<th>Isotherm Specific Constants</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Temperatures (°C)</strong></td>
<td></td>
<td>20</td>
<td>25</td>
<td>40</td>
<td>20</td>
<td>25</td>
<td>40</td>
</tr>
<tr>
<td>Langmuir</td>
<td>(q_e = q_0 K_L C_e )</td>
<td>0.99</td>
<td>0.99</td>
<td>0.96</td>
<td>0.66</td>
<td>1.43</td>
<td>2.37</td>
</tr>
<tr>
<td></td>
<td>(0.003 0.010 0.144)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Freundlich</td>
<td>(q_e = K_F C_e^{(1/n)})</td>
<td>0.98</td>
<td>0.95</td>
<td>0.95</td>
<td>1.57</td>
<td>2.61</td>
<td>2.61</td>
</tr>
<tr>
<td></td>
<td>(0.010 0.04 0.07)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Langmuir-Freundlich</td>
<td>(q_e = q_0 (K_S C_e) )</td>
<td>0.99</td>
<td>0.99</td>
<td>0.98</td>
<td>0.48</td>
<td>1.13</td>
<td>5.23</td>
</tr>
<tr>
<td>(Sips)</td>
<td>(0.003 0.01 0.01)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(q_e\) = amount of adsorbate in the adsorbent at equilibrium (mg/g)

\(q_0\) = theoretical isotherm saturation capacity (mg/g)

\(C_e\) = equilibrium concentration (mg/g)

\(n\) = adsorption intensity

\(K_L\) = Langmuir isotherm constant (L/mg)

\(K_F\) = Freundlich isotherm constant (L/mg)

\(K_S\) = Sips isotherm constant (L/mg)

\(b\) Isotherm fitting curves, isotherm capacities and constant data were generated by local refinement of empirical isotherm equations via the inbuilt Levenberg–Marquardt distant nonlinear regression algorithm in Origin2018b using the average value of 3 replicates for each data point. Significant figures on isotherm specific capacities, constants and regression coefficients are based on the model reported data and may not reflect the actual uncertainties of experimental data.
### A.2.3 C1s and O1s XPS binding energies for model compounds with different carbonyl functionalities

Table A.3  
C1s and O1s XPS binding energies for inorganic and organic or polymeric carbonates, aldehydes, ketones and carboxylic acids.

<table>
<thead>
<tr>
<th>Compound/species</th>
<th>XPS BE (eV)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C1s</td>
<td>O1s</td>
</tr>
<tr>
<td>Group IA carbonates</td>
<td>289.3-288.1</td>
<td>531.8-529.9</td>
</tr>
<tr>
<td>Na₂CO₃</td>
<td>289.5</td>
<td>531.8</td>
</tr>
<tr>
<td>NaHCO₃</td>
<td>290.0</td>
<td>-</td>
</tr>
<tr>
<td>CaCO₃</td>
<td>289.2</td>
<td>531.2</td>
</tr>
<tr>
<td>MgCO₃</td>
<td>-</td>
<td>533.2-533.5</td>
</tr>
<tr>
<td>poly(alkyl carbonate)</td>
<td>286.8</td>
<td>533.9</td>
</tr>
<tr>
<td>diphenyl carbonate</td>
<td>290.7</td>
<td>533.7</td>
</tr>
<tr>
<td>acetophenone</td>
<td>-</td>
<td>532.0</td>
</tr>
<tr>
<td>benzaldehyde</td>
<td>-</td>
<td>532.0</td>
</tr>
<tr>
<td>Keto polymers keto group</td>
<td>287.6-287.9</td>
<td>532.0-532.3</td>
</tr>
<tr>
<td>Biochar -C=O</td>
<td>-</td>
<td>531.5</td>
</tr>
<tr>
<td>Biochar O=O-C-O</td>
<td>289.0</td>
<td>-</td>
</tr>
<tr>
<td>Poly(ether ether ketone) (PEEK) keto group</td>
<td>286.3</td>
<td>533.4</td>
</tr>
<tr>
<td>ethyl acetate</td>
<td>289.2</td>
<td>-</td>
</tr>
<tr>
<td>methyl methacrylate</td>
<td>284.8</td>
<td>533.6</td>
</tr>
<tr>
<td>Stearic, lauric and dodecanedioic acid mixture -COOH group</td>
<td>~288.5</td>
<td>-</td>
</tr>
<tr>
<td>acrylic acid</td>
<td>289.3</td>
<td>533.6</td>
</tr>
<tr>
<td>Isophthalic acid carbonyl</td>
<td>295.2</td>
<td>538.0</td>
</tr>
<tr>
<td>Terephthalic acid</td>
<td>295.2</td>
<td>538.1</td>
</tr>
<tr>
<td>Phthalic acid</td>
<td>295.1</td>
<td>538.1</td>
</tr>
<tr>
<td>Benzoic acid</td>
<td>295.0</td>
<td>537.7</td>
</tr>
</tbody>
</table>
### A.2.4 High resolution (HR) Fe2p XPS data of MBC and As(III)-laden MBC

Table A.4 Amounts of Fe chemical contents found in surface regions of MBC before and after As(III) adsorption XPS

<table>
<thead>
<tr>
<th>Substrate</th>
<th>B.E. (eV)</th>
<th>FWHM (eV)</th>
<th>Atomic Fe %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe 2p₃/₂</td>
<td>721.1</td>
<td>3.5</td>
<td>1.7</td>
</tr>
<tr>
<td>Fe(III) maghemite satellite</td>
<td>718.7</td>
<td>3.0</td>
<td>1.6</td>
</tr>
<tr>
<td>Fe(II) Fe (2p₃/₂) satellite</td>
<td>716.4</td>
<td>2.2</td>
<td>0.8</td>
</tr>
<tr>
<td>Fe (2p₃/₂) satellite</td>
<td>714.7</td>
<td>2.2</td>
<td>1.7</td>
</tr>
<tr>
<td>Fe(III) magnetite</td>
<td>713.0</td>
<td>2.2</td>
<td>3.0</td>
</tr>
<tr>
<td>Fe(III) maghemite</td>
<td>711.5</td>
<td>1.9</td>
<td>3.8</td>
</tr>
<tr>
<td>Fe(III) magnetite</td>
<td>710.5</td>
<td>1.6</td>
<td>2.7</td>
</tr>
</tbody>
</table>

| MBC                                           |           |           |             |
| Fe 2p₃/₂                                      | 721.2     | 3.5       | 1.7         |
| Fe(III) maghemite satellite                   | 718.6     | 3.0       | 1.6         |
| Fe(II) Fe (2p₃/₂) satellite                   | 716.3     | 2.2       | 0.8         |
| Fe (2p₃/₂) satellite                          | 714.5     | 2.2       | 1.6         |
| Fe(III) magnetite                             | 712.8     | 2.2       | 3.0         |
| Fe(III) maghemite                             | 711.2     | 2.0       | 3.9         |
| Fe(III) magnetite                             | 710.2     | 1.4       | 1.9         |

| As loaded MBC                                 |           |           |             |
| Fe 2p₃/₂                                      |           |           |             |
| Fe(III) maghemite satellite                   |           |           |             |
| Fe(II) Fe (2p₃/₂) satellite                   |           |           |             |
| Fe (2p₃/₂) satellite                          |           |           |             |
| Fe(III) magnetite                             |           |           |             |
| Fe(III) maghemite                             |           |           |             |
| Fe(III) magnetite                             |           |           |             |
## A.2.5 Calculated atomic charges for oxygen and iron of MBC and As(III)-laden MBC

Table A.5  O1s and Fe2p core level binding energies\(^c\) for MBC (pH 7) samples and atomic charges of their adsorbent surface species.\(^d\)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Binding Energy (eV)</th>
<th>Calculated atomic charge (Q* (esu))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>O1s</td>
<td>Fe2p</td>
</tr>
<tr>
<td>MBC</td>
<td>530.3</td>
<td>-0.86</td>
</tr>
<tr>
<td></td>
<td>530.8</td>
<td>-0.83</td>
</tr>
<tr>
<td></td>
<td>531.5</td>
<td>-0.78</td>
</tr>
<tr>
<td></td>
<td>533.6</td>
<td>-0.66</td>
</tr>
<tr>
<td></td>
<td>721.1</td>
<td>1.52</td>
</tr>
<tr>
<td>As-laden MBC</td>
<td>530.2</td>
<td>-0.86</td>
</tr>
<tr>
<td></td>
<td>530.7</td>
<td>-0.83</td>
</tr>
<tr>
<td></td>
<td>531.9</td>
<td>-0.76</td>
</tr>
<tr>
<td></td>
<td>533.4</td>
<td>-0.67</td>
</tr>
<tr>
<td></td>
<td>721.1</td>
<td>1.42</td>
</tr>
</tbody>
</table>

\(^c\)Experimental binding energies. These are used to calculate atomic charges with equation 2 and 3.

\(^d\)Fe2p charges are calculated only for core level binding energies.
## HR-XPS data for As(III)- and As(V)-laden MBC under oxic and anoxic conditions

### Table A.6
HR-XPS data for As(III)- and As(V)-laden MBC prepared at pH 2, 7, 12 under oxic and anoxic conditions

<table>
<thead>
<tr>
<th>Initial Oxidation State of Arsenic</th>
<th>Peak/ Chemical State</th>
<th>Argon Purged</th>
<th>Oxic Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>pH 2</td>
<td>pH 7</td>
</tr>
<tr>
<td>2p (Peak I) As(III)</td>
<td>Binding Energy (eV)</td>
<td>1327.2</td>
<td>1326.9</td>
</tr>
<tr>
<td></td>
<td>Atomic Percentage %</td>
<td>1.3</td>
<td>2.3</td>
</tr>
<tr>
<td></td>
<td>FWHM (eV)</td>
<td>1.8</td>
<td>1.9</td>
</tr>
<tr>
<td>2p (Peak II) As(V)</td>
<td>Binding Energy (eV)</td>
<td>1326.2</td>
<td>1326.2</td>
</tr>
<tr>
<td></td>
<td>Atomic Percentage %</td>
<td>1.0</td>
<td>2.2</td>
</tr>
<tr>
<td></td>
<td>FWHM (eV)</td>
<td>1.8</td>
<td>1.6</td>
</tr>
<tr>
<td>As(III)</td>
<td>3d (Peak I) As(III)</td>
<td>Binding Energy (eV)</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Atomic Percentage %</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>FWHM (eV)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>3d (Peak II) As(V)</td>
<td>Binding Energy (eV)</td>
<td>45.7</td>
</tr>
<tr>
<td></td>
<td>Atomic Percentage %</td>
<td>0.7</td>
<td>0.7</td>
</tr>
<tr>
<td></td>
<td>FWHM (eV)</td>
<td>1.8</td>
<td>1.7</td>
</tr>
<tr>
<td></td>
<td>3d (Peak III) As(III)</td>
<td>Binding Energy (eV)</td>
<td>44.4</td>
</tr>
<tr>
<td></td>
<td>Atomic Percentage %</td>
<td>0.4</td>
<td>1.1</td>
</tr>
<tr>
<td></td>
<td>FWHM (eV)</td>
<td>1.6</td>
<td>1.5</td>
</tr>
<tr>
<td></td>
<td>Binding Energy (eV)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>----------------</td>
<td>---------------------</td>
<td>-------</td>
<td>-------</td>
</tr>
<tr>
<td></td>
<td>2p (Peak I)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>As(V)</td>
<td>Binding Energy (eV)</td>
<td>1327.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Atomic Percentage %</td>
<td>1.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>FWHM (eV)</td>
<td>1.6</td>
</tr>
<tr>
<td></td>
<td>2p (Peak II)</td>
<td>Binding Energy (eV)</td>
<td>1327.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Atomic Percentage %</td>
<td>1.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>FWHM (eV)</td>
<td>1.8</td>
</tr>
<tr>
<td></td>
<td>3d (Peak I)</td>
<td>Binding Energy (eV)</td>
<td>46.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Atomic Percentage %</td>
<td>0.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>FWHM (eV)</td>
<td>1.7</td>
</tr>
<tr>
<td></td>
<td>3d (Peak II)</td>
<td>Binding Energy (eV)</td>
<td>45.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Atomic Percentage %</td>
<td>0.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>FWHM (eV)</td>
<td>1.6</td>
</tr>
</tbody>
</table>
A.3 Equations

A.3.1 Dimensionless version of Langmuir adsorption isotherm

\[ R_L = \frac{q_0 - q_e}{q_0} \]  \hspace{1cm} (A.1)

Where, \( R_L \) is the dimensionless separation factor, \( q_0 \) is the maximum adsorption capacity and \( q_e \) is the equilibrium adsorption capacity [19].

\[ R_L = \frac{1}{1 + K_L C_0} \]  \hspace{1cm} (A.2)

\[ Y = \frac{x}{R_L + (1 - R_L)x} \]  \hspace{1cm} (A.3)

\[ R_L = \frac{x(1 - Y)}{Y(1 - x)} \]  \hspace{1cm} (A.4)

\( R_L > 1 \), unfavorable, \( R_L = 1 \) linear, \( 0 < R_L < 1 \), favorable and \( R_L < 0 \), irreversible

Here, \( K_L \) is the Langmuir constant (L/mol), \( C_0 \) is the initial As(III) concentration and \( C_e \) is the equilibrium As(III) concentration.

\[ X = \frac{C_e}{C_0} \]  \hspace{1cm} (A.5)

\[ Y = \frac{q_e}{q_0} \]  \hspace{1cm} (A.6)
A.4 Figures and schemes

A.4.1 SEM-EDX studies of BC, MBC and As(III)-laden MBC

Figure A.1 SEM-EDX spectra of (a) BC, (b) MBC and (c) arsenic-loaded MBC. As-loaded MBC samples were prepared using pH 7, 25.0 mL of 12 mg/L As(III) solution equilibrated with 50 mg of MBC for 1h at 25 °C (2 g/L dose). The EDX-measured surface region weight percent of carbon dropped from ~84% on BC to ~58% on MBC due to Fe₃O₄ particle deposition. The weight percent of Fe varies at different surface locations due to aggregation and other factors inducing heterogeneity (eg ~26% Fe in (c) at a different location. The much smaller As coverage (0.10 wt%) in (c) could not account for this size drop in surface region %Fe.
A.4.2 STEM-EDX studies of BC, MBC and As(III)-laden MBC

Figure A.2 STEM-EDX spectra (a) BC, (b) MBC and (c),(d) arsenic-loaded MBC. As-loaded MBC samples were prepared using pH 7, 25.0 mL of 12 mg/L As(III) solution equilibrated with 50 mg of MBC for 1h at 25 °C (2 g/L dose).
A.4.3 Powder XRD (PXRD) studies of MBC

Figure A.3 The powder XRD spectrum of MBC
A.4.4 As(III) isotherm data and fitted models

Figure A.4 As(III) isotherm data and fitted models a) Langmuir, b) Freundlich and c) Sips for As(III) adsorption on MBC. At 25 °C and pH = 7, 1 h equilibration time. (Error bars represent the standard deviation of 3 replicates).
A.4.5  Dimensionless separation factor ($R_L$)

Figure A.5  Dimensionless separation factor ($RL$) at the temperatures a) 20 °C, b) 25 °C and c) 40 °C. Where $q_e$ is the equilibrium capacity of As(III) on MBC and $Ce$ is the equilibrium As(III) concentration.
A.4.6 Competitive batch sorption results

Figure A.6 Concentrations of As(III) in MBC-treated waste water samples (25.0 mL) after 1 h contact with 100.0 mg of MBC at 25 °C at pH 7. Standard deviation for the average of 3 replicates of samples A, B and C are 0.02, 0.08 and 0.024 mg/L, respectively. Note that the actual, speciation of oxyanions is not presented. Zinc concentrations in sample A and B are ~0.4 mg/L. Chemical laboratory heavy metal contains Cd$^{2+}$, Pb$^{2+}$, Cu$^{2+}$, Fe$^{3+}$ and chromate. 4NA = 4-nitroniline and SA = salicylic acid)
A.4.7 Low resolution XPS-survey spectra for MBC and As(III)-laden MBC

Figure A.7 XPS survey spectra of MBC(a) after As(III) adsorption at pH 7 and (b) before As(III) adsorption. (CPS – counts per second)
A.4.8  Proposed As(III) complexes on the magnetite surface

Figure A.8  Proposed complexes of AsO$_3$ trigonal pyramid on FeO$_6$ octahedra and FeO$_4$ tetrahedra
A.4.9 High resolution (HR) XPS spectra for As(III) and As(V) under oxic and anoxic conditions

Figure A.9 HR-XPS for As(III)- and As(V)-laden MBC under anoxic (pH 2, 7 and 12 and oxic conditions pH = 7). The anoxic conditions were maintained using argon purged solutions in the sorption studies.
A.4.10 Scheme for As(III)-magnetite hydrogen bonding effects

Scheme S1
a) Surface already protonated

b) Neutral surface

Scheme A.1 As(III)-magnetite hydrogen bonding effects
A.5 REFERENCES


APPENDIX B

RHODAMINE B ADSORPTIVE REMOVAL AND PHOTOCATALYTIC DEGRADATION
ON MIL-53-FE MOF/MAGNETIC MAGNETITE/BIOCHAR COMPOSITES
Figure B.1  TEM images and element mapped TEM images of a) MBC, b) MIL-53-Fe MOF, c) MOF-MBC and d) Rh B-laden MOF-MBC
Figure B.2  TEM-EDX spectra (a) MOF, (b) MBC and (c) MOF-MBC and (d) Rh-laden MOF-MBC
Figure B.3  Resolved and assigned HR-XPS spectra for C1s, O1s and Fe2p for BC (CPS – counts per second).
Figure B.4  Resolved and assigned HR-XPS spectra for C1s, O1s and Fe2p for MBC (CPS – counts per second).
Figure B.5  Resolved and assigned HR-XPS spectra for C1s, O1s and Fe2p for MIL-53-Fe MOF (CPS – counts per second).
Figure B.6  Resolved and assigned HR-XPS spectra for C1s, O1s and Fe2p for MOF-MBC (CPS – counts per second).
Figure B.7  Resolved and assigned HR-XPS spectra for C1s, O1s and Fe2p for Rh B-laden MOF-MBC (CPS – counts per second).
Figure B.8  LC-UV Chromatograms for the separation of Rh B from its degradation products for the photocatalysis experiments (in the presence of Cr(VI)) with (a) no catalyst, (b) BC, (c) MBC, (d) MIL-53-Fe MOF and (e) MOF-MBC (UV detection wavelength = 254 nm).
Figure B.9  ESI mass spectra for chromatographic peaks [in the presence of Cr(VI)]; (a) no catalyst, (b) BC, (c) MBC, (d) MIL-53-Fe MOF and (e) MOF-MBC
Figure B.10  Leaching of iron from the adsorbents, BC MBC, MIL-53-Fe MOF and MOF-MBC at pH 1-13 into (a) aqueous Rh B (50 mg/L) and (b) aqueous Rh B + Cr(VI) (50 mg/L) (Each adsorbent 50 mg in 25.0 mL water at the indicated pH was stirred for 3 hrs time at 200 rpm in a shaker).
APPENDIX C

BIOCHAR ADSORBENTS WITH ENHANCED HYDROPHOBICITY FOR OIL SPILL REMOVAL
Figure C.1  Differential scanning calorimetric (DSC) analysis profiles (10 °C/min heating rate under 50 mL/min N₂) of lauric acid, biochar (BC), lauric acid-coated biochar (LBC), Fe₃O₄-modified biochar (MBC), lauric acid-biochar modified with Fe₃O₄ (LMBC) and Fe₃O₄-modified biochar coated with lauric acid (MLBC).
Figure C.2  Magnetic moments of lauric acid-coated biochar (LBC), lauric acid coated magnetic biochar (LMBC) and magnetic biochar-coated with lauric acid (MLBC) at 5 and 300 K by VSM.
C.1 X-ray photoelectron spectroscopy (XPS)

Low resolution wide scan XPS survey spectra for BC, LBC, MBC, LMBC, MLBC and oil-laden adsorbents exhibited in Figure C.3 and summarized in Table C.2. All show Fe2p peaks except BC and LBC where the original iron content in the biochar is low and due only to trace iron compounds present in the original Douglas fir biochar. These survey spectra exhibit iron deposition, as magnetite, onto BC or LBC to give MBC, LMBC and MLBC. The surface region’s Fe atomic percentage in LMBC (~7.0 %) and MLBC (6.7 %) is lower than MBC (~9.3 %), This is because LMBC and MLBC surface contains added lauric acid.

The C1s and O1s high resolution (HR) spectra of BC, LBC, MBC, LMBC and MLBC, both before and after crude oil uptake are given in Figure S4 and S5, respectively. Each were deconvoluted by Avantage v5.932 software provided with the instrument. The C1s and O1s spectra were each deconvoluted into the four peaks which are assigned in Table C.3 for the C1s spectra. Binding energies for C1s at 289.7-288.5 eV, 287.8-286.5 eV, 285.9-285.2 eV and 285.2-284.7 eV range correspond to -CO₂R(H) and CO₃²⁻, C=O, C-O and (C-H, C-C). However, C-C and -CH₃, -CH₂, -C₄- (quaternary) and aromatic ring C (sp² versus sp³ are all found in the 285.2-284.7 eV peak).

The deconvoluted O1s high resolution XPS binding energy (BE) peak ranges of (534.4-533.3) eV, (533.6-531.9) eV, (532.4-530.6) eV and (531.8-529.8) eV (Figure C.5 and assignments in Table C.4) correspond to (CO₃²⁻· O-C=O), O-C, C=O and Fe-O, respectively [1]. LBC shows a slight increase in -CO₂R(H) content in both C1s and O1s HR spectra versus BC. Upon magnetite deposition, Fe-O atomic percentages increased significantly for MBC (12.2 %), LMBC (14.1 %) and MLBC (12.7 %) confirming iron oxide added to their surfaces.
The HR XPS C1s and O1s spectra illustrate that substantial oxygenated functions can be detected in the near surface/surface regions of the adsorbents. BC which appears quite hydrophobic based on contact angle measurements (CA = 122.3°) can still admit water into pores and internal void aided by oxygen-containing functional groups.

Figure C.3  Low resolution (LS) survey scan XPS spectra for biochar (BC), lauric acid-coated biochar (LBC), Fe\textsubscript{3}O\textsubscript{4}-modified biochar (MBC), lauric acid-biochar modified with Fe\textsubscript{3}O\textsubscript{4} (LMBC) and Fe\textsubscript{3}O\textsubscript{4}-modified biochar coated with lauric acid (MLBC) and their crude oil-laden analogues (CPS – counts per second).

The LS-XPS interpretation are on pages 182 and 183.
Table C.2  Low resolution (LS) survey scan XPS data for biochar (BC), lauric acid- coated biochar (LBC), Fe$_3$O$_4$-modified biochar (MBC), lauric acid-biochar modified with Fe$_3$O$_4$ (LMBC) and Fe$_3$O$_4$-modified biochar coated with lauric acid (MLBC) and their crude oil-laden analogues.

<table>
<thead>
<tr>
<th>Peak/Chemical state (LS)-XPS</th>
<th>BC</th>
<th>LBC</th>
<th>MBC</th>
<th>LMBC</th>
<th>MLBC</th>
<th>Crude Oil-laden BC</th>
<th>Crude Oil-laden LBC</th>
<th>Crude Oil-laden MBC</th>
<th>Crude Oil-laden LMBC</th>
<th>Crude Oil-laden MLBC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atomic percentage %</td>
<td>93.9</td>
<td>89.7</td>
<td>68.2</td>
<td>62.94</td>
<td>67.97</td>
<td>87.42</td>
<td>81.75</td>
<td>87.84</td>
<td>76.77</td>
<td>82.97</td>
</tr>
<tr>
<td>FWHM (eV)</td>
<td>2.7</td>
<td>2.71</td>
<td>2.8</td>
<td>2.86</td>
<td>2.78</td>
<td>1.67</td>
<td>2.44</td>
<td>2.52</td>
<td>1.65</td>
<td>2.56</td>
</tr>
<tr>
<td>O Binding energy (eV)</td>
<td>532.84</td>
<td>532.47</td>
<td>531</td>
<td>531.15</td>
<td>531.1</td>
<td>533.23</td>
<td>532.03</td>
<td>533.16</td>
<td>531.71</td>
<td>532.28</td>
</tr>
<tr>
<td>Atomic percentage %</td>
<td>5.65</td>
<td>10.3</td>
<td>21.54</td>
<td>27.62</td>
<td>22.26</td>
<td>10.73</td>
<td>14.12</td>
<td>11.3</td>
<td>15.88</td>
<td>13.9</td>
</tr>
<tr>
<td>FWHM (eV)</td>
<td>3.69</td>
<td>3.5</td>
<td>3.06</td>
<td>3.51</td>
<td>3.53</td>
<td>3.16</td>
<td>3.1</td>
<td>3.17</td>
<td>3.92</td>
<td>4.32</td>
</tr>
<tr>
<td>Fe Binding energy (eV)</td>
<td>-</td>
<td>-</td>
<td>711.56</td>
<td>711.56</td>
<td>711.41</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>711.58</td>
<td>711.32</td>
</tr>
<tr>
<td>Atomic percentage %</td>
<td>-</td>
<td>-</td>
<td>9.31</td>
<td>6.99</td>
<td>6.68</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>3.96</td>
<td>1.82</td>
</tr>
<tr>
<td>FWHM (eV)</td>
<td>-</td>
<td>-</td>
<td>2.82</td>
<td>4.77</td>
<td>4.59</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>2.88</td>
<td>4.6</td>
</tr>
</tbody>
</table>
Figure C.4  High resolution (HR) C1s deconvoluted XPS spectra for (a) biochar (BC), (b) lauric acid-coated biochar (LBC), (c) Fe₃O₄-modified biochar (MBC), (d) lauric acid-biochar modified with Fe₃O₄ (LMBC) and (e) Fe₃O₄-modified biochar coated with lauric acid (MLBC) and (f-j) their crude oil-laden analogues (CPS – counts per second).
Table C.3  High resolution (HR) C1s deconvoluted XPS data for biochar (BC), lauric acid-coated biochar (LBC), Fe$_3$O$_4$-modified biochar (MBC), lauric acid-biochar modified with Fe$_3$O$_4$ (LMBC) and Fe$_3$O$_4$-modified biochar coated with lauric acid (MLBC) and their crude oil-laden analogues

<table>
<thead>
<tr>
<th>Peak/Chemical state (HR)-XPS</th>
<th>BC</th>
<th>LBC</th>
<th>MBC</th>
<th>LMBC</th>
<th>Crude Oil-laden BC</th>
<th>Crude Oil-laden LBC</th>
<th>Crude Oil-laden MBC</th>
<th>Crude Oil-laden LMBC</th>
<th>Crude Oil-laden MLBC</th>
</tr>
</thead>
<tbody>
<tr>
<td>I Binding energy (eV)</td>
<td>289.7</td>
<td>288.9</td>
<td>289.0</td>
<td>288.8</td>
<td>288.5</td>
<td>289.2</td>
<td>288.8</td>
<td>289.1</td>
<td>288.7</td>
</tr>
<tr>
<td>Atomic percentage %</td>
<td>2.4</td>
<td>3.3</td>
<td>3.9</td>
<td>2.8</td>
<td>3.6</td>
<td>4.2</td>
<td>4.4</td>
<td>4.5</td>
<td>3.0</td>
</tr>
<tr>
<td>FWHM (eV)</td>
<td>1.8</td>
<td>1.5</td>
<td>2.0</td>
<td>1.5</td>
<td>1.4</td>
<td>1.0</td>
<td>1.4</td>
<td>1.1</td>
<td>1.4</td>
</tr>
<tr>
<td>II Binding energy (eV)</td>
<td>287.8</td>
<td>287.0</td>
<td>286.7</td>
<td>287.8</td>
<td>286.6</td>
<td>286.8</td>
<td>286.6</td>
<td>286.8</td>
<td>286.7</td>
</tr>
<tr>
<td>Atomic percentage %</td>
<td>3.8</td>
<td>3.6</td>
<td>4.7</td>
<td>4.8</td>
<td>4.5</td>
<td>9.7</td>
<td>4.3</td>
<td>7.3</td>
<td>2.0</td>
</tr>
<tr>
<td>FWHM (eV)</td>
<td>1.8</td>
<td>1.5</td>
<td>2.0</td>
<td>1.5</td>
<td>1.5</td>
<td>1.4</td>
<td>1.5</td>
<td>1.4</td>
<td>1.5</td>
</tr>
<tr>
<td>III Binding energy (eV)</td>
<td>285.9</td>
<td>285.5</td>
<td>285.3</td>
<td>286.4</td>
<td>285.2</td>
<td>285.4</td>
<td>285.3</td>
<td>285.4</td>
<td>285.2</td>
</tr>
<tr>
<td>Atomic percentage %</td>
<td>13.9</td>
<td>24.7</td>
<td>14.9</td>
<td>12.9</td>
<td>30.7</td>
<td>39.4</td>
<td>24.7</td>
<td>34.9</td>
<td>29.1</td>
</tr>
<tr>
<td>FWHM (eV)</td>
<td>1.8</td>
<td>1.4</td>
<td>1.7</td>
<td>1.6</td>
<td>1.4</td>
<td>1.1</td>
<td>1.2</td>
<td>1.2</td>
<td>0.9</td>
</tr>
<tr>
<td>IV Binding energy (eV)</td>
<td>284.5</td>
<td>284.7</td>
<td>284.6</td>
<td>285.2</td>
<td>284.7</td>
<td>285.0</td>
<td>284.9</td>
<td>284.9</td>
<td>284.8</td>
</tr>
<tr>
<td>Atomic percentage %</td>
<td>72.2</td>
<td>58.1</td>
<td>42.7</td>
<td>47.4</td>
<td>33.4</td>
<td>34.8</td>
<td>51.1</td>
<td>41.2</td>
<td>49.9</td>
</tr>
</tbody>
</table>
Figure C.5  High resolution (HR) O1s deconvoluted XPS spectra for (a) Biochar (BC), (b) lauric acid-coated biochar (LBC), (c) Fe$_3$O$_4$-modified biochar (MBC), (d) lauric acid-biochar modified with Fe$_3$O$_4$ (LMBC) and (e) Fe$_3$O$_4$-modified biochar coated with lauric acid (MLBC) and (f-j) their crude oil-laden analogues (CPS – counts per second).
Table C.4  High resolution (HR) O1s deconvoluted XPS data for biochar (BC), lauric acid-coated biochar (LBC), Fe$_3$O$_4$-modified biochar (MBC), lauric acid-biochar modified with Fe$_3$O$_4$ (LMBC) and Fe$_3$O$_4$-modified biochar coated with lauric acid (MLBC) and their crude oil-laden analogues.

<table>
<thead>
<tr>
<th>Peak/Chemical state (HR)-XPS</th>
<th>BC</th>
<th>LBC</th>
<th>MBC</th>
<th>LMBC</th>
<th>MLBC</th>
<th>Oil-laden BC</th>
<th>Oil-laden LBC</th>
<th>Oil-laden MBC</th>
<th>Oil-laden LMBC</th>
<th>Oil-laden MLBC</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Binding energy (eV)</td>
<td>533.9</td>
<td>533.7</td>
<td>533.3</td>
<td>533.9</td>
<td>534.1</td>
<td>535.7</td>
<td>534.1</td>
<td>534.1</td>
<td>533.7</td>
<td>533.5</td>
</tr>
<tr>
<td>Atomic percentage %</td>
<td>1.1</td>
<td>2.3</td>
<td>1.3</td>
<td>1.3</td>
<td>1.6</td>
<td>2.0</td>
<td>2.1</td>
<td>0.8</td>
<td>1.0</td>
<td>4.4</td>
</tr>
<tr>
<td>FWHM (eV)</td>
<td>1.5</td>
<td>1.5</td>
<td>1.4</td>
<td>1.5</td>
<td>1.3</td>
<td>1.3</td>
<td>1.5</td>
<td>1.2</td>
<td>1.3</td>
<td>1.5</td>
</tr>
<tr>
<td>II</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Binding energy (eV)</td>
<td>532.8</td>
<td>532.7</td>
<td>531.9</td>
<td>532.5</td>
<td>532.2</td>
<td>533.5</td>
<td>532.2</td>
<td>533.6</td>
<td>532.2</td>
<td>532.0</td>
</tr>
<tr>
<td>Atomic percentage %</td>
<td>2.2</td>
<td>2.5</td>
<td>4.4</td>
<td>6.1</td>
<td>5.7</td>
<td>3.9</td>
<td>5.5</td>
<td>4.7</td>
<td>4.3</td>
<td>6.4</td>
</tr>
<tr>
<td>FWHM (eV)</td>
<td>1.5</td>
<td>1.2</td>
<td>1.5</td>
<td>1.6</td>
<td>1.5</td>
<td>1.5</td>
<td>1.4</td>
<td>1.5</td>
<td>1.3</td>
<td>1.4</td>
</tr>
<tr>
<td>III</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Binding energy (eV)</td>
<td>531.7</td>
<td>531.8</td>
<td>530.8</td>
<td>531.5</td>
<td>531.3</td>
<td>532.4</td>
<td>531.4</td>
<td>532.4</td>
<td>531.3</td>
<td>530.6</td>
</tr>
<tr>
<td>Atomic percentage %</td>
<td>2.9</td>
<td>3.9</td>
<td>5.4</td>
<td>9.9</td>
<td>7.1</td>
<td>2.8</td>
<td>5.4</td>
<td>1.5</td>
<td>4.9</td>
<td>2.6</td>
</tr>
<tr>
<td>FWHM (eV)</td>
<td>1.5</td>
<td>1.3</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
<td>1.0</td>
<td>1.3</td>
<td>1.0</td>
<td>1.4</td>
<td>1.4</td>
</tr>
<tr>
<td>IV</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Binding energy (eV)</td>
<td>530.5</td>
<td>530.8</td>
<td>530.3</td>
<td>530.2</td>
<td>530.1</td>
<td>531.8</td>
<td>530.7</td>
<td>532.1</td>
<td>529.9</td>
<td>529.8</td>
</tr>
<tr>
<td>Atomic percentage %</td>
<td>1.2</td>
<td>1.4</td>
<td>12.2</td>
<td>14.1</td>
<td>12.7</td>
<td>2.2</td>
<td>1.9</td>
<td>4.2</td>
<td>5.2</td>
<td>1.4</td>
</tr>
<tr>
<td>FWHM (eV)</td>
<td>1.0</td>
<td>1.2</td>
<td>1.1</td>
<td>1.4</td>
<td>1.4</td>
<td>1.0</td>
<td>1.1</td>
<td>1.0</td>
<td>0.8</td>
<td>1.1</td>
</tr>
</tbody>
</table>
C.2 REFERENCES