



**MECHANISTIC STUDY OF ANTIBIOTICS AND
ENDOCRINE DISRUPTORS REMOVAL BY WOOD-
DERIVED BIOCHAR, FUNCTIONALIZED BIOCHAR
AND BIOCHAR COMPOSITE**

By
MOHAMMAD BOSHIR AHMED

**A Dissertation
Submitted in Fulfilment for the Degree of
DOCTOR of PHILOSOPHY
in
Environmental Engineering**

University of Technology Sydney
New South Wales, Australia

June 2018

CERTIFICATE OF ORIGINAL AUTHORSHIP

I, MOHAMMAD BOSHIR AHMED, certify that my research work in this thesis has not previously been submitted anywhere for a degree nor has it been submitted as part of requirements for a degree except as part of the collaborative doctoral degree and/or fully acknowledged within the text.

I also certify that the thesis has thoroughly been written by me. Any kind of help that I have received during my research activities and the preparation of the thesis itself has been acknowledged. Furthermore, I also certify that all information sources and literatures used are indicated in the thesis in the reference section.

Production Note:

Signature removed prior to publication.

SIGNATURE OF STUDENT:

MOHAMMAD BOSHIR AHMED

ACKNOWLEDGMENT

First of all, I owe my deepest gratitude to my principal supervisor, Prof. JOHN L. ZHOU for his continuous supports, guidance, time, patience and inspiration throughout my PhD study. I have learnt a lot from his ideas, critical review of my study plans and papers, knowledge and motivation that encouraged me to overcome many difficulties in the research as well as other aspects of life to achieve this milestone. I also would like to thank my supervisory committee, Prof. HUU HAO NGO for his mentor supports, papers revising and useful comments on this thesis. I would also like to give special thanks to Dr. WENSHAN GUO and Dr. ABU HASAN JOHIR for their contribution for papers revising and useful suggestions on this dissertation.

I gratefully acknowledge the UNIVERSITY OF TECHNOLOGY SYDNEY (UTS) for awarding me the “INTERNATIONAL RESEARCH SCHOLARSHIP” and “FACULTY OF ENGINEERING AND INFORMATION TECHNOLOGY” Scholarships. The financial support from “CENTRE FOR TECHNOLOGY IN WATER AND WASTEWATER” and “BLUE SKY SCHOLARSHIP” is also grateful.

The technical supports and guidance from Dr. ABU HASAN JOHIR, the environmental engineering laboratories, UTS are greatly appreciated. Also, I would like to thank RAMI HADDAD, the manager in civil and environmental engineering laboratories, UTS. Many thanks go to KATIE, HERBERT, MARK and other staff at Microstructure Analysis Unit, UTS. I would like to give special thanks to RONALD SHIMMON, for providing me training to run ^1H NMR in science lab, UTS. I would like to express my appreciation to Kireesan for his technical assistances and useful discussion. I am thankful to my colleagues Ali, Atique, Mahmud, Nawshad Akther, Ben, Lijuan, Dorji, and Nireen for their supports and contributions.

Finally, I am hugely indebted to all my family, colleagues and friends for their emotional supports, unconditional love and guidance.

DEDICATION

This thesis is deeply dedicated to the following people:

To my respective parents, LATE MOHAMMAD NORUL ISLAM & REHENA BEGUM

For their sacrifices, endless love, hard work and inspiration

To my wonderful wife, JASMIN KHTUN

For her constant love, supports and caring

To my lovely uncle and aunt, MD. BELAYET HOSSAIN & SALMA BEGUM

For giving me inspiration, help and hope.

CONTENTS

TABLE OF CONTENTS

MECHANISTIC STUDY OF ANTIBIOTICS AND ENDOCRINE DISRUPTORS REMOVAL BY WOOD-DERIVED BIOCHAR, FUNCTIONALIZED BIOCHAR AND BIOCHAR COMPOSITE	i
CERTIFICATE OF ORIGINAL AUTHORSHIP	ii
ACKNOWLEDGMENT	iii
DEDICATION.....	iv
CONTENTS.....	1
NOMENCLATURES	6
LIST OF FIGURES	11
LIST OF TABLES	11
LIST OF PUBLICATIONS	26
AWARDS.....	30
ABSTRACT.....	31

CHAPTER ONE: INTRODUCTION	37
1.1. Background	37
1.1.1. <i>Adverse Effects of Antibiotic Residues</i>	37
1.1.2. <i>Adverse Effects of EDCs</i>	38
1.1.3. <i>Removal Technologies of Antibiotics and EDCs</i>	39
1.1.4. <i>Removal of Antibiotics and EDCs by Biochar, Functionalized Biochar and Their Composite</i>	40
1.2. Research Hypothesis	41
1.3. Objectives.....	42
1.4. Research significance	43
1.5. Thesis Outline	43
 CHAPTER TWO: LITERATURE REVIEW	 46
2.1. Introduction	46
2.2. Antibiotics and EDCs in the Aquatic Environment	47
2.2.1. <i>Definition, Characteristics, Source, Occurrence and Pollution of Antibiotics in the Aquatic Environment</i>	47
2.2.2. <i>Definition, Characteristics, Source, Occurrences and Pollution of EDCs in the Aquatic Environment</i>	53
2.2.3. <i>Relevant Regulations for Antibiotics and EDCs Residues</i>	59
2.3. Antibiotics and EDCs Removal Technologies.....	60
2.3.1. Biological Treatment Technologies.....	61
2.3.2. Chemical Treatment Technologies	78
2.3.3. Physical Treatment Technologies	94
2.3.4. Hybrid Technologies.....	97
2.4. Biochar and Functionalized Biochar	100
2.5. Adsorption of Antibiotics and EDCs Using Biochar and fBC	102

2.6. Sorption and Reduction of Chloramphenicol Antibiotics Using ZVI and Its Composites	103
2.7. Conclusions and Research Gaps	104
CHAPTER THREE: MATERIALS AND METHODS	108
3.1. Materials.....	108
3.1.1. <i>Experimental Materials</i>	108
3.1.2. <i>Woody Biomass Collection and Processing</i>	108
3.1.4. <i>Stock Solutions of Antibiotics and EDCs</i>	109
3.1.5. <i>Furnace and Reactor for Biochar & Functionalized Biochar Preparation</i>	109
3.1.6. <i>Synthetic Wastewater, MBR Sewage Effluent and Lake Water</i>	109
3.2. Methods.....	110
3.2.1. <i>Preparation and Functionalization of Adsorbents, Synthesis of ZVI & Preparation of Composite</i>	110
3.2.2. <i>Characterization Methods</i>	112
3.2.3. <i>Batch Adsorption Experiments for Removing Antibiotics and EDCs</i>	114
3.2.4. <i>The Analytical Method of the Antibiotic and EDCs Concentrations</i>	115
CHAPTER FOUR: ANTIBIOTICS REMOVAL FROM WATER AND WASTEWATER: MECHANISMS AND APPLICATIONS.....	118
4.1. Single and Competitive Sorption Properties and Mechanism of Functionalized Biochar for Removing Sulfonamide Antibiotics from Water.....	118
4.1.1. <i>Introduction</i>	118
4.1.2. <i>Experimental Section</i>	120
4.1.3. <i>Results and Discussion</i>	125
4.1.4. <i>Concluding Remarks</i>	150
4.2. Competitive Sorption Affinity of Sulfonamides and Chloramphenicol Antibiotics toward Functionalized Biochar for Water and Wastewater Treatment.....	151

4.2.1. Introduction	151
4.2.2. Materials and Methods	152
4.2.3. Results and Discussion	155
4.2.4. Concluding Remarks	167
4.3. Chloramphenicol Interaction with Functionalized Biochar in Water: Sorptive Mechanism, Molecular Imprinting Effect and Repeatable Applications	168
4.3.1. Introduction	168
4.3.2. <i>Materials and Methods</i>	169
4.3.3. Results and Discussion	174
4.3.4. Concluding Remarks	193
4.4. Nano-Fe ⁰ immobilized onto Functionalized Biochar Gaining Excellent Stability During Sorption and Reduction of Chloramphenicol via Transforming to Reusable Magnetic Composite	195
4.4.1. <i>Introduction</i>	195
4.4.2. <i>Materials and Methods</i>	197
4.4.3. Results and Discussion	200
4.4.4. Concluding Remarks	222

CHAPTER FIVE: ENDOCRINE DISRUPTORS REMOVAL BY FUNCTIONALIZED BIOCHAR: MECHANISMS AND APPLICATIONS IN WASTEWATER TREATMENT

223

5.1. Sorptive Removal of Phenolic Endocrine Disruptors by Functionalized Biochar: Competitive Interaction Mechanism, Removal Efficacy and Application in Wastewater	224
5.1.1. Introduction	224
5.1.2. Experimental.....	225
5.1.3. Results and Discussion	230
5.1.4. Concluding Remarks	251

5.2. Sorption of Hydrophobic Organic Contaminants on Functionalized Biochar: Protagonist Role of π - π Electron-Donor-Acceptor Interactions and Hydrogen Bonds	252
5.2.1. Introduction	252
5.2.2. Materials and Methods	254
5.2.3. Results and Discussion	257
5.2.4. Concluding Remarks	276
 CHAPTER SIX: CONCLUSIONS AND RECOMMENDATIONS	278
6.1. Conclusions	278
6.2. Contributions to the Field.....	279
6.3. Recommendations for Further Research	279
 REFERENCES	281

NOMENCLATURES

EDCs = Endocrine disrupting chemicals

SMT = Sulfamethazine

SZT = Sulfatiazole

SMX = Sulfamethoxazole

Al^{3+} = Aluminium ion

E1 = Estrone

E2 = 17β -estradiol

E3 = Estriol

E1 = Estrone

EE2 = 17α -ethynylestradiol

*4t*BP = 4-*tert*-butyl phenol

BPA = Bisphenol A

HNO_3 = Nitric acid

H_2SO_4 = Sulfuric acid

fBC = Functionalized biochar

CNT = Carbon nanotubes

MWCNTs = Multiwalled carbon nanotubes

SWCNTs = Single walled carbon nanotubes

PCPs = Personal care products

AGRs = Antibiotic resistant genes

ECs = Emerging contaminants

K_{ow} = Octanol–water partition coefficient

BC = Biochar

AC = Activated carbon

SEM = Scanning electron microscope

EDS = Energy dispersive spectroscopy

XRD = Powder X-ray diffraction

BET = Brunauer-Emmett-Teller

FTIR = Fourier transform infrared spectroscopy

XPS = X-ray photoelectron spectroscopy

PO_4^{3-} = Phosphate
 Cl^- = Chloride ion
 NO_3^- = Nitrate ion
 SO_4^{2-} = Sulphate ion
CEC = Cationic exchange capacity
H/C = Hydrogen/carbon ratio
 HNO_3 = Nitric acid
 NaOH = Sodium hydroxide
 NaBH_4 = Sodium borohydrate
 M_{dry} = Dried mass
 M_{vm} = Weight of volatile matter
 M_{fc} = Fraction of fixed carbon
 M_{ash} = Weight of ash
 Na_2CO_3 = Sodium carbonate
 CH_3OH = Methanol
 $\text{C}_2\text{H}_5\text{OH}$ = Ethanol
 NaHCO_3 = Sodium bicarbonate
 KCl = Potassium chloride
 NaCl = Sodium chloride
HA = Humic acid
 R^- = Alkyl group
 AlCl_3 = Aluminium chloride
 $\text{CH}_3\text{-CO-CH}_3$ = Acetone
 $\text{C}=\text{C}$ = Carbon-carbon double bonds
 K_2HPO_4 = Potassium biphosphate
 MgSO_4 = Magnesium sulphate
PHEN = Phenanthrene
PABA = para-amino benzoic acid
DNB = 1,3-Dinitro benzene
EDA = Electron donor-acceptor
EDD = Electron-donor-donor
CAP/CP = Chloramphenicol
TAP = Thiamphenicol

FF = Florfenicol
EM = Erythromycin
RTM = Roxithromycin
SD = Sulfadiazine
SM = Sulfamerazine
SP = Sulfapyridine
TC = Tetracycline
CTC = Chlortetracycline
OTC = Oxytetracycline
DXC = Doxycyclinehyclate
NFC = Norfloxacin
CIP = Ciprofloxacin
OFC = Ofloxacin
CARB = Carbadox
LNCM = Lincomycin
TRMP = Trimethoprim
WWTPs = Wastewater treatment plants
DWTPs = Drinking water treatment plants
STPs = Municipal sewage treatment plants
 pK_a = Acid dissociation constant
MBR = Membrane bioreactor
AOPs = Advanced oxidation processes
UV = Ultraviolet
TiO₂ = Titanium dioxide
COD = Chemical oxygen demand
PPCPs = Pharmaceutical personal care products
-OH = Hydroxyl group
-COOH = Carboxylic group
-NH₂ = Amino group
-CH = Alkyl group
-CO = Ketonic group
-COOR = Ester group
ZnO = Zinc oxide

UF = Ultrafiltration

O/C = Oxygen/ carbon ratio

N/C = Nitrogen/carbon ration

CAHB = Charge assisted hydrogen bonds

E^0 = Redox potential

ZVI = Zerovalent iron

nZVI/ Fe^0 = Nonosized zero valent iron

1MbBBC600 = Bamboo derived functionalized biochar (fBC-1)

TGA= Thermogravimetric analysis

K_d = Distribution coefficient

BJH= Barrett-Joyner-Halenda

DI= Deionised water

PFO = Pseudo first order

PSO = Pseudo second order

IDM = Intraparticle diffusion

Q_{max} = Maximum sorption capacity

K_L = Langmuir fitting constant

$Q_{max(total)}$ = Summerized Langmur maximum sorption capacity

$K_F(total)$ = Summerized freundilich constant

$C_6H_5^-$ = Aryl group

ΔG = Free energy change

K_{aw} = Water dissociation constant

TDS = Total dissolved solid

I_G/I_D = Raman spectroscopy D and G band ratio

k = Rate constant

NO= Nitroso

HOAM = Hydroxlamino

m/z = Mass to charge ratio

DO = Dissolved oxygen

RP = Reverse phase

C18 = 18 C-12

Vis = Visible

LC-MS_(Qtof) = Triple quad liquid chromatography-mass spectroscopy

ESI = Electrospray ionisation
PTFE = Poly tetrafluoro ethylene
MP-AES = Microwave plasma-atomic emission spectroscopy
IC = Ion chromatography
EAA = Electron acceptor-acceptor
 ΔpH = pH change
LOD = Limit of detection
CMs = Carbonaceous materials
HOCs = Hydrophobic organic contaminants
 ^1H NMR = Proton nuclear magnetic resonance spectroscopy
 δ = Chemical shifts in NMR
PMM = Polanyi-Mane Model
 C_s = Solubility of compound
 S_v = Sorbed volume
 ρ_{HOC} = Density of HOC compounds
 K_{HD} = Hexadecane partition coefficient
2,4-D = 2,4-Dichlorophenoxyacetic acid
MCPA = 2-methyl-4-chlorophenoxyacetic acid

LIST OF FIGURES

Figure 1.1: The price of different adsorbents [57].	41
Figure 2.1: Sources of Antibiotics [24].	50
Figure 2.2: Chemical structures of EDCs and resonance form of phenolic group in EDCs..	54
Figure 2.3: Routes of potential exposure of sex steroids from livestock [96].	55
Figure 2.4: Routes of potential exposure to sex steroids from livestock [100].	56
Figure 2.5: Figure demonstrates that all hormone-sensitive physiological systems are vulnerable to EDCs [1].	59
Figure 2.6: ECs removal achieved by activated sludge process with the corresponding reference after the compound name. a = antidepressant, b = contrast agent, c = gastroesophageal, d = vasodilator, e = antineoplastic, f = diuretic. The concentrations are in mg L ⁻¹ for empty columns.	71
Figure 2.7: Constructed wetlands for wastewater treatment. a CW with free-floating plants (FFP). b CW with free water surface and emergent macrophytes (FWS). c CW with horizontal subsurface flow (HSSF, HF). d CW with vertical subsurface flow (VSSF, VF) [113].	75
Figure 2.8: Comparative average removal efficiency of ECs with standard deviation (error bar) for wastewater treatment (activated sludge, biologically activated carbon, microalgae, MBR and constructed wetlands) and sludge treatment (aerobic and anaerobic).	78
Figure 2.9: ECs removal efficiencies achieved by ozonation process with the corresponding reference after the compound name. Concentrations are in mg L ⁻¹ for empty columns and in g L ⁻¹ for dark columns.	83

Figure 2.10: ECs removal efficiencies achieved by ozonation in the presence of H₂O₂ (a) and UV in the presence of H₂O₂ (b), with the corresponding reference after the compound name. Concentrations are in mg L⁻¹ for empty columns and g L⁻¹ for dark columns. 1 = corrosion inhibitor, 2 = pain reliever, 3 = contrast agent, 4 = anti-inflammatory.84

Figure 2.11: ECs removal efficiencies achieved by Fenton process (Figure 2.10a) and by UV photolysis (Fig. 2.10b). Concentrations are in mg L⁻¹ for empty columns and in g L⁻¹ for clofibrilic acid. 1 = corrosion inhibitors, 2 = anti-diabetics, 3 = contrast agents, 4 = anti-inflammatory, 5 = pain reliever, 6 = anticonvulsant, 7 = lipid regulators.86

Figure 2.12: ECs removal efficiencies achieved by photo-Fenton (a) and UV photocatalysis (UV/TiO₂) (b), with the corresponding reference after the compound name. Concentrations are in mg L⁻¹ for empty columns and in g L⁻¹ for chloramphenicol. 1 = pesticide, 2 = corrosion inhibitor, 3 = contrast agent, 4 = antidepressant, 5 = anti-diabetic, 6 = gastroesophageal, 7 = lipid regulator, 8 = diuretic, 9 = beta blocker, 10 = pain reliever, 11 = NSAID, 12 = stimulant [225].92

Figure 2.13: Comparative average removal efficiency of ECs with standard deviation (error bar) by different chemical treatment technologies.94

Figure 3.1: Fixed bed pyrolyser (reactor) for pyrolysis of biomass. 110

Figure 4.1.1: Molecular structures of sulfonamides antibiotics and their equilibrium species. 119

Figure 4.1.2: DSC-TGA graph for biomass raw material (bamboo). 122

Figure 4.1.3: The chemical speciation of (a) sulfamethoxazole modified from Fukahori et al. [308]; (b) sulfathiazole took from Pei et al. [309], and (c) sulfamethazine modified from Teixidó et al. [59]. 126

Figure 4.1.4: (a) Effect of pH on the distribution coefficient (K_d) with standard deviation (error bars) for removal of sulfonamide antibiotics; (b) single and competitive sorption kinetics data

with PSO and IDM kinetics model fittings (initial concentration of sulfonamide antibiotics being 10 mg L^{-1} for single solute, and 3.33 mg L^{-1} for each competitive solute at room temperature using 100 mg L^{-1} functionalized biochar dosages)..... 127

Figure 4.1.5: Pseudo first order (PFO) kinetic model for the kinetics of sulfonamide sorption on functionalized biochar, in single and competitive mode (model fitted to origin pro version 9.1 software). 128

Figure 4.1.6: STZ adsorption isotherm plots and model fits from single solute (initial concentration $0.5\text{--}50 \text{ mg L}^{-1}$), and from mixtures (initial individual concentrations were $0.33\text{--}16.67 \text{ mg L}^{-1}$) at pH 3.5 and different temperatures..... 132

Figure 4.1.7: SMX adsorption isotherm and model fits (Langmuir and Freundlich) at different temperatures using initial concentrations of $0.5\text{--}50 \text{ mg L}^{-1}$ at pH 3.25 for single solutes, and at $1\text{--}50 \text{ mg L}^{-1}$ in mixture mode at pH 3.5. 133

Figure 4.1.8: SMT adsorption isotherm and model fits (Langmuir and Freundlich) at different temperatures using initial concentrations of $0.5\text{--}50 \text{ mg L}^{-1}$ at pH 4.5 for single solutes, and at $1\text{--}50 \text{ mg L}^{-1}$ in mixture mode at pH 3.5. 134

Figure 4.1.9: Change of K_d values (with SD as error bars) against equilibrium concentrations for (a) competitive solutes with total initial solution concentrations (C_o) at $1\text{--}50 \text{ mg L}^{-1}$ and each solute concentration was $0.33\text{--}16.67 \text{ mg L}^{-1}$ (i.e. $C_o/3$), and for (b) single solute ($C_o = 0.5\text{--}50 \text{ mg L}^{-1}$). 136

Figure 4.1.10: Proposed sorption mechanism for single and competitive antibiotics (R1 for SMT, R2 for STZ, R3 for SMX) on functionalized biochar with possible resonance effects for $\pi\text{--}\pi$ interactions. 137

Figure 4.1.11: Change of pH for blank samples (without antibiotics) at different adsorbent dosages leading to proton release in solution. 140

Figure 4.1.12: FTIR spectra for raw bamboo biomass, biochar (BBC380), and functionalized biochar (1MbBBC600) for the sorption of single and competitive solutes (before and after adsorption).	142
Figure 4.1.13: Raman spectra with band ratio (I_D/I_G) for biochar (BBC380), and functionalized biochar (1MbBBC600 i.e. fBC-1) before and after sorption of single and competitive solutes.	144
Figure 4.2.1: Effect of pH on K_d (with standard deviation) during the removal of sulfonamides and chloramphenicol antibiotics using fBC (80 mg L^{-1}) with initial individual antibiotic concentration of 1.0 mg L^{-1} at 25°C (a). Competitive sorption kinetics data with PSO and PFO model fitting using 1.0 mg L^{-1} initial antibiotics concentration and 80 mg L^{-1} of fBC at pH 4.0–4.25 (b).....	156
Figure 4.2.2: Zeta potential values of fBC and pH shift during pH effect study.....	157
Figure 4.2.3: Sorption isotherm plots and model fitting for mixtures of antibiotics (initial concentration of each antibiotic was $0.250\text{--}20.0 \text{ mg L}^{-1}$) at pH 4.0–4.25 using fBC dosage of 80 mg L^{-1}	160
Figure 4.2.4: FTIR (a) and Raman spectra (b) with band ratio (I_D/I_G) of fBC before and after sorption experiments for competitive solutes in mixture mode.....	162
Figure 4.2.5: Possible resonance structures of antibiotics and different functional groups in fBC and their electron donor and acceptor sites.	163
Figure 4.2.6: Proposed sorption mechanisms for the removal of antibiotics in competitive mode using fBC.	163
Figure 4.2.7: Sorption of antibiotics (%) in mixture mode with 1.0 mg L^{-1} initial concentration of each antibiotic from lake water (a) and synthetic wastewater (b) with different dosages of fBC at pH 4.0–4.25 and 25°C	167

Figure 4.3.1: Nitrogen sorption isotherm for fBC-1 and fBC-2 (a). Barret-Joyner-Halenda (BJH) surface/volume mesopore analysis (adsorption/desorption) with cumulative pore size distribution of fBC-1 and fBC-2 (b). 175

Figure 4.3.2: (a) FTIR spectra of biochar and fBC, (b) Raman spectra of fBCs (with band intensity ratio, I_G/I_D) before and after chloramphenicol sorption. 176

Figure 4.3.3: Effect of pH on the equilibrium K_d of chloramphenicol on biochar, fBC-1 and fBC-2 at 25 °C, using initial chloramphenicol concentration of 15.5 $\mu\text{M L}^{-1}$, 50–60 mg L^{-1} fBCs or 100 mg L^{-1} biochar. Error bars indicate the standard deviation. 177

Figure 4.3.4: Effects of (a) humic acid concentration, (b) salt concentration, and (c) soil concentration on the equilibrium K_d of chloramphenicol at 25 °C, using 50–60 mg L^{-1} fBC-2 at pH 4.0–4.5. 179

Figure 4.3.5: (a) Sorption isotherm plots and model fitting with initial chloramphenicol concentrations of 0.774–154.7 $\mu\text{M L}^{-1}$ at pH 4.25, 25 °C using 50–60 mg L^{-1} fBC or 100 mg L^{-1} biochar over 40 h. (b) Change of K_d values (with SD as error bars) against equilibrium concentrations from isotherm studies. 182

Figure 4.3.6: Proposed sorption mechanism for the removal of chloramphenicol from different water using fBC. 184

Figure 4.3.7: Effects of competitors phenanthrene and PABA on the adsorption of chloramphenicol at pH 1.82–1.85 (a), pH 4.20–4.56 (b), and pH 9.15–9.60 (c) in deionized water. Phenanthrene and PABA concentrations at 1.0 mg L^{-1} , chloramphenicol concentration at $\sim 3.10 \mu\text{M L}^{-1}$, fBC-2 dosage at 40–50 mg L^{-1} . Error bars represent the standard deviation. 186

Figure 4.3.8: Sorption of PABA and phenanthrene in the presence or absence of chloramphenicol [65] in deionized water at different pH values. Solution compositions: phenanthrene and PABA concentrations at 1.0 mg L^{-1} , CP concentration at $\sim 3.10 \mu\text{M L}^{-1}$, fBC-2 dosage at 40–50 mg L^{-1} . Error bars represent the standard deviation. 188

Figure 4.3.9: (a) Sorption of chloramphenicol (initial concentration $3.10 \mu\text{M L}^{-1}$) from deionized water, lake water and synthetic wastewater at different dosages of fBC-2 against residual concentrations at pH 4.0–4.5, 25 °C (contact time was 18 h). (b) Reusability of fBC-2 (on percentage basis) for the removal of chloramphenicol under the same condition from different water samples. 191

Figure 4.3.10: Percentage of regeneration of chloramphenicol. 193

Figure 4.4.1: SEM cross-sectional images of fBC, nZVI-fBC and nFe₃O₄-fBC composite (after application of nZVI-fBC), respectively (a–c) using scanning electron microscope (SEM) with energy dispersive spectrometer (EDS) and XRD pattern of nZVI (d).....202

Figure 4.4.2: SEM image of nZVI.202

Figure 4.4.3: EDS plot of nZVI.203

Figure 4.4.4: XPS analysis of nZVI-fBC composite before sorption experiments. Spectra were obtained by plotting counts against binding energy for C1s (a), O1s (b), Fe2p (c) and overall survey (d) in a wide scan.204

Figure 4.4.5: FTIR spectroscopy of nZVI-fBC composite before and after the sorption of chloramphenicol.....205

Figure 4.4.6: XRD pattern of fBC, nZVI-fBC and nFe₃O₄-fBC (a). Raman spectra of nZVI and nZVI-fBC composite (with band ratio, I_G/I_D) for the removal of chloramphenicol before and after experiments (b).206

Figure 4.4.7: XPS analysis of nZVI-fBC (after 1st cycle). Spectra were obtained by plotting counts against binding energy for C1s (a), O1s (b), Fe2p (c) and overall survey (d) in a wide scan.207

Figure 4.4.8: Percentage removal (\pm , standard deviation) of chloramphenicol with time using nZVI (a) and nZVI-fBC composite (b). The initial concentration of chloramphenicol was $3.10 \mu\text{M L}^{-1}$, pH 4.0–4.5, 25 °C from different water matrices with different dosages of nZVI and nZVI-fBC composite.....208

Figure 4.4.9: Sorption of chloramphenicol by fBC and Fe_3O_4 -fBC composite with the Freundlich and Langmuir model fit.212

Figure 4.4.10: Proposed reduction and dechlorination mechanisms for the removal of chloramphenicol from water and wastewater.213

Figure 4.4.11: Reduced products of chloramphenicol as identified by LC-MS/QTOF from deionized water, synthetic wastewater and lake water using nZVI only (sample collected after 8 h).214

Figure 4.4.12: Chloramphenicol transformation by-products identified by their retention times (2.1 min, 2.7 min) in LC and mass spectra by LC-MS/QTOF from deionized water (a) and lake water (b) using nZVI only (sample collected after 8 h). LC-MS/QTOF method run for 13 min and data plotted up to 5 min.....215

Figure 4.4.13: Chloramphenicol transformation products highlighted by their retention times after 10 min (a), 30 min (b), 150 min (c), and 12 h (d) using nZVI-fBC in synthetic wastewater during the 1st cycle application. LC-MS/QTOF method run for 13 min and data plotted up to 5 min.215

Figure 4.4.14: The 2nd cycle application of nZVI-fBC (nZVI-fBC transformed to nFe_3O_4 -fBC) for the removal of chloramphenicol from synthetic wastewater. Small fraction of reduced product indicates that sorption was dominating in the 2nd and subsequent cycles.216

Figure 4.4.15: Chloramphenicol sorption mechanisms at pH 4.0-4.5.219

Figure 4.4.16: Percentage of sorption and reduction (cumulative basis, after excluding the amount of recoverable chloramphenicol) using nZVI-fBC composite (in the 1st cycle) followed

by sorption only onto nFe₃O₄-fBC composite (a). Reusability of nFe₃O₄-fBC composite for the repetitive applications (up to 7th cycle) for the removal of chloramphenicol (3.10 µM L⁻¹ initial concentration) at pH 4.0–4.5, 25 °C from different water (b).220

Figure 4.4.17: Sorption of methylene blue by nFe₃O₄-fBC with the Langmuir and Freundlich model fit.221

Figure 4.4.18: Use of a magnet bar to demonstrate easy separation of nFe₃O₄-fBC composite after experiments.....222

Figure 5.1.1: SEM image of fBC-2 before (a) and after (b) sorption of EDCs.230

Figure 5.1.2: Nitrogen adsorption–desorption isotherm for fBC-2: Barret-Joyner-Halenda (BJH) surface/volume mesopore analysis (a), and cumulative pore size distribution (b).233

Figure 5.1.3: Raman spectra for fBC-2 before and after sorption experiments. Raman shifts measurement was carried out using Renishaw inVia Raman spectrometer equipped with a 17 mW Renishaw Helium-Neon Laser 633 nm and CCD array detector at 50% laser intensity.234

Figure 5.1.4: XPS analysis of fBC-2. Spectra were obtained by plotting counts against binding energy in a wide scan for C1s (a), O1s (b), P 2p(c) and overall survey (d).....235

Figure 5.1.5: Effect of pH on solid phase concentration (µg g⁻¹) during EDCs sorption in competitive mode using fBC-2 at a dosage of 80 mg L⁻¹ at 25 °C (a). Zeta potential values of fBC-2 using 0.01 M KCl solution at different pH with fBC-2 dosage of 400 mg L⁻¹ together with initial and equilibrium pH values (b).236

Figure 5.1.6: Kinetic model fit for EDCs adsorption on fBC-2 at 25 °C. (a) Weber-Morris plots, (b) external mass transfer plots, and (c) Boyd plots.....237

Figure 5.1.7: Solid phase concentration vs. aqueous concentration at equilibrium for the sorption of EDCs using 100 mg L⁻¹ of fBC-2 at 25 °C.....240

Figure 5.1.8: The Langmuir isotherm model fits for sorption of EDCs onto fBC-2.....241

Figure 5.1.9: Logarithm plot of distribution coefficient (K_d) vs aqueous equilibrium concentration for the sorption of EDCs using 100 mg L⁻¹ of fBC-2 at 25 °C.....242

Figure 5.1.10: Resonance structures of EDCs and different functional groups in fBC-2. ...245

Figure 5.1.11: Sorption of EDCs in mixture mode with initial concentration of each EDC at ~500 µg L⁻¹ from MBR sewage effluent at different dosages of fBC-2 at pH 3.0–3.25, 25 °C.249

Figure 5.2.1: (a) Adsorption isotherms of estrone (E1), 17 β -estradiol (E2), estriol (E3), 17 α -ethynylestradiol (EE2) and bisphenol A (BPA) on fBC-2 at pH 3.0-3.5. Solid lines are the polynomial fitting curves using PMM. (b) Effect of pH on solid phase concentration (µg kg⁻¹) during HOC sorption (initial concentration of each HOC was ~500 µg L⁻¹) by fBC-2 with dosage of 40-60 mg L⁻¹, 25 °C.259

Figure 5.2.2: PMM Sorption Isotherm Fitting for HOCs. Isotherm Parameters were Normalized by the Primary Solute Solubility with $b=1$, and S_e of Single-Solute Isotherms.259

Figure 5.2.3: Individual sorption of different concentrations of (a) phenanthrene (PHEN) and (b) 1,3-dinitrobenzene (DNB) on fBC-2 at different pH, 25 °C using fBC-2 dosage of 18-25 mg L⁻¹ and 40-60 mg L⁻¹, respectively for PHEN and DNB.262

Figure 5.1.4: Removal percentage NON-2 during sorption by fBC-2 (30-35 mg L⁻¹) at different pH, highlighting the role of π -H-bonding and H-bonding with fBC-2.....263

Figure 5.2.5: (a) Comparison of K_d/K_{HW} between phenanthrene (PHEN) and HOCs such as estrone (E1), 17 β -estradiol (E2), estriol (E3), 17 α -ethynylestradiol (EE2) and bisphenol A (BPA). K_d/K_{HW} was calculated at $C_e = 0.002 C_s$. The K_d/K_{HW} values of solutes were directly labelled on their respective bars due to the off-scale values. The differences among them are

consistent with the explanation that π - π bonds played a major role after eliminating hydrophobic effects. The π - π bonds formed among HOCs and fBC-2 were a donor/acceptor system, and much stronger than those between PHEN and fBC-2. (b) Relationship between $\log K_{HW}$ vs $\log K_d$ as calculated at $C_e = 0.002 C_s$264

Figure 5.1.6: Sorption performance of (a) estrone (E1) and (b) bisphenol A (BPA) in the absence and presence of competitor such as π -electron-donor phenanthrene (PHEN) and π -electron-acceptor 1,3-dinitrobenzene (DNB). Their interactions indicated the role of co-solutes and the role of π - π electron-donor-donor or donor-acceptor multi-system on the sorption performance of HOCs by fBC-2. Error bar representing the standard deviation. Sorption performance of 17β -estradiol (E2), estriol (E3) and 17α -ethynylestradiol (EE2) in the absence and presence of π -electron-donor-acceptor system is represented in Figure 5.2.7. Each HOC initial concentration was $\sim 1000 \mu\text{g L}^{-1}$ and fBC-2 dosage was maintained $40\text{-}60 \text{ mg L}^{-1}$266

Figure 5.2.7: Sorption performance of (a) 17β -estradiol (E2), (b) estriol (E3), and (b) 17α -ethynylestradiol (EE2) in the absence and presence of competitors such as π -electron-donor phenanthrene (PHEN) and π -electron-acceptor 1,3-dinitrobenzene (DNB). Their interactions indicated the role of co-solutes and the role of π - π electron-donor-donor or donor-acceptor multi-system on the sorption performance of HOCs by fBC-2. Error bar representing the standard deviation. The initial concentration of HOC was $\sim 1000 \mu\text{g L}^{-1}$ and fBC-2 dosage was maintained $40\text{-}60 \text{ mg L}^{-1}$ 267

Figure 5.2.9: Sorption performance of (a) estrone (E1) and (b) bisphenol A (BPA) in the absence and presence of competitors such as π -electron-donor phenanthrene (PHEN) and π -electron-acceptor *p*-amino benzoic acid (PABA). Their interactions indicated the role of co-solutes and the role of π - π electron-donor-donor or donor-acceptor multi-system on the sorption performance of HOCs by fBC-2. Error bar representing the standard deviation. The initial concentration of HOC was $\sim 1000 \mu\text{g L}^{-1}$ and fBC-2 dosage was maintained $40\text{-}60 \text{ mg L}^{-1}$. 269

Figure 5.2.10: Sorption performance of (a) 17β -estradiol (E2), (b), estriol (E3), and (b) 17α -ethynylestradiol (EE2) in the absence and presence of competitors such as π -electron-donor phenanthrene (PHEN) and π -electron-acceptor *p*-amino benzoic acid (PABA). Their interactions indicated the role of co-solutes and the role of π - π electron-donor-donor or donor-

acceptor multi-system on the sorption performance of HOCs by fBC-2. Error bar representing the standard deviation. The initial concentration of HOC was $\sim 1000 \mu\text{g L}^{-1}$ and fBC-2 dosage was maintained $40\text{-}60 \text{ mg L}^{-1}$270

Figure 5.2.11: UV-Vis spectra difference in the acceptor-donor mixture showing the charge-transfer absorption band of π - π complexes. (a) Donor-phenanthrene (PHEN), acceptor 1,3-dinitrobenzene (DNB) and their mixing interaction, (b) Donor-PHEN, acceptor-DNB and HOC-estrone (E1) interactions, (c) Donor-PHEN, acceptor-DNB and HOC-estriol (E3) interactions, and (d) Donor- PHEN, acceptor-DNB and HOC-BPA interactions clearly indicating the difference of absorption band of π - π complexes.....271

Figure 5.2.12: ^1H NMR observed frequency shift for different protons in specific carbon bonded protons in the respective structure of structure of E1, BPA, DNB, and PHEN (Figures a-c). ΔHz of each proton in each component in their mixture specified within first bracket. Data obtained from a series of combine mixing solution of solutes and their increased shielding by extra-nuclear electrons (i.e. increasing magnetic field at fixed frequency) from a fixed concentration of solute in methanol- d_4 solvent. Observed frequency shift (ΔHz) for each solute in solution was measured by multiplying the chemical shift (δ) of each solute and spectrophotometer frequency for different proton positions (marked as green color) as shown in figure (d). Structural proton positions were labelled based on ^1H NMR peaks accessible at http://sdb.sdb.aist.go.jp/sdb/cgi-bin/cre_result.cgi?STSI=151281072529897. (d) Illustration of offset geometry of HOCs in which proton number lies in the structure.....273

Figure 5.2.13: Sorption of PABA at different concentrations and different pH using fBC-2 dosage of $40\text{-}60 \text{ mg L}^{-1}$ 276

LIST OF TABLES

Table 2.1: Physicochemical properties of major types of antibiotics investigated by different studies.	51
Table 2.2: Physicochemical properties of the target EDCs.	57
Table 2.3: Advantages and challenges of different technologies in the removal of ECs.	62
Table 2.4: ECs removal efficiency by nitrification and denitrification treatment technologies.	65
Table 2.5: ECs removal efficiency by biological activated carbon [131].	66
Table 2.6: ECs removal efficiency from WWTPs by different biological treatment technologies.	67
Table 2.7: ECs removal efficiency by aerobic, anaerobic and facultative processes.	72
Table 2.8: ECs removal efficiency by biosorption and MBR based systems.	73
Table 2.9: ECs removal efficiency by different constructed wetland processes.	76
Table 2.10: ECs removal efficiency by gamma radiation (conventional) and AOPs based treatment technologies.	87
Table 2.11: The removal efficiency of EDCs, pesticides and beta blockers achieved by hybrid systems.	98
Table 2.12: Pharmaceuticals removal efficiency by hybrid systems.	99
Table 3.1: Yield of biochar prepared from different biomass.	112

Table 4.1.1: Physicochemical properties of the antibiotics investigated in this study.....	119
Table 4.1.2: The basic properties, zeta potential and EDS data of biomass and biochar samples.	122
Table 4.1.3: Summary of BET and BJH physical parameters for biochar and functionalized biochar.....	123
Table 4.1.4: Summary of the kinetic model parameters for sulfonamide antibiotic adsorption on functionalized biochar.....	129
Table 4.1.5: Summary of the Freundlich isotherm parameters for sulfonamide antibiotic adsorption on functionalized biochar.....	129
Table 4.1.6: Summary of the Langmuir isotherm parameters for sulfonamide antibiotic adsorption on functionalized biochar.....	130
Table 4.1.7: pH shift for different species of SMT, SMX and STZ antibiotics on functionalized biochar.....	139
Table 4.1.8: ΔG_o values calculated from water dissociation constant (K_{aw}) at different temperatures.....	145
Table 4.1.9: Summary of Raman spectroscopy peak assignment in char [51, 317] and observed in this study before and after adsorption.....	149
Table 4.2.1: Physicochemical properties of the antibiotics investigated in this study.....	153
Table 4.2.2: Summary of the kinetic model parameters for antibiotics sorption on fBC at 25 ± 0.5 °C.	158
Table 4.2.3: Summary of the Freundlich and Langmuir isotherm parameters for competitive antibiotic sorption on fBC at 25 ± 0.5 °C.	159

Table 4.3.1: Physicochemical properties of chloramphenicol.	169
Table 4.3.2: EDS analysis data of biochar and fBC.....	172
Table 4.3.3: Physicochemical properties of lake water and synthetic wastewater.	173
Table 4.3.4: The Freundlich and Langmuir isotherm parameters for the sorption of chloramphenicol by biochar and functionalized biochar.	181
Table 4.3.5: Zeta potential values of fBC-1 and fBC-2.....	183
Table 4.4.1: Zeta potential values (mV) of Fe ₃ O ₄ -fBC composite and nZVI.....	199
Table 4.4.2: Chemical composition of synthetic wastewater.....	200
Table 4.4.4: EDS of fBC, nZVI and nZVI-fBC.....	201
Table 4.4.5: Reduction kinetic parameters of chloramphenicol in different water types using nZVI.....	209
Table 4.4.6: The Freundlich and Langmuir isotherm parameters for the sorption of chloramphenicol using fBC and Fe ₃ O ₄ -fBC.....	212
Table 5.1.1: Physicochemical characteristics of synthetic wastewater and MBR sewage effluent.	227
Table 5.1.2: Limit of detection (LOD) of EDCs by HPLC equipped with UV and fluorescence detectors.	228
Table 5.1.3: Summary of BET and BJH physical parameters for fBC-2.....	231

Table 5.1.4: Kinetic parameters calculated from the PSO and Waber-Morris kinetic models for the sorption of EDCs on fBC-2 at 25 °C.....	238
Table 5.1.5: Summary of the Langmuir isotherm parameters for EDCs sorption on fBC-2 at 25±0.5 °C.	242
Table 5.1.6: Calculated ΔG^0 (kJ mole ⁻¹) values for EDCs at 25 °C with initial concentrations of each EDC at 250-3000 µg L ⁻¹ . K_d values were taken as L kg ⁻¹	243
Table 5.1.7: ΔG^0 values calculated from water dissociation constant (K_{aw}) at 25 °C.	247
Table 5.1.8: EDC removal from synthetic wastewater with different dosages of fBC-2 at 46 h, 50 h and 64 h. (LOD = limit of detection)	250
Table 5.2.1: Physicochemical Properties of Selected HOCs.	253
Table 5.2.2: XPS Spectra Summery for fBC-2 [25, 397].	255
Table 5.2.3: Summary of the Freundlich Isotherm Parameters for Each HOC Adsorption on fBC-2 at 25 ± 0.5 °C.	258
Table 5.2.4: Summary of the PMM Isotherm Parameters for Each HOC Adsorption on fBC-2 at 25 ± 0.5 °C (d=1).	258
Table 5.2.5: Hexadecane-Water Partition Coefficient and Sorption Coefficient Relationship.	264

LIST OF PUBLICATIONS

Peer-Reviewed Publications

- *(1). Mohammad Boshir Ahmed,** John L Zhou, Huu Hao Ngo, Wenshan Guo, Md Abu Hasan Johir, Kireesan Sornalingam, M. Sahedur Rahman. "Chloramphenicol interaction with functionalized biochar in water: sorptive mechanism, molecular imprinting effect and repeatable application". *Sci. Total Environ.* 609 (2017): 885-895.
- *(2). Mohammad Boshir Ahmed,** John L Zhou, Huu Hao Ngo, Wenshan Guo, Md Abu Hasan Johir, Kireesan Sornalingam, Dalel Belhaj, Monem Kallel. "Nano-Fe⁰ immobilized onto functionalized biochar gaining excellent stability during sorption and reduction of chloramphenicol via transforming to reusable magnetic composite". *Chem. Eng. J.* 322 (2017): 571-581.
- (3). Mohammad Boshir Ahmed,** Md Abu Hasan Johir, John L Zhou, Huu Hao Ngo, Wenshan Guo, Kireesan Sornalingam. "Photolytic and photocatalytic degradation of organic UV filters in contaminated water". *Curr. Opin. Green Sustain. Chem.* 6 (2017): 85-92. (Special issue on catalysis).
- *(4). Mohammad Boshir Ahmed,** John L Zhou, Huu Hao Ngo, Wenshan Guo, Md Abu Hasan Johir, Dalel Belhaj. "Competitive sorption affinity of sulfonamides and chloramphenicol antibiotics toward functionalized biochar for water and wastewater treatment". *Bioresour. Technol.* 238 (2017): 306-312.
- * (5). Mohammad Boshir Ahmed,** John L. Zhou, Huu Hao Ngo, Wenshan Guo, Md Abu Hasan Johir, Kireesan Sornalingam "Single and competitive sorption properties and mechanism of functionalized biochar for removing sulfonamide antibiotics from water". *Chem. Eng. J.* 311 (2017), 348-358.
- *(6). Mohammad Boshir Ahmed,** John L. Zhou, Huu Hao Ngo, and Wenshan Guo. "Adsorptive removal of antibiotics from water and wastewater: progress and challenges". *Sci. Total Environ.* 532 (2015): 112-126. (Hot Paper & Highly cited paper according to web of science)
- *(7). Mohammad Boshir Ahmed,** John L. Zhou, Huu Hao Ngo, and Wenshan Guo "Insight into biochar properties and its cost analysis". *Biomass Bioenerg.* 84 (2016): 76-86.
- *(8). Mohammad Boshir Ahmed,** John L. Zhou, Huu Hao Ngo, Wenshan Guo and Mengfang Chen "Progress in the preparation and application of modified biochar for improved contaminant removal from water and wastewater. *Bioresour. Technol.* 214 (2016), 836-851.

- * (9). **Mohammad Boshir Ahmed**, John L. Zhou, Huu Hao Ngo, Wenshan Guo, Nikolaos S Thomaidis, Jiang Xu "Progress in the biological and chemical treatment technologies for emerging contaminant removal from wastewater: a critical review". *J. Hazard. Mater.* 323 (2017), 274-298 (*on special issue, most downloaded paper in J. Hazard. Mater.*). (*Hot Paper & Highly cited paper according to web of science*).
- *(10). **Mohammad Boshir Ahmed**, Huu Hao Ngo, Md Abu Hasan Johir, Kireesan Sornalingam. "Sorptive removal of phenolic endocrine disruptors by functionalized biochar: competitive interaction mechanism, removal efficacy and application in wastewater". *Chem. Eng. J.* (2017), 335, 801-811.
- (11). Kireesan Sornalingam, Andrew McDonagh, John L Zhou, Md A Johir, **Mohammad Boshir Ahmed**. "Photocatalysis of estrone in water and wastewater: Comparison between Au-TiO₂ nanocomposite and TiO₂, and degradation by-products". *Sci. Total Environ.* 610 (2018): 521-530.
- (12). Dalel Belhaj, Donyez Frikha, Khaled Athmouni, Bouthaina Jerbi, **Mohammad Boshir Ahmed**, Zouhaier Bouallagui, Monem Kallel, Sami Maalej, John Zhou, Habib Ayadi. "Box-Behnken design for extraction optimization of crude polysaccharides from Tunisian *Phormidium versicolor* cyanobacteria (NCC 466): partial characterization, in vitro antioxidant and antimicrobial activities." *Int. J. Biological Macromol.* (2017).
- (13). Narottam Saha, M. Safiur Rahman, **Mohammad Boshir Ahmed**, John L. Zhou, Huu Hao Ngo, and Wenshan Guo "Industrial metal pollution in water and probabilistic assessment of human health risk." *J. Environ. Manage.* 185 (2017): 70-78.
- (14). Bentuo Xu, **Mohammad Boshir Ahmed**, John L. Zhou, Ali Altaee, Minghong Wu, Gang Xu. "Photocatalytic removal of perfluoroalkyl substances from water and wastewater: Mechanism, kinetics and controlling factors." *Chemosphere*, 189 (2017), 717-729.
- (15). **Mohammad Boshir Ahmed**, A.T. M. Kamrul Hasan, Md. Mohiuddin, Mohammad Asadullah, Md. Sahedur Rahman, A. Khaleque. "Effects of heating rate and heating up time to central of biomass particles for bio-oil production." *Bangladesh J. Sci. Indust. Res.* 51(2017), 13-22.
- (16). Marwa Mohsen, **Mohammad Boshir Ahmed**, John L. Zhou. "Particulate Matter Concentrations and Heavy Metal Contamination Levels in the Railway Transport System of Sydney, Australia". *Transport. Res. Part D: Transport. Environ.* 62, 112-124. 62(2018), 112-124.
- (17). Bentuo Xu, **Mohammad Boshir Ahmed**, John L. Zhou, Ali Altaee, Minghong Wu, Gang Xu. "Graphitic carbon nitride (g-C₃N₄) based nanocomposites for the photocatalysis of

organic contaminants under visible irradiation: progress, limitations and future directions". *Sci. Total Environ.* 633 (2018), 546-559.

- (18). Dalel Belha, Khaled Athmouni, **Mohammad Boshir Ahmed**, Nissaf Aoiadni, Abdelfattah El Feki, John L. Zhou, Habib Ayadi. "Polysaccharides from *Phormidium versicolor* (NCC466) protecting HepG2 human hepatocellular carcinoma cells and rat liver tissues from cadmium toxicity: evidence from in vitro and in vivo tests". *Int. J. Biological Macromol.* 113 (2018), 813-920.

List of Submitted Journal Articles:

*(19). **Mohammad Boshir Ahmed**, John L Zhou, Huu Hao Ngo, Md. Abu Hasan Johir, Liying Sun, Mohammad Asadullah, Dalel Belhaj. "Sorption of Hydrophobic Organic Contaminants on Functionalized Biochar: Protagonist Role of π - π Electron-Donor-Acceptor Interactions and Hydrogen bonds". *J. Hazard. Mater.* (2018).

(20). Tanjina Nur, Paripurnanda Loganathan, **Mohammad Boshir Ahmed**, Mohammad Johir, Jaya Kandasamy, Saravanamuthu Vigneswaran*. Struvite production using membrane-bioreactor wastewater effluent and seawater. *Desalination* (2018), *Short Communication*.

(22). Bouthaina Jerbi, Dalel Belhaj, Sikandar I Mulla, Khaled Athmouni, **Mohammad Boshir Ahmed**, John L Zhou, Habib Ayadi, Monem Kallel. Uptake, accumulation, biochemical responses and health risk of heavy metals in soil-tomato system through urban sewage sludge amendment: A case study in Sfax, Tunisia. *Environ. Sci. Pollut. Res.* (2018).

*[Publications made during the PhD candidature including articles not entirely related to this Thesis. *Articles related to the Thesis.]*

Contribution to Scientific Forums:

*(1). **Mohammad Boshir Ahmed**, John L. Zhou, Huu Hao Ngo, and Wenshan Guo "Removal of sulfamethazine and sulfathiazole from water using modified bamboo biochar". 22nd -25th of August, 2016. The Synergy of Science and Industry: Biochar's Connection to Ecology, Soil, Food and Energy. Oregon State University, Portland, Oregon, USA.

(2). Dalel Belhaj, Bouthaina Jerbi, Khaled Athmouni, **Mohammad Boshir Ahmed**, Sikandar Mulla, John Zhou, Habib Ayadi. Ecotoxicological effect s of 17 α -ethinylestradiol (EE2) and its removal by monoculture of phytoplankton species and their consortium. May 2018. 3rd

International Conference on Integrated Environmental Management for Sustainable Development (ICIEM-2018), Sousse, Tunisia. <http://www.iciem-conference.com>

***(3). Mohammad Boshir Ahmed,** John L Zhou, Huu Hao Ngo, Wenshan Guo, Md Abu Hasan Johir, Kireesan Sornalingam, Dalel Belhaj, Monem Kallel. "Nano-Fe⁰ immobilized onto functionalized biochar gaining excellent stability during sorption and reduction of chloramphenicol via transforming to reusable magnetic composite". July 26-27, 2018. 6th Edition of International Conference on “Water Pollution and Sewage Management”- Be a part of Solution, Not the Pollution!!, Rome, Italy.

***(4). Mohammad Boshir Ahmed,** John L Zhou, Huu Hao Ngo. “Interactions of emerging contaminants-antibiotics with functionalized biochar”. August 20-23, 2018. Biochar 2018 - “The Carbon link in Watershed Ecosystem Services”, Wilmington, Delaware USA.

[Presentation made during the PhD candidature including proceedings and oral presentations.]

[*Presentation related to the Thesis]

AWARDS

1. Finalist for “**NSW Young Water Professional of the Year Award**”, the **Australian Water Association**, NSW, and Australia.
2. “**Top 35 of the Antibiotics Travel Awards 2017**” shortlisted by “**Antibiotics**” journal authority from worldwide applications.
3. **2017 HDR Students “Publication Award and Certificate”** from Faculty of Engineering and Information Technology, University of Technology Sydney (UTS), Sydney, Australia for publishing in high quality Journals.
4. **2016 HDR Students “Publication Award and Certificate”** from Faculty of Engineering and Information Technology, University of Technology Sydney (UTS), Sydney, Australia for publishing in high quality Journals.
5. **2015 HDR Students “Publication Award and Certificate”** from Faculty of Engineering and Information Technology, University of Technology Sydney (UTS), Sydney, Australia for publishing in high quality Journals.
6. **International Research Scholarship and Faculty of Engineering & Information Technology Scholarship** from University of Technology Sydney (UTS), Sydney, Australia.
7. **FEIT Travel funds** for the year of 2016 and 2018 from UTS.
8. **Vice Chancellor Travel fund** in 2018 from UTS.
9. **One-Off-Scholarship** from UTS in 2018.

ABSTRACT

In the last few decades, water pollution by different organic and inorganic species has become one of the most critical issues in many regions of the world. The consumption of the contaminated water is of major human health concern. The presence of antibiotics and EDCs in the aquatic environment causes critical problems to human health and aquatic organisms. The efficacy for removing antibiotics and EDCs in traditional wastewater treatment plants is not satisfactory by considering technology, cost and overall performance. On the other hand, adsorptive materials are cost effective and highly suitable for removal of antibiotics and EDCs. In this study, different adsorptive materials such as biochar, functionalized biochar and a biochar composite sorbent were prepared by the utilization of woody biomasses (bamboo and eucalyptus) and scrap iron material. Biochar was prepared at 380-400 °C via pyrolysis process and then modified using H_3PO_4 to produce functionalized biochar (fBC) at 600 °C. The functionalized biochars were named as fBC-1 (prepared from bamboo) and fBC-2 (prepared from eucalyptus globules). Finally, fBC-2 was used to prepare a biochar composite with zero-valent-iron (synthesized from scrap iron). These materials were used to remove antibiotics and EDCs in single and competitive mode.

Single and competitive sorption properties and mechanism of functionalized biochar for removing sulfonamide antibiotics from water:

Single and competitive sorption of ionisable sulphonamides sulfamethazine, sulfamethoxazole and sulfathiazole on functionalized biochar was highly pH dependent. The equilibrium data were well represented by both Langmuir and Freundlich models for single solutes, and by the Langmuir model for competitive solutes. Sorption capacity and distribution coefficient values decreased as sulfathiazole > sulfamethoxazole > sulfamethazine. The sorption capacity of each antibiotic in competitive mode is about three times lower than in single solute sorption. The kinetics data were best described by the pseudo second-order model for single solutes, and by PSO and intra-particle diffusion models for competitive solutes. Adsorption mechanism was governed by pore filling through diffusion process. The findings from pH shift, FTIR spectra and Raman band shift showed that sorption of neutral sulfonamide species occurred mainly due to strong H-bonds followed by $\pi^+ - \pi$ electron-donor-acceptor (EDA), and by Lewis acid-

base interaction. Moreover, EDA was the main mechanism for the sorption of positive sulfonamides species. The sorption of negative species was mainly regulated by proton exchange with water forming negative charge assisted H-bond (CAHB), followed by the neutralization of -OH groups by H^+ released from functionalized biochar surface; in addition, π - π electron-acceptor-acceptor (EAA) interaction played an important role.

Competitive sorption affinity of sulfonamides and chloramphenicol antibiotics toward functionalized biochar for water and wastewater treatment:

Competitive sorption of sulfamethazine (SMT), sulfamethoxazole (SMX), sulfathiazole (STZ) and chloramphenicol toward functionalized biochar (fBC) was highly pH dependent with maximum sorption at pH \sim 4.0–4.25. The Langmuir and Freundlich models well represented equilibrium data in the order $\text{STZ} > \text{SMX} > \text{CP} > \text{SMT}$. Kinetics data were slightly better fitted by the pseudo-second-order model than pseudo first-order and intra-particle-diffusion models. Maximum sorptive interactions occurred at pH 4.0–4.25 through H-bonds formations for neutral sulfonamides species and negative charge assisted H-bond (CAHB) formation for CP, in addition to π - π electron-donor-acceptor (EDA) interactions. EDA was the main mechanism for the sorption of positive sulfonamides species and CP at pH < 2.0 . Sorption of negative sulfonamides species and CP at pH > 7.0 was regulated by H-bond formation and proton exchange with water by forming CAHB, respectively. The results suggested fBC to be highly efficient in removing antibiotics mixture.

Chloramphenicol interaction with functionalized biochar in water: sorptive mechanism, molecular imprinting effect and repeatable application:

Biochar and functionalized biochar (fBC-1 and fBC-2) were prepared and applied to remove antibiotic chloramphenicol from deionized water, lake water and synthetic wastewater. Results showed that chloramphenicol removal on biochar was pH dependent and maximum sorption occurred at pH 4.0–4.5. The sorption data of chloramphenicol fitted better with the Langmuir isotherm model than the Freundlich isotherm model with the maximum Langmuir sorption capacity of $233 \mu\text{M g}^{-1}$ using fBC-2. Chloramphenicol sorption on fBC-2 followed the trend: deionized water $>$ lake water $>$ synthetic wastewater. The presence of humic acid decreased the sorption distribution

coefficient (K_d) while the presence of low ionic strength and soil in solution increased K_d value significantly. The mechanism of sorption on fBC mainly involved electron-donor-acceptor (EDA) interactions at $\text{pH} < 2.0$; formation of charge-assisted hydrogen bond (CAHB) and hydrogen bonds in addition to EDA in the $\text{pH} 4.0\text{--}4.5$; and CAHB and EDA interactions at $\text{pH} > 7.0$. Additionally, solvent and thermal regeneration of fBC-2 for repeatable applications showed excellent sorption of chloramphenicol under the same condition, due to the creation of a molecular imprinting effect in fBC-2. Consequently, fBC-2 can be applied with excellent reusability properties to remove chloramphenicol and other similar organic contaminants.

Nano-Fe⁰ immobilized onto functionalized biochar gaining excellent stability during sorption and reduction of chloramphenicol via transforming to reusable magnetic composite:

The widely used nano-sized zero-valent iron (nZVI or nFe^0) particles and their composite material lose reductive nature during application, and the stability of transformed composite material for repeatable application is not addressed to date. To shed light on this, nZVI was synthesized from scrap material and immobilized on functionalized biochar (fBC) to prepare nZVI-fBC composite. Comparative study between nZVI and nZVI-fBC composite on the removal of chlorinated antibiotic chloramphenicol from different water types was conducted. The results suggested that nZVI was solely responsible for reduction of chloramphenicol. Whereas nZVI-fBC could be applied once, within a few hours, for the reduction of chloramphenicol (29–32.5%) and subsequently sorption (67.5–70.5%) by transforming to a fully magnetic composite ($\text{nFe}_3\text{O}_4\text{-fBC}$) gaining stability with synergistic sorption performance. In both cases, two reduction by-products were identified namely 2-chloro-N-[1,3-dihydroxy-1-(4-aminophenyl)propan-2-yl]acetamide (m/z 257) and dechlorinated N-[1,3-dihydroxy-1-(4-aminophenyl)propan-2-yl]acetamide (m/z 223). The complete removal of $3.1\ \mu\text{M L}^{-1}$ of chloramphenicol in different water was faster by nZVI-fBC ($\sim 12\text{--}15\ \text{h}$) than by stable $\text{nFe}_3\text{O}_4\text{-fBC}$ composite ($\sim 18\ \text{h}$). Both nZVI-fBC and $\text{nFe}_3\text{O}_4\text{-fBC}$ composites removed chloramphenicol in the order: deionized water > lake water > synthetic wastewater. $\text{nFe}_3\text{O}_4\text{-fBC}$ showed excellent reusability after regeneration, with the regenerated $\text{nFe}_3\text{O}_4\text{-fBC}$ composite (after 6 cycles of application) showing significant performance for methylene blue

removal ($\sim 287 \text{ mg g}^{-1}$). Therefore, the transformed nFe_3O_4 -fBC composite is a promising and reusable sorbent for the efficient removal of organic contaminants.

Sorptive removal of phenolic endocrine disruptors by functionalized biochar: Competitive interaction mechanism, removal efficacy and application in wastewater:

Sorptive removal of six phenolic endocrine disrupting chemicals (EDCs) estrone (E1), 17β -estradiol (E2), estriol (E3), 17α -ethynylestradiol (EE2), bisphenol A (BPA) and 4-*tert*-butylphenol (4*t*BP) by functionalized biochar (fBC-2) through competitive interactions was investigated. EDC sorption was pH dependent with the maximum sorption at pH 3.0–3.5 due to hydrogen bonds and π - π interactions as the principal sorptive mechanism. Sorption isotherm of the EDCs was fitted to the Langmuir model. Sorption capacities and distribution coefficient values followed the order $\text{E1} > \text{E2} \geq \text{EE2} > \text{BPA} > 4\text{tBP} > \text{E3}$. The findings suggested that EDC sorption occurred mainly through pseudo-second order and external mass transfer diffusion processes, by forming H-bonds along with π - π electron-donor–acceptor (EDA) interactions at different pH. The complete removal of $\sim 500 \mu\text{g L}^{-1}$ of each EDC from different water decreased in the order: deionised water > membrane bioreactor (MBR) sewage effluent > synthetic wastewater. The presence of sodium lauryl sulphonate and acacia gum in synthetic wastewater significantly suppressed sorption affinity of EDCs by 38–50%, hence requiring more fBC to maintain removal efficacy.

Sorption of Hydrophobic Organic Contaminants on Functionalized Biochar: Protagonist Role of π - π Electron-Donor-Acceptor Interactions and Hydrogen Bonds:

Sorption of five potent endocrine disruptors as representative hydrophobic organic contaminants (HOCs) namely estrone (E1), 17β -estradiol (E2), estriol (E3), 17α -ethynylestradiol (EE2) and bisphenol A (BPA) on functionalized biochar (fBC-2) was systematically examined, with a particular focus on the importance of π -electron-donor (phenanthrene: PHEN) and π -electron-acceptors (1,3-dinitrobenzene: DNB, *p*-amino benzoic acid: PABA) on sorption. Experimental results suggested that hydrogen-bond formations and π - π -electron-donor-acceptor (EDA) interactions were the dominant sorption mechanisms. The sorption of HOCs followed the order of $\text{E1} > \text{E2} > \text{EE2} > \text{E3} > \text{BPA}$ based on the Freundlich and Polanyi-Mane-models. The comparison of adsorption coefficient (K_d) normalized against

hexadecane-water partition coefficient (K_{HW}) between HOCs and PHEN indicated strong π - π -EDA interactions. π - π interactions among DNB, PHEN and HOCs in methanol- d_4 were verified by the observed upfield frequency shifts using proton nuclear magnetic resonance (^1H NMR) which identified the specific direction of π - π interactions. UV-vis spectra showed charge-transfer bands for π -donors (PHEN and HOCs) with the model π -acceptor (DNB) also demonstrating the role of π - π EDA interactions. The role of π -electron-donor and π -electron-acceptor domains in fBC was identified at different solution pH. Therefore, π - π EDA interaction together with hydrogen-bond formation were the key mechanism responsible for sorptive removal of HOCs.