UNIVERSITY OF TECHNOLOGY SYDNEY

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

By
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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.

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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 ^{1}H 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

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 walledcarbon nanotubes

PCPs = Personal care products

AGRs = Antibiotic resistant genes

ECs = Emerging contaminants

Kow = Octanol–water partition coefficient

BC = Biochar

AC = Activated carbon

SEM = Scanning electron microscope

EDS = Energy dispervise 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 mas

M_{vm} = Weight of volatime matter

M_{fc} = Fraction of fixed carbon

M_{ash} = Weight of ash

Na_2CO_3= Sodium carbonate

CH_3OH =Methanol

C_2H_5OH= Ethanol

$NaHCO_3$ = Sodium bicharbonate

KCl = Potassium chloride

NaCl = Sodium chloride

HA = Humic acid

R^- = Alkyel group

$AlCl_3$ = Aluminium chloride

CH_3-CO-CH_3 = Acetone

C=C = Carbon-carbon double bonds

K_2HPO_4 = Potassium biphosphote

$MgSO_4$ = 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 = Carbodox

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

TiO_2 = Titanium dioxide

COD = Chemical oxygen deman

PPCPs = Pharmaceutical personal care products

-OH= Hydroxyl group

-COOH = Carboxylic group

$-NH_2$ = 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

$LC\text{-}MS_{(Qtof)}$ = Triple quad liquid chromatography-mass spectroscopy

ESI = Electrospray ionisation

PTFE = Poly tetraflouro ethylene

MP-AES = Microwave plasma-atomic emission spectroscopy

IC = Ion chromatography

EAA = Electon acceptor-acceptor

ΔpH = pH change

LOD = Limit of detection

CMs = Carbonaceous materials

HOCs = Hydrophobic organic contaminants

^{1}H NMR = Proton nuclear magnatic resonance spectroscopy

δ = Chemical shifts in NMR

PMM = Polanyi-Mane Model

Cs = Solubility of compound

S_v = Sorbed volumn

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

LIST OF TABLES

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-Fe^0 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.

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(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.

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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-Fe^0 immobilized onto functionalized biochar gaining excellent stability during sorption and reduction of chloramphenicol via transforming to reusable magnetic composite". July 26-27, 2018. 6^{th} 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 biorchar, functionlaized 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 ^{0}C via pyrolysis process and then modified using *o*H_3PO_4 to produce functionalized biochar (fBC) at 600 ^{0}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 antiobiotics 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 π^+-π 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 ∼4.0–4.25. The Langmuir and Freundlich models well represented equilibrium data in the order STZ > SMX > CP > 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 $\mu M\ g^{-1}$ 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 pH < 2.0; formation of charge-assisted hydrogen bond (CAHB) and hydrogen bonds in addition to EDA in the pH 4.0–4.5; and CAHB and EDA interactions at 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 (nFe_3O_4-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 μM L^{-1} of chloramphenicol in different water was faster by nZVI-fBC (∼12–15 h) than by stable nFe_3O_4-fBC composite (∼18 h). Both nZVI-fBC and nFe_3O_4-fBC composites removed chloramphenicol in the order: deionized water > lake water > synthetic wastewater. nFe_3O_4-fBC showed excellent reusability after regeneration, with the regenerated nFe_3O_4-fBC composite (after 6 cycles of application) showing significant performance for methylene blue

removal (~287 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 E1 > E2 ≥ EE2 > BPA > 4*t*BP > 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 ~500 μg 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), 17*β*-estradiol (E2), estriol (E3), 17*α*-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 E1 > E2 > EE2 > E3 > 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 (^{1}H 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.