



**PLASMA MODIFIED STEEL PROCESSING
BY-PRODUCT FOR REMOVING HEAVY
METALS AND ANTIBIOTICS FROM WATER**

By

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A dissertation

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CERTIFICATE OF ORIGINAL AUTHORSHIP

I certify that the work in this thesis has not previously been submitted 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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TABLE OF CONTENTS

CERTIFICATE OF ORIGINAL AUTHORSHIP.....	ii
ACKNOWLEDGMENT.....	iii
DEDICATION.....	iv
TABLE OF CONTENTS.....	v
NOMENCLATURES.....	xiv
ABBREVIATIONS.....	xvii
LIST OF TABLES.....	xviii
LIST OF FIGURES.....	xxi
LIST OF RESEARCH OUTCOMES.....	xxvii
PhD DISSERTATION ABSTRACT.....	xxix
CHAPTER 1 INTRODUCTION.....	1
1.1. Problem statement.....	2
1.1.1. Heavy metals and antibiotics pollution in water and health risk.....	2
1.1.2. Removal technologies of heavy metals and antibiotics from water.....	3
1.1.3. Adsorption of heavy metals and antibiotics by steel shavings.....	4
1.2. Research hypotheses.....	6
1.3. Objectives.....	6
1.4. Research significance.....	7
1.5. Thesis outline.....	8
CHAPTER 2 LITERATURE REVIEW.....	11
2.1. Introduction.....	12
2.2. Heavy metal and antibiotics pollution in water.....	12
2.2.1. Heavy metals pollution in water.....	12

A. Definition, characteristics.....	12
B. Sources and occurrence of HMs in the environment	13
C. Adverse effects of the HMs pollution	14
D. HMs relevant regulations	15
2.2.2. Antibiotics pollution in water.....	15
A. Definition, characteristics.....	15
B. Sources and occurrence of ABs in the environment	16
C. Adverse effects of the ABs pollution	21
D. ABs relevant regulations	22
2.3. Technologies for the removal of heavy metals and antibiotics from water	
.....	23
2.3.1. Heavy metals removal technologies	23
A. Chemical precipitation	24
B. Ion exchange	24
C. Adsorption	25
D. Membrane filtration	25
E. Coagulation-flocculation	26
F. Flotation	26
G. Electrochemical	27
H. Electrodialysis.....	27
K. Photocatalysis	28
2.3.2. Antibiotics removal technologies	28
A. Conventional methods.....	30
B. Oxidation and advanced oxidation processes	30

C. Adsorption processes	34
D. Membrane processes	34
E. Combined processes.....	36
2.3.3. Adsorption of HMs and ABs using typical low cost materials	36
A. Natural minerals	37
B. Agricultural waste and by-products.....	42
C. Industrial waste and by-products.....	51
2.4. Adsorption of HMs and ABs using magnetic materials (iron-based adsorbents).....	54
2.4.1. Introduction.....	54
2.4.2. Uptake mechanism of HMs and ABs from water by iron-based adsorbents.....	56
A. Removal pathway of HMs	56
B. ABs abatement mechanism.....	57
2.4.3. Application of iron adsorbents for removing heavy metals from aqueous solution	57
2.4.4. Application of iron adsorbents for removing antibiotics from aqueous solution.....	58
2.4.5. Steel shavings as a novel adsorbent	63
2.5. Gas plasma for modifying iron materials.....	64
2.5.1. Introduction.....	64
2.5.2. Employed gas in plasma modification	66
2.5.3. The usage of gas plasma for adsorbent modification.....	66
2.6. Conclusion and research gap	67

2.6.1. Main findings from literature review.....	67
2.6.2. Research gaps.....	70
CHAPTER 3 MATERIALS AND METHODS.....	72
3.1. Materials.....	73
3.1.1. Steel shavings.....	73
3.1.2. Solutions of heavy metals.....	73
3.1.3. Solutions of antibiotics.....	74
3.2. Methods.....	74
3.2.1. Preparation of adsorbents.....	74
A. Raw steel shavings.....	75
B. Plasma modified material.....	76
C. Comparison with a commercial iron material.....	77
3.2.2. Characterization methods.....	78
A. SEM-EDS.....	79
B. XRD.....	79
C. XPS.....	79
D. BET.....	80
E. Zeta potential and particle size distribution.....	80
F. FTIR.....	81
3.2.3. Development of adsorbents from steel shavings.....	82
A. Particle size.....	82
B. Employed gas in plasma modification.....	82
3.2.4. Batch adsorption experimental set-up for removing HMs.....	82
A. Affecting factors on HMs adsorption from aqueous solutions.....	82

B. Isotherms and kinetics models of HMs adsorption	84
C. Competitive adsorption of HMs on raw and modified StS	85
D. Desorption and regeneration	87
3.2.5. Batch adsorption experimental set-up for removing antibiotics.....	87
A. Affecting factors on antibiotics adsorption from aqueous solutions...	87
B. Isotherms and kinetics models of antibiotics adsorption	89
C. Competitive adsorption of ABs on raw and modified StS.....	90
D. Desorption and regeneration	91
3.2.6. Semi-pilot scale experimental set up for removing HMs and ABs from synthesized wastewater.....	92
A. Selecting the treatment designs for HMs and ABs removal.....	92
B. A column design for HMs removal by nitrogen plasma modified steel shavings	97
C. A column design for ABs removal by nitrogen plasma modified steel shavings	100
3.2.7. Heavy metals analysis method.....	101
3.2.8. Analytical method of the antibiotic concentrations	102
3.2.9. Statistical analysis	102
CHAPTER 4 DEVELOPMENT OF ADSORBENTS FROM STEEL SHAVINGS FOR HEAVY METALS AND ANTIBIOTICS REMOVAL.....	104
4.1. Introduction.....	105
4.2. Effects of particle size, employed gas to adsorptive removal of HMs...	105
4.2.1. Particle size.....	106
4.2.2. Employed gas in plasma modification	106

4.3. Effects of particle size, employed gas to adsorptive removal of ABs ...	107
4.3.1. Particle size	107
4.3.2. Employed gas in plasma modification.....	108
4.4. Characterization of adsorbents	109
4.4.1. Surface morphology.....	110
4.4.2. Elementary composition	110
4.4.3. XRD spectrums	113
4.4.4. BET.....	114
4.4.5. XPS	115
4.4.6. FTIR.....	118
4.4.7. Zeta potential.....	118
4.4.8. Particle size distribution.....	119
4.5. Conclusion.....	121
CHAPTER 5 RAW AND PLASMA MODIFIED STEEL SHAVINGS FOR REMOVING HEAVY METALS FROM AQUEOUS SOLUTION: A BATCH STUDY.....	124
5.1. Introduction	125
5.2. Affecting factors to removal efficiencies	126
5.2.1. Solution pH	126
5.2.2. Adsorbent dosage.....	129
5.2.3. Temperature/thermodynamic	130
5.3. Modeling of adsorption isotherm and kinetics.....	132
5.3.1. Adsorption isotherm	132
5.3.2. Adsorption kinetics.....	135

5.4. Competitive adsorption of multi-metals solutions on the adsorbents...	138
5.4.1. Competitive adsorption isotherms	138
5.4.2. Competitive adsorption kinetics	140
5.5. Uptake mechanisms of heavy metals by steel shavings	143
5.6. Desorption and regeneration of the HMs loaded adsorbents	144
5.6.1. Selecting desorption reagent.....	144
5.6.2. Adsorption-desorption cycles	145
5.7. Conclusion	147
CHAPTER 6 RAW AND PLASMA MODIFIED STEEL SHAVINGS FOR REMOVING ANTIBIOTICS FROM AQUEOUS SOLUTION: A BATCH STUDY .	149
.....	149
6.1. Introduction.....	150
6.2. Affecting factors to removal efficiencies.....	153
6.2.1. pH.....	153
6.2.2. Adsorbent dosage	156
6.2.3. Temperature/thermodynamic.....	158
6.3. Modeling of adsorption isotherms and kinetics.....	159
6.3.1. Adsorption isotherms	159
6.3.2. Adsorption kinetics	160
6.4. Competitive adsorption of multi-antibiotics solution on the adsorbents....	165
.....	165
6.4.1. Competitive adsorption isotherms	165
6.4.2. Competitive adsorption kinetics	165
6.5. Desorption and regeneration of the ABs loaded adsorbents.....	170

6.5.1. Selecting desorption reagent	170
6.5.2. Adsorption-desorption cycles	171
6.6. Proposed mechanisms of ABs removal by steel shavings	173
6.7. Conclusions	180
CHAPTER 7 DEVELOPMENT OF A SEMI-PILOT TREATMENT DESIGN FOR REMOVING HMs AND ABs USING NITROGEN PLASMA MODIFIED STEEL SHAVINGS	182
7.1. Introduction	183
7.2. Selecting treatment unit.....	185
7.2.1. Removal of HMs by different treatment designs	185
7.2.2. Removal of ABs by different treatment designs	188
7.3. HMs removal in the column design	189
7.3.1. Affecting factors	189
A. Flow rate.....	189
B. Bed height.....	192
7.3.2. Breakthrough curves modeling.....	195
A. Adams–Bohart model.....	195
B. Thomas model.....	196
C. Yoon–Nelson model.....	196
D. BDST model	198
7.4. ABs removal in the column design	200
7.4.1. Affecting factors	200
A. Flow rate.....	200
B. Bed height.....	202

7.4.2. Breakthrough curves modeling.....	204
A. Adams–Bohart model.....	204
B. Thomas model.....	205
C. Yoon–Nelson model.....	205
D. BDST model.....	207
7.5. Conclusion.....	208
CHAPTER 8 CONCLUSIONS AND RECOMMENDATIONS.....	210
8.1. Overall conclusion.....	211
8.1.1. Major findings.....	211
8.1.2. Contributions to the field.....	214
8.2. Recommendations for future works.....	215
REFERENCES.....	216
APPENDICES.....	243
Appendix A - SEM images.....	244
Appendix B - EDS spectrums.....	246

NOMENCLATURES

Symbol	Description	Unit
Å	Angstrom	
Ar	Argon	
As	Arsenic	
C_{ad}	The different in the adsorbate concentration at the initial time and time t caused by adsorption	mg/L
C_b	Adsorbate concentration at breakthrough time	mg/L or $\mu\text{g/L}$
Cd^{2+}	Cadmium	
C_e	Concentration at equilibrium	mg/L
C_o	Initial concentration	mg/L
C_b	Desired effluent concentration of BDST model	mg/L or $\mu\text{g/L}$
Cr^{3+}	Chromium	
C_t	Concentration of adsorbate at time (t)	mg/L or $\mu\text{g/L}$
Cu^{2+}	Copper	mg/L
CH_3COOH	Acetic acid	
cm^3/g	Cubic centimeter per gram	
CP	Chloramphenicol	
F	Linear velocity	cm/min
Fe_2O_3	Iron (III) oxide	
g/L	Gram per liter	
H_2	Hydrogen	
HCL	Hydrochloric acid	
HNO_3	Nitric acid	
HRT	Hydraulic retention time	
H_2SO_4	Sulfuric acid	
k_{1p}	Equilibrium rate constant of PFO	1/min
k_{2p}	Equilibrium rate constant of PSO	1/min
k_{AB}	Adams-Bohart kinetic constant	
k_b	Rate constant of BDST model	L/(mg.h)
k_F	Freundlich isotherm constant	

k_i	Equilibrium rate constant of IDM	mg/g.min or $\mu\text{g/g.min}$
k_L	Langmuir isotherm constant	
k_{Th}	Thomas rate constant	
k_{YN}	Yoon-Nelson rate velocity constant	
L/h	Liter per hour	
M	The amount of $M_3\text{-pIN}_2$ packed in the column	g
mg/L	Milligram per liter	
min	Minute	
mL/min	Milliliter per minute	
m^2/g	Square meter per gram	
m^3/day	Cubic meter per day	
mmol/g	milimol per gram	
n	Freundlich constant	
N_0	Saturation adsorbate concentration	
N_2	Nitrogen	
NaOH	Sodium hydroxide	
Ni	Nikel	
O_2	Oxygen	
Pb^{2+}	Lead	
ppm	Part per million	
Q	Volumetric flow rate	mL/min
q_0	Column adsorption capacity	mg/g or $\mu\text{g/g}$
q_b	Amount of adsorbate adsorbed per unit of dry weight of adsorbent at breakthrough time	mg/g or $\mu\text{g/g}$
q_e	Adsorption capacity at equilibrium	mg/g or $\mu\text{g/g}$
$q_{exp.}$	Experimental adsorption capacity	mg/g or $\mu\text{g/g}$
q_{max}	Langmuir maximum adsorption capacity of the adsorbent	mg/g or $\mu\text{g/g}$
q_s	Amount of adsorbate adsorbed per unit of dry weight of adsorbent at saturation/exhaustion time	mg/g or $\mu\text{g/g}$

q_t	Amount of adsorbate adsorbed per unit of dry weight of adsorbent at time t	mg/g or $\mu\text{g/g}$
r^2	Correlation constant	
R_b	Removal percentage of adsorbate at breakthrough time	%
R_s	Removal percentage of adsorbate at saturation/exhaustion time	%
RF	Radio frequency	
rpm	Revolutions per minute	
SCCM	Standard cubic centimeters per minute	
SMT	Sulfamethazine	
t	Service time of column	
TC	Tetracycline	
V	Volume	
V_b	Volume of water treated at breakthrough time	L
Z	Bed height	cm
Zn^{2+}	Zinc	
ΔG	Change in Gibbs free energy	J/mol
ΔH	Change in enthalpy	J/mol
ΔS	Change in entropy	J/mol/K
μm	Micro meter	
τ	The time required for 50% adsorbate breakthrough	min

ABBREVIATIONS

Symbol	Description
HMs	Heavy metals
ABs	Antibiotics
StS	Steel shavings
BDST	Bed depth service time
M ₁ , M ₂ , M ₃ , M _x -pN ₂ , M _x -pAr, M _x pO ₂ , M _x pH ₂	Steel shavings with particles sizes 0-75; 75-150 and 150-425µm; modified steel shavings with plasma in N ₂ , Ar, O ₂ and H ₂ gases
RO	Reverse osmosis
SEM-EDS	Scanning electron microscopy - energy-dispersive X-ray spectroscopy
SEM- SUPRA 55VP	Scanning electron microscopy SUPRA 55V
XRD	Powder X-ray diffraction
XPS	X-ray photoelectron spectroscopy
BET	Brunauer emmett teller
FTIR	Fourier transform infrared spectroscopy
MP-AES	Microwave plasma-atomic emission spectrometry
HPLC	High-performance liquid chromatography

LIST OF TABLES

Table 2.1 Chemical structure and properties of the study antibiotics (Ahmed et al., 2015; Adams et al., 2002; Homem and Santos, 2011; Xia et al., 2014; Pubchem, 2017).....	18
Table 2.2 Common methods for HMs removal from aqueous solution (Rahimi et al., 2015; Nguyen et al., 2013; Atta et al., 2015; Simate and Ndlovu, 2015).....	23
Table 2.3 Common methods for removing ABs from aqueous solution (Homem and Santos, 2011).....	29
Table 2.4 Prices of low-cost adsorbents (Bailey et al., 1999; Bhattacharyya and Gupta, 2008; Rafatullah et al., 2010; Olivella et al., 2012; Tran et al., 2015).....	36
Table 2.5 Heavy metals of adsorption capacity (mg/g) of biosorbents	47
Table 2.6 ABs adsorption capacities of raw/modified biosorbents	50
Table 2.7 Removal mechanisms of metal ions with Fe ⁰ (O'Carroll et al., 2013)	56
Table 2.8 Synthesis/preparation and characterization of iron adsorbents and HMs adsorption isotherms, kinetics, experimental conditions.....	60
Table 2.9 Synthesis/preparation and characterization of iron adsorbents and ABs adsorption isotherms, kinetics, experimental conditions.....	62
Table 3.1 Summary of adsorbents preparation steps	75
Table 3.2 Summary of adsorbents characterization studies.....	78
Table 3.3 Kinetic and isotherm models of HMs adsorption on StS	84
Table 3.4 Kinetic and isotherm models of antibiotics adsorption on StS.....	89
Table 3.5 The elution program applied in the antibiotics analysis using HPLC.....	103
Table 4.1 Removal efficiencies of HMs and ABs on different sizes of raw and plasma modified StS.....	109

Table 4.2 Elementary composition of different kinds of adsorbents	113
Table 4.3 Summary comparison in characterisations of raw and plasma modified StS with N ₂	115
Table 4.4 Binding energy, chemical state, relative peak area and atomic percentage of peaks in narrow scan of C1s region of M ₃ -pIN ₂ scan of O1s region Fe2p3/2 region	117
Table 5.1 Thermodynamic parameters for HMs adsorption on M ₃ and M ₃ -pIN ₂	131
Table 5.2 Isotherm and kinetic parameters using the non-linear regression method for HMs adsorption onto raw and N ₂ treated plasma M ₃ particles.....	137
Table 5.3 Isotherm and kinetic parameters using the non-linear regression method for competitive HMs adsorption onto raw and N ₂ treated plasma M ₃ particles.....	142
Table 6.1 Thermodynamic parameters for ABs adsorption on M ₃ and M ₃ -pIN ₂	159
Table 6.2 Isotherm and kinetic parameters using the non-linear regression method for antibiotics adsorption onto M ₃ and M ₃ -pIN ₂	164
Table 6.3 Isotherm and kinetic parameters using the non-linear regression method for competitive adsorption kinetics and isotherms of ABs on M ₃ and M ₃ -pIN ₂	169
Table 6.4 Binding energy, chemical state, relative peak area and atomic percentage of peaks in narrow scan of C1s region of the adsorbent before and after adsorption	176
Table 6.5 Binding energy, chemical state, relative peak area and atomic percentage of peaks in narrow scan of O1s region of the adsorbent before and after adsorption	178

Table 6.6 Binding energy, chemical state, relative peak area and atomic percentage of peaks in narrow scan of Fe2p3/2 region of the adsorbent before and after adsorption.....	180
Table 7.1 Breakthrough curve parameters for HMs adsorption onto M ₃ -pIN ₂ at different operating conditions	194
Table 7.2 Adams–Bohart, Thomas and Yoon-Nelson model constants for HMs adsorption onto M ₃ -pIN ₂ column	197
Table 7.3 BDST model constants for HMs adsorption onto M ₃ -pIN ₂	200
Table 7.4 Breakthrough curve parameters for ABs adsorption onto M ₃ -pIN ₂ at different operating conditions	203
Table 7.5 Adams–Bohart, Thomas and Yoon-Nelson model constants for ABs adsorption onto M ₃ -pIN ₂ column	206
Table 7.6 BDST model constants for ABs adsorption onto M ₃ -pIN ₂	207

LIST OF FIGURES

Figure 2.1 Sources of antibiotics in the environment (Adapted from Homem and Santos, 2011).....	20
Figure 2.2 symptom of aplastic anemia (Pinterest, 2017).....	22
Figure 2.3 Average chemical composition of some typical lignocellulose (% dry weight) (Tran et al., 2015).....	43
Figure 2.4 Molecular structure of chitosan (adapted from Celis et al., 2012).....	46
Figure 2.5 Schematic representation of the magnetic adsorbents separation (Adapted from Oliveira et al., 2004b).....	55
Figure 2.6 The generation of steel shavings from a steel processing machine (Dreamstime, 2017).....	63
Figure 2.7 diagram of multi-step process in plasma surface cleaning (Belkind and Gershman, 2008)	65
Figure 2.8 Scheme of plasma cleaning with oxygen (Plasma electronic, 2017).....	65
Figure 3.1 Steel shavings at the steel processing laboratory, UTS.....	73
Figure 3.2 Flowchart for the preparation of adsorbents from StS	74
Figure 3.3 Images of steel shavings: (A) after washing and drying; (B) after grinding by a pug and ring crusher	75
Figure 3.4 Chamber window of plasma equipment: (A) before; (B) in action	76
Figure 3.5 Radio frequency (RF) plasma configuration with nitrogen for the surface treatment of StS	77
Figure 3.6 SEM-EDS instruments: (A) Zeiss Evo SEM and (B) Supra 55VP SEM.	79
Figure 3.7 XRD and XPS instruments: (A) Seimens D5000 X-ray Diffractometer and (B)Thermo Scientific ESCALAB 250Xi.....	80

Figure 3.8 BET system instruments: (A) micrometrics tristar III system, and (B) Micrometrics VacPrep 061 Sample Degas	81
Figure 3.9 Zeta potential and FTIR instruments: (A) Nano-ZS Zeta-sizer (Malvern, Model: ZEN3600) and (B) MIRacle 10, Shimadzu	82
Figure 3.10 Schematic diagram of treatment system using nitrogen plasma modified steel shavings design 1	94
Figure 3.11 Schematic diagram of treatment system using nitrogen plasma modified StS design 2.....	95
Figure 3.12 Schematic diagram of treatment system using nitrogen plasma modified StS design 3.....	96
Figure 3.13 MP-AES and HPLC instruments: (A) 4100-MP-AES, Agilent Technologies and (B) Jasco HPLC-UV.....	102
Figure 3.14 (A) Chromatograph of SMT, CP and TC by HPLC- UV and (B) Analytical standard lines of SMT, TC and CP.....	103
Figure 4.1 SEM results of raw and nitrogen plasma modified adsorbent A: M ₃ ; B: M ₃ -pN ₂ (M ₃ : StS<75 μm; M ₃ -pN ₂ : StS<75 μm was plasma modified with N ₂)...	110
Figure 4.2 EDS results of raw and nitrogen plasma modified adsorbents (A) M ₃ ; (B) M ₃ -pN ₂ (M ₃ : StS<75 μm; M ₃ -pN ₂ : StS<75 μm was plasma modified with N ₂)...	112
Figure 4.3 XRD patterns of adsorbents: (A) M ₃ ; (B) M ₃ -pN ₂ ; (C) M ₃ -pAr (M ₃ : StS<75 μm; M ₃ -pN ₂ , M ₃ -pAr: StS<75 μm was plasma modified with N ₂ , Ar)....	114
Figure 4.4 The XPS spectra of N ₂ plasma modified steel shavings (M ₃ -pN ₂): (A) full survey; (B) narrow scan of C1s region; (C) narrow scan of O1s region; (D) narrow scan of Fe2p region	117
Figure 4.5 FTIR spectra of M ₃ and M ₃ -pN ₂	118

Figure 4.6 Zeta potential as a function of pH solution: (A) M ₃ ; (B) M ₃ -pIN ₂	121
Figure 4.7 Particle size distribution of grinded steel shavings.....	121
Figure 5.1 Effect of factors to removal efficiency of metal ions: (A) pH-M ₃ ; (B) dose-M ₃ ; (C) pH-M ₃ -pIN ₂ ; (D) dose-M ₃ -pIN ₂	130
Figure 5.2 Adsorption isotherm of HMs on (A) M ₃ and (B) M ₃ -pIN ₂ (initial concentration 0-500 mg/L single metal ion; pH 5, dose 5g/L; at 130 rpm; at 25 ⁰ C; for 24 hours).....	134
Figure 5.3 Adsorption kinetic models of HMs on (A) M ₃ and (B) M ₃ -pIN ₂ (initial concentration: 100 mg/L single metal ion; no pH adjustment; dose 5g/L; at 130 rpm shaking speed; at room temperature).....	136
Figure 5.4 Competitive adsorption isotherms of HMs on (A) M ₃ and (B) M ₃ -pIN ₂ (total initial concentration 0-500 mg/L; 0-166.67 mg/L single metal ion; pH 5; dose 5g/L; at 130 rpm; at 25 ⁰ C; for 24 hours).....	139
Figure 5.5 Competitive adsorption kinetics of HMs on (A) M ₃ and (B) M ₃ -pIN ₂ (total initial concentration: 100 mg/L, 20mg/L single metal ion; no pH adjustment; dose 5g/L; at 130 rpm shaking speed; at room temperature).....	141
Figure 5.6 Removal mechanisms of metals and chlorinated compounds with Fe ⁰ (O'Carroll et al. 2013).....	143
Figure 5.7 Regeneration of M ₃ -pIN ₂ after adsorption of Pb ²⁺ , Cu ²⁺ , Cd ²⁺ , Cr ³⁺ and Zn ²⁺	145
Figure 5.8 Adsorption and desorption cycles for HMs on M ₃ -pIN ₂	146
Figure 6.1 Effect of pH on adsorption of the antibiotics on (A) M ₃ ; (B) M ₃ -pIN ₂ ..	156
Figure 6.2 Effect of dose on antibiotics adsorption efficiency using (A) M ₃ ; (B) M ₃ -pIN ₂	157

Figure 6.3 Langmuir and Freundlich adsorption of SMT, TC, CP on M ₃ and M ₃ -pIN ₂ (initial concentration: 100 - 20000 µg/L; pH 3 was adjusted for SMT, CP; pH 5 for TC; adsorbent dose of 2g/L; at 25 ⁰ C).....	162
Figure 6.4 Sorption kinetics of SMT, TC and CP on M ₃ and M ₃ -pIN ₂ (initial concentration: 1000 µg/L; no pH adjustment; adsorbent dose of 2g/L; at room temperature).....	163
Figure 6.5 Competitive adsorption isotherm of ABs on M ₃ and M ₃ -pIN ₂ (total multi-antibiotics initial concentration: 0 - 20000 µg/L, each solute concentration: 0-6666.67 µg/L; pH 3; adsorbent dose of 2g/L; at 25 ⁰ C).....	167
Figure 6.6 Competitive adsorption kinetics of ABs on M ₃ and M ₃ -pIN ₂ (total competitive initial concentration: 1000 µg/L, each solute concentration is 333.33 µg/L; no pH adjustment; adsorbent dose of 2g/L; at room temperature).....	168
Figure 6.7 Regeneration of M ₃ -pIN ₂ after adsorption of ABs	171
Figure 6.8 Adsorption and desorption cycles for ABs on M ₃ -pIN ₂ using methanol 0.1N	172
Figure 6.9 FTIR spectrums for M ₃ , M ₃ -pIN ₂ and antibiotics loaded M ₃ -pIN ₂	174
Figure 6.10 Full survey of N ₂ plasma modified steel shavings before and after adsorption.....	175
Figure 6.11 XPS narrow scan of C1s region for M ₃ -pIN ₂ (A) before adsorption and (B) after adsorption	176
Figure 6.12 XPS narrow scan of O1s region for M ₃ -pIN ₂ (A) before adsorption and (B) after adsorption	177
Figure 6.13 XPS narrow scan of Fe2p region for M ₃ -pIN ₂ (A) before adsorption; (B) after adsorption; (C) combined spectrums of before and after adsorption	180

Figure 7.1 Remaining concentrations of HMs in the outlet flow after treatment using nitrogen plasma modified StS ($M_3\text{-plN}_2$) with different designs: (A) Pb^{2+} ; (B) Cu^{2+} ; (C) Cd^{2+} ; (D) Cr^{3+} and (E) Zn^{2+}	187
Figure 7.2 Remaining concentrations of ABs in the outlet flow after semi-pilot scale treatment units using $M_3\text{-plN}_2$: (A) SMT; (B) TC and (C) CP	189
Figure 7.3 Effects of flow rate on the breakthrough curve of HMs adsorption on $M_3\text{-plN}_2$: (A) Pb^{2+} ; (B) Cu^{2+} ; (C) Cd^{2+} ; (D) Cr^{3+} and (E) Zn^{2+} (natural pH, bed height = 35 cm; initial concentrations (C_0) of HMs: Pb^{2+} 5.94; Cu^{2+} 4.74; Cd^{2+} 6.48; Cr^{3+} 6.44 and Zn^{2+} 5.18 mg/L)	191
Figure 7.4 Effects of bed height (Z) on the breakthrough curve of HMs adsorption on $M_3\text{-plN}_2$: (A) Pb^{2+} ; (B) Cu^{2+} ; (C) Cd^{2+} ; (D) Cr^{3+} and (E) Zn^{2+} (natural pH, flow rate = 3.47 L/min; initial concentrations (C_0) of HMs: Pb^{2+} 5.94; Cu^{2+} 4.74; Cd^{2+} 6.48; Cr^{3+} 6.44 and Zn^{2+} 5.18 mg/L)	193
Figure 7.5 BDST model plots for 10% and 90% breakthrough of Pb^{2+} , Cu^{2+} , Cd^{2+} , Cr^{3+} , Zn^{2+} adsorption onto $M_3\text{-plN}_2$ column at different bed heights (natural pH, flow rate = 3.47 L/min; initial concentrations (C_0) of HMs: Pb^{2+} 5.94; Cu^{2+} 4.74; Cd^{2+} 6.48; Cr^{3+} 6.44 and Zn^{2+} 5.18 mg/L)	199
Figure 7.6 Effects of flow rate on the breakthrough curve of ABs adsorption on $M_3\text{-plN}_2$: (A) SMT; (B) TC and (C) CP (natural pH, bed height = 35 cm; initial concentrations (C_0) of ABs: SMT 100.1; TC 97.3 and CP 99.5 $\mu\text{g/L}$).....	201
Figure 7.7 Effects of bed height (Z) on the breakthrough curve of ABs adsorption on $M_3\text{-plN}_2$: (A) SMT; (B) TC and (C) CP (natural pH, flow rate = 3.47 L/min; initial concentrations (C_0) of ABs: SMT 100.1; TC 97.3 and CP 99.5 $\mu\text{g/L}$)	203

Figure 7.8 BDST model plots for 10% and 90% breakthrough of SMT, TC and CP adsorption onto M_3 -pIN₂ column at different bed heights (natural pH, flow rate = 3.47 L/min; initial concentrations (C_0) of ABs: SMT 100.1; TC 97.3 and CP 99.5 $\mu\text{g/L}$)..... 208

LIST OF RESEARCH OUTCOMES

Peer-reviewed journal papers

1. **Tran, V.S.**, Ngo, H.H., Guo, W., Zhang, J., Liang, S., Ton-That, C., Zhang, X., 2015. Typical low cost biosorbents for adsorptive removal of specific organic pollutants from water. *Bioresource technology*, 182, pp.353-363.
2. **Tran, V.S.**, Ngo, H.H., Guo, W., Ton-That, C., Li, J., Li, J., Liu, Y., 2017. Removal of antibiotics (sulfamethazine, tetracycline and chloramphenicol) from aqueous solution by raw and nitrogen plasma modified steel shavings. *Science of The Total Environment*, 601, pp.845-856.
3. **Tran, V.S.**, Guo W.S., Ngo, H.H., Li, J., Liu, Y., Li, J., Ton-That, C., 2017. Enhancement of steel shavings' heavy metal adsorption capacity by a novel plasma modification method. *Journal of Industrial and Engineering Chemistry* (Submitted and under reviewing).

Contribution to scientific forums

1. **Tran, V.S.**, Ngo, H.H., Guo, W.S., Ton-that, C., 2017. Single and competitive adsorption of antibiotics (sulfamethazine, tetracycline and chloramphenicol) onto nitrogen plasma modified steel shavings (oral presentation). The Inaugural International Conference on Green Technologies for Sustainable Water (GTSW). Hanoi, Vietnam, 13-16 October, 2017 (accepted).

Awards

1. 2015 HDR Students publication Award from Faculty of Engineering and Information Technology (FEIT), University of Technology Sydney (UTS) for publishing in high quality Journals.
2. 2014 one-off scholarship from Centre for Technology in Water and Wastewater (CTWW), University of Technology Sydney (UTS).

PhD DISSERTATION ABSTRACT

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Thesis title: Plasma modified steel processing by-product for removing heavy metals and antibiotics from water

School: Civil and Environmental Engineering

Supervisors: Prof. Dr. Huu Hao Ngo (Principal supervisor)
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Abstract:

The presence of heavy metals (HMs) and antibiotics (ABs) in the aquatic environment causes critical problems to human health and the environment. The adsorptive removal of HMs and ABs onto cost-effective adsorbents has a high potential. In this study, adsorbents were prepared from steel shavings (StS), a by-product generated from the steel processing industries. Among adsorbents, nitrogen plasma modified StS ($M_3\text{-pIN}_2$) has highest adsorption capacities of HMs and ABs. Adsorption and co-precipitation were the mechanisms for HMs removal by the adsorbents, while main driving forces for ABs adsorption were hydrogen bonding, electrostatic and non-electrostatic interactions, and redox reaction. Thermodynamic data demonstrated that both adsorption processes of HMs and ABs onto the adsorbents were feasible, spontaneous and endothermic. Solution pH, particle size, adsorbent dose and contact time exerted great influences on the adsorption process. Optimal conditions for the adsorptive removal of HMs were pH 5, adsorbent dose

5g/L, at 25°C. The best removal of sulfamethazine (SMT) and chloramphenicol (CP) was observed at pH 3, while tetracycline (TC) was ultimately removed at pH 5 (with the same adsorbent dose of 2 g/L and at 25°C). The Pseudo-first-order kinetic and Pseudo-second-order kinetic models described the adsorptive kinetics of HMs and ABs very well. The Langmuir maximum single adsorption capacities of Pb^{2+} , Cu^{2+} , Cd^{2+} , Cr^{3+} and Zn^{2+} onto $\text{M}_3\text{-pIN}_2$ were: 27.04, 20.64, 16.87, 14.89 and 18.47 mg/g, respectively. In competitive adsorption of multi-metals solutions, each competitive solute adsorption capacities were approximately 2-fold less than the single adsorption capacities. However, the total of competitive adsorption capacities was higher than those of single solute sorption. Single Langmuir adsorption capacities of SMT, TC and CP onto $\text{M}_3\text{-pIN}_2$ were 2702.55, 2158.36 and 2920.11 $\mu\text{g/g}$, respectively. Adsorption capacities of mixed-ABs onto the adsorbents were nearly 2-fold less than individual adsorption capacities. Furthermore, the metals-loaded $\text{M}_3\text{-pIN}_2$ was well regenerated using sulphuric acid 0.1N after 5 cycles of adsorption-desorption, while the most effective reagent to regenerate ABs-loaded $\text{M}_3\text{-pIN}_2$ was methanol 0.1N solution after 2-3 adsorption-desorption cycles. The semi-pilot scale experiments confirmed that fixed-bed column using $\text{M}_3\text{-pIN}_2$ could efficient abate both HMs and ABs from water with the highest removal efficiencies at a flow rate of 3.47 L/min and bed height of 35 cm. The column adsorption data was well described by The Thomas, Yoon-Nelson and BDST models. Overall, the application of $\text{M}_3\text{-pIN}_2$ for removing HMs and ABs from aqueous solution can provide tremendous benefits in treating water and reducing solid wastes.

Key words: Heavy metals, Antibiotics, Removal, Adsorption, Mechanism, Desorption, regeneration, Industrial waste/by-product, Steel shavings (StS), Gas plasma, Nitrogen plasma modified steel shavings (M₃-pIN₂), Characterization.

Graphical Abstract



