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.

I also certify that the thesis has been written by me. Any help that I have received in my research work and the preparation of the thesis itself has been acknowledged. In addition, I certify that all information sources and literature used are indicated in the thesis.

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DEDICATION

This thesis is deeply dedicated to the following people:

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For their sacrifices, endless love, hard work and inspiration

To my wonderful wife, Thi Thuan Tran
For her constant love, supports and caring

To my lovely daughter and son, Ha Linh & Huy Phong
For bringing joy and hope

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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 µg/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 µg/L
Cr^{3+}	Chromium	
C_t	Concentration of adsorbate at time (t)	mg/L or µg/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 µg/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-plN_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_o	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_o	Column adsorption capacity	mg/g or µg/g
q_b	Amount of adsorbate adsorbed per unit of dry weight of adsorbent at breakthrough time	mg/g or µg/g
q_e	Adsorption capacity at equilibrium	mg/g or µg/g
$q_{exp.}$	Experimental adsorption capacity	mg/g or µg/g
q_{max}	Langmuir maximum adsorption capacity of the adsorbent	mg/g or µg/g
q_s	Amount of adsorbate adsorbed per unit of dry weight of adsorbent at saturation/exhaustion time	mg/g or µg/g

q_t	Amount of adsorbate adsorbed per unit of dry weight of adsorbent at time t	mg/g or µg/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-plN_2, M_x-plAr, $M_x$plO_2, $M_x$plH_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

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LIST OF RESEARCH OUTCOMES

Peer-riewed 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 competive 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

Author: Van Son Tran

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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)

Dr. Wenshan Guo (Alternative supervisor)

Assoc. Prof. Dr. Cuong Ton-that (Co-supervisor)

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-plN_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^{o}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^{o}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 M_3-plN_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 M_3-plN_2 were 2702.55, 2158.36 and 2920.11 µg/g, respectively. Adsorption capacities of mixed-ABs onto the adsorbents were nearly 2-fold less than individual adsorption capacities. Furthermore, the metals-loaded M_3-plN_2 was well regenerated using sulphuric acid 0.1N after 5 cycles of adsorption-desorption, while the most effective reagent to regenerate ABs-loaded M_3-plN_2 was methanol 0.1N solution after 2-3 adsorption-desorption cycles. The semi-pilot scale experiments confirmed that fixed-bed column using M_3-plN_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 M_3-plN_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 (M_3-plN_2), Characterization.

Graphical Abstract