Detoxification of heavy metal ions from aqueous solutions using a novel lignocellulosic multi–metal binding biosorbent

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 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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Thank you

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DEDICATION

To my loveliest love, my most favourite boy in the world;

My dearest ***Darian***

Who spent whole days and nights of this project beside me!

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2. **Abdolali, A.**, Ngo, H.H., Guo, W.S., (2013). Detoxification of heavy metal–bearing effluents on a novel multi–metal binding biosorbent, Accepted article in the 6thInternational Conference on the "Challenges in Environmental Science and Engineering" (CESE–2013), Daegu, Korea, 29th October–2nd November 2013.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF ILLUSTRATIONS

NOMENCLATURES

Symbol	Description	Unit
a	Dose Response model exponent	
A	Column area	cm^2
Å	Angstrom	
a_S	Sips model constants	L/mg
b_L	Langmuir constant	L/mg
C=C–C	Asymmetric stretching aromatic rings	
$C_2H_4O_2S$	Mercapto–acetic acid	
$C_2H_4O_2S$	Thioglycolic acid	
C_2H_6O	Ethanol	
C_3H_6O	Acetone	
$C_6H_8O_7$	Citric acid	
$Ca(OH)_2$	Calcium hydroxide	
$CaCl_2$	Calcium chloride	
CaO	Calcium oxide	
C_{ads}	Adsorbed metal concentration	mg/L
C_b	Breakthrough concentration,	mg/L
$Cd(NO_3)_2{\cdot}4H_2O$	Cadmium nitrate tetrahydrate	
C_e	Effluent metal ion concentration	mg/L
C_{eq}	Equilibrium metal concentration	mg/L
C_f	Equilibrium metal concentrations	mg/L
CF_p	Overall sorption process concentration factor	
CH_2O	Formaldehyde	
CH_2O_2	Formic Acid	
CH_3COOH	Acetic Acid	
CH_3OH	Methanol	
C_i	Initial/ Influent metal concentrations	mg/L
–C–O–C=O	Symmetric stretching of ester groups	
–COOH	Carboxyl groups	
C_p	Eluted metal concentration at t_p	mg/L

Symbol	Description	Unit
CS_2	Carbon disulfide	
$Cu_3(NO)_2{\cdot}3H_2O$	Copper nitrate trihydrate	
D_i	Inner diameter	cm
E	Mean free energy of adsorption calculated by Dubinin–Radushkevich isotherm	kJ/mol
g	gram	
g/L	gram per litre	
H_2O_2	Hydrogen peroxide	
H_2SO_4	Sulphuric acid	
H_3PO_4	Phosphoric acid	
H–C–H	Asymmetric and symmetric stretch	
HCl	Hydrochloric acid	
HFO	Iron(III) oxy–hydroxide	
HNO_3	Nitric acid	
hr	hour(s)	
K	Kelvin	
K_1	The first–order reaction rate equilibrium constant	min^{-1}
K_2	The second–order reaction rate equilibrium constant	$g\ mg^{-1}\ min^{-1}$
K_2MnO_4	Potassium manganate	
k_{BDST}	BDST adsorption rate constant that describes the mass transfer from the liquid to the solid phase	L/mg h
K_F	Freundlich constant	L/g
K_p	Intra–particle diffusion kinetic model constant	$mg\ g^{-1}min^{-0.5}$
K_{RP}	Redlich–Peterson model constants	L/g
K_S	Sips model constants	L/g
k_{Th}	Thomas rate constant	mL/ mg min
k_{Y-N}	Yoon–Nelson proportionality constant	1/min

Symbol	Description	Unit
L	litre	
L	Bed height	cm
$L_{critical}$	Critical bed depth	cm
M	Molarity	mol/L
m	Mass of biosorbent in batch system	g
M	Total mass of the biosorbent in the column	g
m_{total}	Amount of metal ions sent to the column at different time	mg
mg/g	milligram of adsorbate per gram of adsorbent	
$MgCl_2$	Magnesium chloride	
$MgSO_4$	Magnesium sulphate	
min	minute(s)	
mol/g	mol per gram	
n	Freundlich exponent	
Na_2CO_3	Sodium carbonate	
NaCl	Sodium chloride	
$NaHCO_3$	Sodium bicarbonate	
$NaNO_3$	Sodium nitrate	
NaOH	Sodium hydroxide	
N_{BDST}	BDST biosorption capacity	mg/L
NH_4^+	Ammonium	
NH_4OH	Ammonium hydroxide	
$Pb(NO_3)_2$	Lead nitrate	
Q	Volumetric flow rate	mL/min
q_c	Column capacity (mg)	
q_{D-R}	Maximum adsorption capacity for heavy metal ions calculated by Dose Response model	mg/g
q_e	Metal adsorbed at equilibrium	mg/g
$q_{e,d}$	gram of desorbed metal per gram of adsorbent in column	mg/g

Symbol	Description	Unit
$q_{m,L}$	Langmuir maximum metal biosorption capacity	mg/g
q_t	Metal adsorbed at time t	mg/g
q_{Th}	Thomas maximum adsorption capacity for heavy metal ions	mg/g
rpm	round(s) per minute	
t	time	min
t_b	Breakthrough time (C_e/C_i = 10%)	min
t_p	The time when the elution rate reaches the peak	min
t_{sat}	Saturation or exhaustion time (C_e/C_i = 90%)	min
t_{total}	Total flow time	min
v	Solution volume in batch mode	L
v	Superficial velocity or the linear flow velocity of metal solution through the bed	cm/min
$V_{W,b}$	Treated water volume	L
$Zn(NO_3)_2{\cdot}6H_2O$	Zinc nitrate hexahydrate	
$ZnCl_2$	Zinc chloride	
ΔG°	Gibbs free energy change	kJ/mol
ΔH°	Enthalpy change	kJ/mol
ΔS°	Entropy change	kJ/mol K
%E	Elution efficiency	%
%R	Metal removal (%)	%
$[H_3O]^+$	Hydronium	
˚C	Degree Celsius	

ABBREVIATIONS

Symbol	Description
BDST	Bed Depth Service Time
CSTR	Continuous Stirred–Tank Reactor
AER	Adsorbent exhaustion rate in column
ANOVA	Analysis of Variance
AP	Apple peel
AV	Avocado peel
BET	Brunauer Emmett Teller
BOD	Biological Oxygen Demand
CC	Corncob
COD	Chemical Oxygen Demand
CP	Coir peat
CW	Coffee waste
EBCT	Empty Bed Contact Time (min)
EDTA	Ethylene diamine triacetic acid
EDTAD	Ethylene diamine tetraacetic dianhydride
EDX	Energy Dispersive X–Ray
ES	Egg shell
EU	Eucalyptus leave
FTIR	Fourier Transform Infrared Spectroscopy
GG	Garden grass
GS	Grape stalk
HLR	Hydraulic Loading Rate (m^3/m^2 hr)
LC	Lychee rind
MG	Mango skin
ML	Maple leave
MMBB	Multi–Metal Binding Biosorbent
MP	Mandarin peel
MP–AES	Microwave Plasma–Atomic Emission Spectrometer
MTZ	Mass Transfer Zone (cm)

Symbol	Description
OP	Orange peel
pH	potential Hydrogen
ppm	Part per million
PS	passion fruit skin
R^2	Coefficient of determination
RMSE	Residual Root Mean Square Error
RO	Reverse Osmosis
SC	Sugarcane bagasse
SD	Sawdust
SEM/EDS	Scanning electron microscopy with X–ray microanalysis
SSE	Error Sum of Square
TEM	Transmission Electron Microscopy
TOC	Total Organic Carbon
TSS	Total Suspended Solids
TW	Tea waste
WWTP	Water and Wastewater Treatment Plant
XPS	X–ray Photoelectron Spectroscopy

GREEK SYMBOLS

Symbol	Description	Unit
β_{RP}	Redlich–Peterson model exponent	
β_S	Sips model exponent	
μ	micro	
τ	the time required for retaining 50% of the initial adsorbate	min

PhD DISSERTATION ABSTRACT

Author: ATEFEH ABDOLALI

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Thesis title: Detoxification of heavy metal ions from aqueous solutions using a novel lignocellulosic multi–metal binding biosorbent

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School: Civil and Environmental Engineering

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

Dr Wenshan Guo (Co–supervisor)

Keywords: Agro–industrial waste; Biosorption; Breakthrough curve; Chemical Modification; Fixed–bed column; Heavy metal; Kinetics; Modeling

Abstract

Since, the availability of a biomass at a low cost is a key factor dictating its selection for a biosorption, thus agro–industrial wastes and by–products are considered as alternatives for heavy metal biosorption development. Utilizing potentials of combination of common agro–industrial wastes and by–products let us have different kinds of active binding sites at same time in wastewater treatment. In order to make the biosorption process more suitable for heavy metal removal, both batch and continuous systems have been studied. Two breakthrough multi–metal binding biosorbent made from a combination of tea wastes, maple leaves and mandarin peel (MMBB1) and a mixture of tea waste, sawdust and corncob (MMBB2) were applied to evaluate their biosorptive potential of heavy metal removal from synthetic multi–metal solutions. FTIR and SEM were conducted, before and after biosorption, to explore the intensity and position of the available functional groups and changes in adsorbent surface morphology. Carboxylic and hydroxyl groups were found to be the principal functional groups for the sorption of metals. MMBB1 exhibited better performance at pH 5.5 with maximum sorption capacities of 41.48, 39.48, 94.0 and 27.23 mg/g for Cd(II), Cu(II), Pb(II) and Zn(II), respectively. In batch system, MMBB1 was selected for further process optimization, modification, characterization and thermodynamic studies. The data indicated that Langmuir isotherm and pseudo–second order kinetics model describe the experimental data very well. The maximum amounts of biosorption capacity of modified MMBB increased to 69.56, 127.70, 345.20 and 70.55 mg/g for Cd(II), Cu(II), Pb(II) and Zn(II), respectively. Then a continuous fixed–bed study was carried out by utilizing the modified MMBB for cadmium, copper, lead and zinc removal from synthetic solution and real wastewater. The effect of operating conditions i.e. influent flow rate, metal concentration and bed depth was investigated at optimal pH (5.5±0.1) for a synthetic wastewater. Results confirmed that the total amount of metal adsorption decreased with increasing influent flow rate and also increased with increasing each metal concentration. The maximum biosorption capacity of 38.25, 63.37, 108.12 and 35.23 mg/g for Cd, Cu, Pb and Zn, respectively, were attained at 31 cm bed height, 10 mL/min flow rate and 20 mg/L initial concentration. The Thomas model found better describing the whole dynamic behaviour of the column. Finally, desorption studies indicated that metal–loaded biosorbent could be used after three consecutive sorption, desorption and regeneration cycles by applying a semi–simulated real wastewater.

Graphical abstract: