STUDIES ON THE DEVELOPMENT OF NATURAL CATION EXCHANGER FOR HEAVY METALS REMOVAL

A Thesis Submitted to the Central Department of Chemistry Institute of Science and Technology Tribhuvan University, Nepal For the Award of Doctor of Philosophy (Ph. D.) Degree in Chemistry

By

PUSPA LAL HOMAGAI Central Department of Chemistry Kirtipur, Kathmandu, Nepal 2012 AD (2069 BS)

BOARD OF EXAMINERS

Approved By

.....

Assoc. Prof. Dr. Kedar Nath Ghimire Supervisor & Head of Department Central Department of Chemistry Tribhuvan University, Kirtipur, Kathmandu, Nepal

Examined By

.....

Dr. Prem Ratna Sthapit External Examiner Ex-Deputy Director General Department of Plant Resources, Nepal Government

RECOMMENDATION

This is to certify that **Mr. Puspa Lal Homagai** has completed this dissertation work entitled **Studies on the Development of Natural Cation Exchanger for Heavy Metals Removal** for the award of **Doctor of Philosophy (Ph. D.) Degree in Chemistry** under my supervision, to my knowledge this work has not been submitted for any other degree.

Date: 2012.04.27

.....

Assoc. Prof. Dr. Kedar Nath Ghimire

Supervisor

Central Department of Chemistry

Tribhuvan University

.

Kirtipur, Kathmandu, Nepal

CERTIFICATE OF APPROVAL

On the recommendation of **Dr. Kedar Nath Ghimire**, this dissertation work of **Mr. Puspa Lal Homagai** is forwarded for the examination and is submitted to the Tribhuvan University for the award of **Doctor of Philosophy (Ph. D.) Degree in Chemistry.**

.....

Assoc. Prof. Dr. Kedar Nath Ghimire

Head

Central Department of Chemistry Tribhuvan University Kirtipur, Kathmandu, Nepal Dedicated to my Parents

ACKNOWLEDGEMENTS

My heartfelt thanks go to my supervisor Assoc. Prof. Dr. Kedar Nath Ghimire for his kind guidance, practical wisdom, unwavering support, and warm friendship throughout my research period. His words of encouragement boosted my confidence and self-esteem.

Gratitude and credit goes to Professor Katsutoshi Inoue, for providing laboratory facilities to do partial works in Saga University, Japan. I am grateful to Prof. JK Shrestha, Prof. MB Gewali and Assoc. Prof. MR Pokhrel for their helpful discussions and encouragement. I am also thankful to Dr. SK Kalauni, Dr. AP Yadav and Dr. BK Jha for their generous help during my studies.

Warm thanks also go to Dr. HN Luitel, Dr. R Chanda, Dr. B Bastakoti and Dr. S Guragain for their all-around support during my stay in Saga University, Japan.I would like to thank Mr. Rajan Dahal for his kind cooperation in designing my thesis.

The financial support by the National Academy of Science and Technology (NAST, Nepal) as the PhD scholarship is gratefully acknowledged. I also acknowledge Coordination Division T.U. Kirtipur for providing partial financial support for my research work.

I would also like to thank all teaching and non-teaching staffs of the Central Department of Chemistry for their generous help. I would like to thank Mrs. J Kour and Mrs. B Shrestha for their continuous support in the research works. Warm thanks go to my sons Vaskar and Prasanna for their endeavor help in typing the thesis in time.

Finally, special thanks go to my wife, Laxmi for her endless support, continued patience and encouragement throughout the course of my studies.

Puspa Lal Homagai Ph.D.Scholar Central Department of Chemistry Kirtipur, Kathmandu, Nepal 2012

ABSTRACT

Two types of novel bioadsorbents such as charred xanthated sugarcane bagasse (CXSB) and charred aminated sugarcane bagasse (CASB) are investigated. This research work elucidates the uptake performance of biosorbent for the sequestration of heavy metal ions such as Cd²⁺, Pb²⁺, Cu²⁺, Ni²⁺ and Zn²⁺, respectively. Xanthated and aminated biosorbent prepared from sugarcane bagasse under specific experimental conditions were characterized with FT-IR, TGA/DTA, SEM, Zeta potential and Elemental analysis.

Batch adsorption experiments were performed at eight different initial metal ion concentrations (25, 50,100, 200, 400, 600, 800, 1000 mg/L), at 293K temperature, while pH of the solutions was varied from 1 to 7. The results indicated that the uptake performance of CXSB and CASB biosorbent significantly changed with pH, concentration of metal ions and temperature. The selectivity order in the removal of heavy metals at pH around 4 follows the order Pb> Cu > Ni > Cd >Zn for CXSB whereas the order Pb> Cd > Zn > Ni >Cu for CASB. Moreover Irwing- Williams Series support the bindings' mechanism for Cu²⁺, Cd²⁺,Pb²⁺, Zn²⁺and Ni²⁺ ions onto both the modified biopolymers.

Adsorption of heavy metal ions onto both CXSB and CASB biosobents followed pseudosecond order kinetics with faster adsorption within 15minutes to 40 minutes. All the obtained data well followed the Langmuir adsorption isotherm. The positive value of enthalpy change (Δ H) and negative of free energy change (Δ G) shows the adsorption process is endothermic and spontaneous. Moreover, the obtained positive entropy changes (Δ S) shows that an increase in randomness, is associated with the adsorption of metal ions onto the CXSB and CASB biosorbents.

As in the case of plastic materials like commercial synthetic cation exchanger, the CXSB and CASB based on sugarcane bagasse developed in our laboratory revealed to be an efficient cation exchanger for removing cadmium, lead, copper, nickel and zinc ions from the aqueous solution.

Keywords: Adsorption, xanthation, amination, heavy metals, sugarcane bassage.

TABLE OF CONTENTS

Title Page	i
Dedication	ii
Recommendation	iii
Certificate of Approval	iv
Board of Examiners	V
Acknowledgement	vi
Abstract	vii
List of Abbreviations	viii-ix
List of Tables	xiii
List of figures	xiv-xv
List of Photograph	xvi
1. Introduction	1-13
1.1 Statement of Pollution Problem	
1.2 Effects of Heavy Metals on Human Health	7
1.3 Common Method Used for the Treatment of Heavy from	
metals from Wastewater	9
1.3.1 Chemical Precipitation	9
1.3.2 Coagulation-Flocculation	9
1.3.3 Reverse Osmosis	10
1.3.4 Ultra filtration	11
1.3.5 Electrodialysis	11

1.3.6 Flotation	11	
1.3.7 Ion Exchange	12	
1.4 Scopes of the study	12	
2. Objectives of the study	14-16	
3. Literature Review	17-32	
3.1 Fundamentals of Adsorption		
4. Materials and Methods		
4.1 Chemicals	33	
4.2 Preparation of Adsorbents		
4.2.1 Preparations of Charred Xanthated		
Sugarcane Bagasse (CXSB)	34	
4.2.2 Preparations of Charred Aminated		
Sugarcane Bagasse (CASB)	35	
4.3 Effect of pH on Metals Removal		
4.4 Adsorption Experiments		
4.5 Kinetic Studies		
4.6 Desorption Studies		
4.7 Analysis	39	
4.7.1 Elemental Analysis	39	
4.7.2 Scanning Electron Microscope Analysis	40	
4.7.3 Zeta Potential Analysis	40	
4.7.4 IR Spectroscopy		

4.7.5 Thermal Gravimetric Analysis	43
4.7.6 Atomic Absorption Spectrometry	44
5. Results and Discussions	
5.1 SEM Analysis	46
5.2 FTIR Spectra Analysis	48
5.3 Elemental Analysis	51
5.4 Thermal Analysis	52
5.5 Effect of pH	55
5.6 Point of Zero Charge	57
5.7 Adsorption Isotherms	59
5.8 Sorption Kinetics	63
5.9 Adsorption Thermodynamics	68
5.10 Plausible Adsorption Mechanism	70
5.11 Desorption and Recycling Studies	
5.12 Comparisons of CXSB and CASB against other	
adsorbents	73
6. Conclusions	75-77
7. Summary and Recommendations	78-79
References	
Appendices	
Appendix-I : Participation in Conferences/ Seminars	

Appendix-II : List of Publications and Publications

LIST OF TABLES

- Table 1
 General distribution of heavy metals in Particular Industrial Effluents
- Table 2Different properties of some heavy metals of interest
- Table 3Major sources, health effects of heavy metals and WHO drinking water standards
- Table 4
 Adsorption capacities (mg/g) of some inorganic substances for some heavy metals removal
- Table 5Sorption of heavy metals by bacteria, fungi and algae
- Table 6Sorption of heavy metals by waste products of higher plants
- Table 7Specific wavelengths and AAS analysis conditions for heavy metal ions.
- Table 8
 IR Assignments of Functional groups on carbon surfaces
- Table 9Elemental analysis of sugarcane bagasse before and after modification
- Table 10Solubility of metal ions at different pH
- Table 11
 Effect of pH of metal ions adsorption onto CXSB and CASB
- Table 12Langmuir adsorption isotherm model parameters and experimental qmax of CXSB
- Table 13Langmuir adsorption isotherm model parameters and experimental qmax of CASB
- Table 14Sorption kinetics of pseudo second order for several metal ions onto CXSB
- Table 15Sorption kinetics of pseudo-second order for several metal ions onto CASB
- Table 16Thermodynamic parameters of CXSB and CASB
- Table 17Comparison of adsorption capacities (mg/g) of different biosorbents with CXSB and
CASB for the removal of various metal ions reported in the literatures.

LIST OF FIGURES

Figure 1	Cellulosic structure of sugarcane bagasse
Figure 2	Hetero atoms and groups on carbon surface
Figure 3	(a) Proposed ring opening of monomeric unit of cellulose contained in
Figure 4	Batch adsorption experiment
Figure 5	Schematic representation of zeta potential. (Source WEB_6 2007)
Figure 6	A typical plot of zeta potential versus pH (Source WEB_ 6 2007)
Figure 7	SEM images showing the surface morphologies of (a) CSB before modification (b) CXSB and (c) CASB after modification
Figure 8	FTIR of CSB (before modification) and CXSB (after modification)
Figure 9	FTIR of CSB (before modification) and CASB (after modification)
Figure 10	TG-DTA curves of CSB (before modification) and CXSB (after modification)
Figure 11	TG-DTA curves of CSB (before modification) and CASB (after modification)
Figure 12	Effect of pH in the adsorption of Cd(II), Pb(II), Ni(II), Zn(II) and Cu(II) onto CXSB
Figure 13	Effect of pH in the adsorption of Cd(II), Pb(II), Ni(II), Zn(II) and Cu(II) onto CASB

 $Figure \ 14 \qquad Point \ of \ zero \ charge \ (pH_{pzc} \) \ curve \ of \ RSB \ and \ CXSB$

- Figure 15 Point of zero charge (pH_{pzc}) curve of RSB and CASB
- Figure 16 Adsorption isotherm plot for the adsorption of several metal ions onto CXSB
- Figure 17 Adsorption isotherm plot for the adsorption of several metal ions onto CASB
- Figure 18 Langmuir isotherm plot for the adsorption of several metal ions onto CXSB
- Figure 19 Langmuir isotherm plot for the adsorption of several metal ions onto CASB
- Figure 20 Amounts of adsorption versus adsorption times for Cd(II), Pb(II), Ni(II), Zn(II) and Cu(II) onto CXSB
- Figure 21 Amounts of adsorption versus adsorption times for Cd(II), Pb(II), Ni(II), Zn(II) and Cu(II) onto CASB
- Figure 22 Pseudo second order sorption kinetics of Cd(II), Pb(II), Ni(II), Zn(II) and Cu(II) onto CXSB
- Figure 23 Pseudo second order sorption kinetics of Cd(II), Pb(II), Ni(II), Zn(II) and Cu(II) onto CASB
- Figure 24 Thermodynamic parameter of Cu (II) and Zn(II) for adsorption onto CXSB
- Figure 25 Thermodynamic parameter of Cu (II) and Zn(II) for adsorption onto CASB
- Figure 26 Plausible adsorption mechanism of metal ion onto monomeric cellulose unit contained in CXSB.

LIST OF PHOTOGRAPHS

- Photograph 1: Me taking Scanning Electron Microscope (SEM)
- Photograph 2: Me working in Saga laboratory
- Photograph 3: Me working in lab taking concentration of solution by AAS
- Photograph 4: Me working in CDC Lab. with Supervisor

LIST OF ABBREVIATIONS

AAS	Atomic absorption spectrometry
С	Centigrade
CASB	Charred animated sugarcane bagasse
CSB	Charred sugarcane bagasse
cm	centimeter
CXSB	Charred Xanthated Sugarcane Bagasse
dm ³	Decimeter cube
DTA	Differential Gravimetric Analysis
FT-IR	Fourier Transform Infrared Spectroscopy
g	gram
Κ	Kelvin
L	Litre
m	meter
mg	milligram
μg	microgram
μm	micrometer
mL	milliliter
mm	millimeter
рН	power of hydrogen

rpm	rotation per minute
RSB	Raw sugarcane bagasse
SB	Sugarcane bassage
SEM	Scanning Electron Microscopy
TGA	Thermo Gravimetric Analysis