

Contents

List of Figures	xx
List of Tables	xxiii
List of Abbreviations	xxiv
Abstract	xxvii
1 Introduction	1
1.1 Background	1
1.2 Sources of Heavy Metals	3
1.3 Heavy Metals Exposure and Poisoning	4
1.4 Mechanism of Heavy Metals Toxicity	4
1.5 Heavy Metal Removal Technologies	8
1.6 Motivation	10
1.7 Objectives of the Present Work	11
1.8 Thesis Outline	12
2 Literature Review	14
2.1 Background	14
2.2 Nickel	17
2.2.1 History	17
2.2.2 Properties	18
2.2.3 Nickel's presence in the Environment	19

2.2.4	Health Effects	19
2.2.5	Environmental Impacts	20
2.3	Copper	21
2.3.1	Background	21
2.3.2	History	22
2.3.3	Properties	22
2.3.4	Copper’s presence in the Environment	23
2.3.5	Health Effects	23
2.3.6	Environmental Impacts	24
2.4	Zinc	24
2.4.1	Background	24
2.4.2	History	24
2.4.3	Properties	25
2.4.4	Zinc’s presence in the Environment	25
2.4.5	Health Effects	26
2.4.6	Environmental Impacts	27
2.5	Techniques for removal of copper, nickel and zinc from contaminated water	27
2.5.1	Ion Exchange	28
2.5.2	Chemical Precipitation	29
2.5.3	Electrochemical Methods	31
2.5.4	Adsorption	33
2.6	Properties of an Adsorbent	35
2.7	Adsorption Mechanisms	35
2.7.1	Chemical Adsorption	36
2.7.2	Physical Adsorption	37
2.7.3	Ion Exchange	37
2.7.4	Precipitation	38
2.7.5	Complexation and Chelation	38
2.8	Raw Adsorbents	39

2.8.1	Bentonite	39
2.8.1.1	History	39
2.8.1.2	Chemical Properties of Bentonite clay	40
2.8.1.3	Application of Bentonite Clay	41
2.8.2	Red Ochre	42
2.8.3	<i>Tectona grandis</i> Sawdust	43
2.8.4	<i>Azadirachta indica</i> Twig Ash	44
2.8.5	Natural Soil	44
3	Material and Methods	46
3.1	Instruments Used in Experimentation	46
3.2	Characteristic Analysis of Novel Adsorbents	47
3.2.1	Proximate and Ultimate Analysis	47
3.2.2	Yield (%)	47
3.2.3	Bulk Density	48
3.2.4	Iodine Number	48
3.2.5	Brunauer-Emmett-Teller Surface Area	48
3.2.6	pH _{ZPC}	48
3.2.7	Surface Characteristics	49
3.2.8	Crystallinity and Thermostabilization Characteristics	49
3.3	Experimental Procedure for Adsorption Study	50
3.3.1	Standards and Reagents Preparation	50
3.3.2	Selection of Adsorbents for Preparing Novel Adsorbents	51
3.3.2.1	Composite of Bentonite Clay and Red Ochre	51
3.3.2.2	<i>Azadirachta indica</i> Twig Ash (ATA)	52
3.3.2.3	Activated Carbon derived from <i>Tectona grandis</i>	53
3.3.2.4	Mould	54
3.4	Batch Adsorption Study	55
3.5	Factors Affecting Adsorption	56
3.5.1	Contact Time	56

3.5.2	pH	56
3.5.3	Initial Concentration	57
3.5.4	Adsorbent dose	57
3.5.5	Temperature	57
3.6	Adsorption Dynamics	57
3.6.1	Derivation of Dimensionless Numbers	59
3.7	Mechanistic Modeling	60
3.7.1	Bangham Model	60
3.7.2	Boyd Model	61
3.7.3	Mass Transfer Model	61
3.8	Adsorption Kinetics	61
3.8.1	PFO Kinetic Model	62
3.8.2	PSO Kinetic Model	62
3.8.3	Elovich Model	63
3.8.4	IPD Model	63
3.9	Adsorption Isotherm	63
3.9.1	Langmuir Isotherm	64
3.9.2	Redlich-Peterson (R-P) Isotherm	64
3.9.3	Flory-Huggins (F-H) Isotherm	65
3.9.4	Temkin Isotherm	65
3.9.5	Toth Isotherm	65
3.9.6	Hill Isotherm	66
3.9.7	Sip Isotherm	66
3.9.8	Koble-Corrigan (K-C) Isotherm	66
3.9.9	Fritz Schlunder-5 (FS-5) Isotherm	67
3.9.10	Khan Isotherm	67
3.9.11	Radke-Prausnitz Isotherm	67
3.9.12	Dubinin-Radushkevich (D-R) Isotherm	68
3.9.13	Fowler-Guggenheim (F-G) Isotherm	68

3.9.14	Elovich Isotherm	69
3.9.15	Freundlich Isotherm	69
3.9.16	Halsey Isotherm	69
3.10	Thermodynamics	70
3.11	Artificial Neural Network (ANN) Modeling	70
3.12	Desorption Study	72
4	Adsorption using Composite	73
4.1	Removal of Cu^{2+} , Ni^{2+} and Zn^{2+} ions by Composite	73
4.2	Results and discussion	75
4.2.1	Physicochemical characterization	75
4.2.1.1	SEM	75
4.2.1.2	FTIR	76
4.2.1.3	XRD	78
4.2.1.4	BET Surface Area	79
4.2.1.5	Ultimate Analysis	79
4.2.2	pH_{ZPC}	80
4.2.3	Adsorption Dynamics	80
4.2.4	ANN Modelling	81
4.2.5	Adsorption Kinetics	83
4.2.6	Adsorption Isotherm	85
4.2.7	Thermodynamics	86
4.2.8	Optimization Study	88
4.2.8.1	Effect of pH	88
4.2.8.2	Effect of Composite Dose	89
4.2.8.3	Effect of Initial Concentration	90
4.2.8.4	Effect of Contact Time	91
4.2.8.5	Effect of Temperature	92
4.3	Adsorption Mechanism for composite	92
4.4	Comparative Study	94

4.5	Conclusion	95
5	Adsorption using ATA	96
5.1	Adsorption of Cu^{2+} , Ni^{2+} and Zn^{2+} ions by ATA	96
5.2	Results and Discussion	98
5.2.1	Characterization	98
5.2.1.1	SEM-EDX	98
5.2.1.2	FTIR	100
5.2.1.3	XRD	101
5.2.1.4	BET Surface Area	103
5.2.1.5	Proximate and Ultimate Analysis	103
5.2.1.6	Bulk Density	103
5.2.2	pH_{ZPC}	104
5.2.3	Adsorption Dynamics	104
5.2.4	ANN Modeling	105
5.2.5	Adsorption Kinetics	107
5.2.6	Adsorption Isotherm	109
5.2.7	Thermodynamics Study	111
5.2.8	Optimization Study	112
5.2.8.1	Effect of pH	112
5.2.8.2	Effect of ATA Dose	113
5.2.8.3	Effect of Initial Concentration	114
5.2.8.4	Effect of Contact Time	115
5.2.8.5	Effect of Temperature	116
5.3	Adsorption mechanism for ATA	117
5.4	Comparative Study	119
5.5	Conclusion	120
6	Adsorption using AC	121

6.1	Removal of Cu^{2+} , Ni^{2+} and Zn^{2+} ions by Activated Carbon derived from <i>Tectona grandis</i>	121
6.2	Results and Discussion	122
6.2.1	Characterization	122
6.2.1.1	SEM-EDX	122
6.2.1.2	FTIR	124
6.2.1.3	XRD	126
6.2.1.4	TGA	128
6.2.1.5	BET Surface Area	129
6.2.1.6	Proximate analysis	129
6.2.1.7	Yield (%)	130
6.2.1.8	Bulk Density	130
6.2.1.9	Iodine Number	130
6.2.2	pH_{ZPC}	131
6.2.3	Adsorption Dynamics	132
6.2.4	ANN Modeling	132
6.2.5	Adsorption Kinetics	135
6.2.6	Adsorption Isotherm	136
6.2.7	Thermodynamics	138
6.2.8	Optimization Study	139
6.2.8.1	Effect of pH	139
6.2.8.2	Effect of AC Dose	140
6.2.8.3	Effect of Initial Concentration	141
6.2.8.4	Effect of Contact Time	142
6.2.8.5	Effect of Temperature	143
6.3	Adsorption mechanism for AC	144
6.4	Comparative Study	145
6.5	Biodegradability Study	152
6.6	Conclusion	152

7 Adsorption using mould	154
7.1 Removal of Cu ²⁺ , Ni ²⁺ and Zn ²⁺ ions by Mould	154
7.2 The Ganga River Bank (Ghat) in Varanasi	156
7.3 Results and Discussion	156
7.3.1 Physicochemical Characterization	156
7.3.1.1 SEM-EDS	156
7.3.1.2 FTIR	158
7.3.1.3 XRD	160
7.3.1.4 Proximate Analysis	162
7.3.1.5 TGA	162
7.3.2 Adsorption Dynamics	163
7.3.3 ANN Modeling	164
7.3.4 Adsorption Kinetics	166
7.3.5 Adsorption Isotherm	169
7.3.6 Thermodynamics Study	171
7.3.7 Optimization Study	173
7.3.7.1 Effect of pH	173
7.3.7.2 Effect of Initial Concentration	175
7.3.7.3 Effect of Temperature	176
7.3.7.4 Effect of Contact Time	177
7.4 Adsorption mechanism for mould	178
7.5 Comparative Study	180
7.6 Conclusion	182
8 Comparison of Novel Adsorbents, Desorption and Application of Spent Ad- sorbent	183
8.1 Comparison of Novel Adsorbents	183
8.2 Desorption Study	185
8.3 Application of Spent Adsorbent	186

9 Conclusion	188
Appendix	194
A.1 Removal of Nickel using Composite	194
A.2 Results and Discussion	196
A.2.1 Physico-chemical Characterization	196
A.2.1.1 SEM-EDX	196
A.2.1.2 XRD	197
A.2.1.3 FTIR	199
A.2.2 Mechanistic Study	200
A.2.3 Adsorption Dynamics	202
A.2.4 Optimization Study	202
A.2.4.1 Effect of pH	202
A.2.4.2 Effect of Composite Dose	203
A.2.4.3 Effect of Initial Concentration of Ni ²⁺ Ions	204
A.2.4.4 Effect of Temperature	205
A.2.4.5 Effect of Agitation Rate	206
A.2.4.6 Effect of Contact Time	207
A.2.5 Adsorption Kinetics	208
A.2.6 Adsorption Isotherm	209
A.2.7 Thermodynamic Study	212
A.3 Comparative Study	213
A.4 Conclusion	215
References	293
List of Publications	294
Media Coverage of Research Work	297
COPYRIGHT ©	298

List of Figures

1.1	Copper toxicity and its mechanisms of action	5
1.2	Nickel-induced oxidative stress	6
1.3	Regulation of zinc homeostasis in cells and its effects on cytotoxicity	7
1.4	Removal technologies for heavy metals from contaminated water	9
1.5	Outline of this work	13
2.1	Different mechanisms of Adsorption (AE and AM: molecules with exchangeable ions and metal ions, C: chelating agents, M+: heavy metal ions, Tp: transport protein)	36
2.2	Structure of bentonite clay	40
3.1	Stock solution of Ni ²⁺ , Cu ²⁺ and Zn ²⁺ ions	50
3.2	Composite beads made from bentonite clay and red ochre	52
3.3	Process of preparation of ATA	52
3.4	<i>Tectona grandis</i> sawdust	53
3.5	Activated carbon derived from <i>Tectona grandis</i> sawdust	53
3.6	Process for producing activated carbon from <i>Tectona grandis</i> sawdust	54
3.7	(a) Mould preparation by the potter and (b) Final Product (Mould)	55
4.1	SEM of composite before and after adsorption of ternary metal ions	75
4.2	EDX of composite before adsorption of ternary metal ions	76
4.3	EDX of composite after adsorption of ternary metal ions	76
4.4	FTIR of composite before and after adsorption of ternary metal ions	77

4.5	XRD of composite before and after adsorption of ternary metal ions	78
4.6	pH_{zpc} of composite	80
4.7	Performance between number of epochs and MSE for prediction of (a) Cu^{2+} , (b) Ni^{2+} and (c) Zn^{2+} ions removal using composite as adsorbent	81
4.8	Regression plot for prediction of (a) Cu^{2+} , (b) Ni^{2+} and (c) Zn^{2+} ions removal using composite as adsorbent	82
4.9	Correlation plot for the experimental and ANN predicted values for ternary metal ions removal using composite as adsorbent	83
4.10	a) PFO b) PSO and c) IPD kinetic models for composite as adsorbent	84
4.11	a) Langmuir b) Freundlich and c) D-R isotherms for composite as adsorbent	85
4.12	Plot of $\ln K_d$ vs. $1/T$ for composite as adsorbent	87
4.13	Effect of pH on % removal of ternary metal ions and adsorption capacity of composite (-Q is adsorption capacity and -R is % Removal)	88
4.14	Effect of composite dose on % removal of ternary metal ions and adsorption capacity of composite	89
4.15	Effect of initial concentration of ternary metal ions on % removal and adsorption capacity of composite	90
4.16	Effect of contact time on % removal of ternary metal ions and adsorption capacity of composite	91
4.17	Effect of temperature on % removal of ternary metal ions and adsorption capacity of composite	92
5.1	SEM of ATA before adsorption of ternary metal ions	98
5.2	SEM of ATA after adsorption of ternary metal ions	98
5.3	EDX of ATA	99
5.4	FTIR Spectrum of ATA before and after adsorption of ternary metal ions	100
5.5	XRD of ATA before and after adsorption of ternary metal ions	102
5.6	pH_{zpc} of ATA	104
5.7	Performance between number of epochs and MSE for prediction of (a) Cu^{2+} , (b) Ni^{2+} and (c) Zn^{2+} ions removal using ATA as adsorbent	105

5.8	Regression plot for prediction of (a) Cu^{2+} , (b) Ni^{2+} and (c) Zn^{2+} ions removal using ATA as adsorbent	106
5.9	Correlation plot for the experimental and ANN predicted values for ternary metal ions removal using ATA as adsorbent	107
5.10	(a) PFO, (b) PSO and (c) IPD model for ATA as adsorbent	108
5.11	a) Langmuir, b) Freundlich and c) D-R isotherm models for ATA as adsorbent	109
5.12	Plot of $\ln K_d$ vs. $1/T$ for ATA as adsorbent	111
5.13	Effect of pH on percentage removal of ternary metal ions using ATA	112
5.14	Effect of ATA dose on percentage removal of ternary metal ions and adsorption capacity of ATA	113
5.15	Effect of initial Cu^{2+} , Ni^{2+} and Zn^{2+} ions concentration on percentage removal and adsorption capacity of ATA	115
5.16	Effect of contact time on percentage removal of ternary metal ions and adsorption capacity of ATA	116
5.17	Effect of temperature on percentage removal of of ternary metal ions	116
6.1	SEM of AC	123
6.2	EDX of AC	123
6.3	FTIR of TG and AC (before and after adsorption of ternary metal ions)	125
6.4	XRD analysis of AC	127
6.5	TGA of AC	128
6.6	pH_{zpc} of AC	131
6.7	Performance between number of epochs and MSE for prediction of (a) Ni^{2+} , (b) Cu^{2+} and (c) Zn^{2+} ions removal using AC	133
6.8	Regression plot for (a) Ni^{2+} , (b) Cu^{2+} and (c) Zn^{2+} ions	134
6.9	Correlation plot for the experimental and ANN predicted values	135
6.10	(a) PFO, (b) PSO and (c) IPD model for AC as adsorbent	135
6.11	(a) Langmuir, (b) Freundlich and (c) D-R model for AC as adsorbent	137
6.12	Plot of $\ln K_d$ vs $1/T$ for AC	138
6.13	Effect of pH on percentage removal of ternary metal ions using AC	140

6.14	Effect of AC dose on percentage removal of ternary metal ions and adsorption capacity of AC	141
6.15	Effect of initial concentration of Ni ²⁺ , Cu ²⁺ and Zn ²⁺ ions on percentage removal and adsorption capacity of AC	142
6.16	Effect of contact time on percentage removal of ternary metal ions and adsorption capacity of AC	142
6.17	Effect of temperature on percentage removal and adsorption capacity of AC	143
7.1	(a) SEM of unloaded mould and (b) SEM of metal ions-loaded mould . . .	157
7.2	EDX of mould before adsorption	158
7.3	EDX of mould after adsorption of ternary metal ions	158
7.4	FTIR spectrum of mould before and after adsorption of ternary metal ions	159
7.5	XRD of mould before and after adsorption of ternary metal ions	161
7.6	TGA and DTG curves of mould	163
7.7	Performance between number of epochs and MSE for prediction of (a) Ni ²⁺ , b) Cu ²⁺ and (c) Zn ²⁺ ions removal using mould as adsorbent	164
7.8	Regression plot for prediction of (a) Ni ²⁺ , (b) Cu ²⁺ and (c) Zn ²⁺ ions removal using mould as adsorbent	165
7.9	Correlation plot for the experimental and ANN predicted values for ternary metal ions removal using mould as adsorbent	166
7.10	Adsorption kinetics for Ni ²⁺ ions using mould as adsorbent	167
7.11	Adsorption kinetics for Cu ²⁺ ions using mould as adsorbent	167
7.12	Adsorption kinetics for Zn ²⁺ ions using mould as adsorbent	168
7.13	Adsorption isotherm for Ni ²⁺ ions	169
7.14	Adsorption isotherm for Cu ²⁺ ions	170
7.15	Adsorption isotherm for Zn ²⁺ ions	170
7.16	Plot of ln K _d vs 1/T for Ni ²⁺ ions	172
7.17	Plot of ln K _d vs 1/T for Cu ²⁺ ions	172
7.18	Plot of ln K _d vs 1/T for Zn ²⁺ ions	173
7.19	Effect of pH on % removal of ternary metal ions	174

7.20	Effect of initial concentration on % removal of ternary metal ions and adsorption capacity of mould	175
7.21	Effect of temperature on % removal of ternary metal ions and adsorption capacity of mould	176
7.22	Effect of contact time on % removal and adsorption capacity of mould . . .	177
8.1	Percentage desorption of novel adsorbents	185
A.1	SEM of composite after adsorption of Ni ²⁺ ions	196
A.2	EDX of composite after adsorption of Ni ²⁺ ions	197
A.3	XRD of composite before and after adsorption of Ni ²⁺ ions	198
A.4	FTIR of composite before and after adsorption of Ni ²⁺ ions	200
A.5	Mechanistic models for adsorption of Ni ²⁺ ions	201
A.6	Effect of pH on the removal of Ni ²⁺ ions	203
A.7	Effect of composite dose on % removal and adsorption capacity	204
A.8	Effect of the initial concentration of Ni ²⁺ on removal and uptake capacity	204
A.9	Effect of temperature on the removal of Ni ²⁺ ions	205
A.10	Effect of agitation rate on the removal of Ni ²⁺ ions	206
A.11	Effect of contact time on the removal of Ni ²⁺ ions	207
A.12	(a) PFO, (b) PSO model and (c) Elovich kinetic models for removal of Ni ²⁺ ions using composite	208
A.13	Adsorption isotherm models for removal of Ni ²⁺ ions using composite . . .	211
A.14	Plot of ΔG vs. T for removal of Ni ²⁺ ions using composite	213

List of Tables

1.1	Permissible limit (mg/ L) of Copper, Nickel and Zinc in drinking water [5]–[7]	2
1.2	Concentration (mg/ L) of copper, nickel and zinc in various industrial discharge	3
2.1	General information about copper, nickel and zinc with their possible toxic effects [1], [4]	15
2.2	Key characteristics of Nickel	18
2.3	Key characteristics of copper	22
2.4	Key characteristics of Zinc	26
2.5	Permissible limit (mg/ L) of Copper, Nickel and Zinc in drinking water [5]–[7]	28
3.1	Instruments used in experimental work	46
4.1	Dimensionless numbers and diffusivity coefficients for composite	81
4.2	Adsorption kinetic model parameters for composite as adsorbent	84
4.3	Adsorption isotherm model parameters for composite as adsorbent	85
4.4	Thermodynamic parameters for composite as adsorbent	87
4.5	Comparison of adsorption capacities of inorganic adsorbents and composite synthesized in the present work	94
5.1	X-Ray Diffraction analysis of ATA	102
5.2	Value of dimensionless numbers for ternary metal ions	105

LIST OF TABLES

5.3	Adsorption kinetic model parameters for ATA as adsorbent	108
5.4	Adsorption isotherm model parameters for ATA as adsorbent	110
5.5	Thermodynamic parameters for ATA as adsorbent	111
5.6	Comparison of different adsorbents with ATA based on adsorption capacity	119
6.1	Percentage of elemental weight from AC's EDX	124
6.2	Table of FTIR comparisons before and after activation of sawdust	126
6.3	XRD analysis of AC	128
6.4	Proximate analysis of TG	130
6.5	Value of dimensionless numbers for ternary metal ions	132
6.6	Adsorption kinetic model parameters for AC as adsorbent	136
6.7	Adsorption isotherm model parameters for AC as adsorbent	138
6.8	Thermodynamic parameters for ternary metal ions adsorption	139
6.9	Comparative analysis of the physico-chemical features of AC with those of other activated carbons	146
6.10	Comparison of various adsorbents with AC	148
7.1	FTIR band positions of the prepared mould before and after adsorption . . .	160
7.2	Calculated values of D and FWHM for the corresponding absorption peaks	161
7.3	Proximate analysis of mould	162
7.4	Dimensionless numbers and diffusivity coefficients for the adsorption of metal ions in mould	163
7.5	Kinetic parameters	168
7.6	Isotherm parameters	169
7.7	Thermodynamic parameters for ternary metal ions adsorption	174
7.8	Comparison of mould with other adsorbents	180
8.1	Comparative study of Novel Adsorbents	184
A.1	EDX of composite after adsorption	197
A.2	Diffraction major peaks parameters	198
A.3	Mechanistic model parameters	201

A.4	Adsorption kinetic models parameters for Ni ²⁺ ions removal	209
A.5	Adsorption isotherm model parameters for removal of Ni ²⁺ ions using composite	209
A.6	Thermodynamic parameters for Ni ²⁺ ions adsorption	213
A.7	Comparison of composite adsorption capacity with other adsorbents . . .	214

List of Abbreviations

AAS	Atomic Absorption Spectrophotometer
ACGIH	American Conference of Governmental Industrial Hygienists
AC/ACTG	Activated carbon derived from <i>Tectona grandis</i>
ANN	Artificial Neural Network
ASTM	American Society for Testing and Materials
ATA	Azadirachta indica Twig Ash
ATSDR	Agency for Toxic Substances and Disease Registry
BET	Brunauer–Emmett–Teller
BIS	Bureau of Indian Standards
CPCB	Central pollution Control Board
Cu	Copper
D-R	Dubinin–Radushkevich
DTG	Derivative Thermogravimetry
ECEF	Electrocoagulation-Electroflotation
EDX	Energy-dispersive X-ray spectroscopy
F	Feldspar
FTIR	Fourier-transform infrared spectroscopy

FWHM	Full Width at Half Maxima
I	Illite
IARC	International Agency for Cancer Research
ICMR	Indian Council of Medical Research
L-M	Levenberg-Marquardt
M	Montmorillonite
MSE	Mean Square Error
MT	Metallothionein
Ni	Nickel
NTP	National Toxicology Program
OFI	Opuntia Ficus-indica
PIO	Pseudo First Order
PSO	Pseudo Second Order
Q	Quartz
Q	Reactive Oxygen Species
RSM	Response Surface Methodology
SEM	Scanning Electron microscopy
SRT	Statistical Rate Theory
TG	<i>Tectona grandis</i> Sawdust
TGA	Thermogravimetric analysis
USA	The United States of America
USEPA	United States Environmental Protection Agency
WHO	World Health Organization

LIST OF ABBREVIATIONS

XRD X-ray Diffraction

ZiP Zinc Importer

Zn Zinc

ZnT Zinc Transporter