

**REMOVAL OF LEAD, CADMIUM AND NICKEL BY SAWDUST-
MODIFIED TROPICAL CLAY FOR USE AS LANDFILL LINER
MATERIAL**

By

AKINWUMI, ISAAC IBUKUN

Matric. Number: CUGP080208

July, 2017

**REMOVAL OF LEAD, CADMIUM AND NICKEL BY SAWDUST-
MODIFIED TROPICAL CLAY FOR USE AS LANDFILL LINER
MATERIAL**

By

AKINWUMI, ISAAC IBUKUN
B.Eng. Civil Engineering (Akure)
M.Eng. Civil Engineering (Ota)
Matric. Number: CUGP080208

A THESIS SUBMITTED TO THE DEPARTMENT OF CIVIL
ENGINEERING, COLLEGE OF ENGINEERING, COVENANT
UNIVERSITY, OTA, OGUN STATE, NIGERIA IN PARTIAL
FULFILMENT OF THE REQUIREMENTS FOR THE AWARD OF
DOCTOR OF PHILOSOPHY (Ph.D) DEGREE IN CIVIL
ENGINEERING

July, 2017

ACCEPTANCE

This is to attest that this thesis is accepted in partial fulfilment of the requirements for the award of the degree of Doctor of Philosophy in Civil Engineering in the Department of Civil Engineering, College of Engineering, Covenant University, Ota.

Philip John Ainwokhai

(Secretary, School of Postgraduate Studies)

.....

Signature & Date

Professor Samuel T. Wara

(Dean, School of Postgraduate Studies)

.....

Signature & Date

DECLARATION

I, **AKINWUMI, ISAAC IBUKUN** (CUGP080208), declare that this research was carried out by me under the supervision of Dr. Oluwapelumi O. Ojuri of the Department of Civil and Environmental Engineering, Federal University of Technology Akure and Dr. Adebajji S. Ogbiye of the Department of Civil Engineering, Covenant University, Ota. I attest that the thesis has not been presented either wholly or partly for the award of any degree elsewhere. All sources of data and scholarly information used in this thesis are duly acknowledged.

AKINWUMI, ISAAC IBUKUN

.....

Signature & Date

CERTIFICATION

We certify that this thesis titled “Removal of Lead, Cadmium and Nickel by Sawdust-modified Tropical Clay for use as Landfill Liner Material” is an original work carried out by AKINWUMI, ISAAC IBUKUN (CUGP080208), in the Department of Civil Engineering, College of Engineering, Covenant University, Ota, Ogun State, Nigeria, under the supervision of Dr. Oluwapelumi O. Ojuri and Dr. Adebajji S. Ogiye. We have examined and found the work acceptable as part of the requirements for the award of Doctor of Philosophy (Ph.D) degree in Civil Engineering (Geotechnical Engineering Option).

Dr. Oluwapelumi O. Ojuri
(Supervisor) Signature & Date

Dr. Adebajji S. Ogiye
(Co-Supervisor) Signature & Date

Dr. David O. Olukanni
(Head of Department) Signature & Date

Professor Emmanuel A. Okunade
(External Examiner) Signature & Date

Professor Samuel T. Wara
(Dean, School of Postgraduate Studies) Signature & Date

DEDICATION

This research work is dedicated to the Producer of the ‘movie’ of my life, the Ultimate Deliverer, the Way Maker, the Capable One, the King over all storms, the All Sufficient One, the Father of the fathers and the Father to the fatherless, the Great Provider, the Ever-loving One, the Never-erring but Forgiver of all sins, and the Timeless One that is always right on time - the Almighty God.

ACKNOWLEDGEMENTS

The Almighty God preserved, strengthened, and blessed me during this research work. He directed people and organisations to provide support to me during the course of this study. I give HIM all the glory.

My profound appreciation goes to the Chancellor and Chairman of the Board of Regents, Covenant University, Dr. D. O. Oyedepo, for the academic and spiritual platform created. I sincerely thank the Vice-Chancellor, Professor A. A. A. Atayero and all the management team for running with the vision. I also appreciate the leadership of the School of Postgraduate Studies led by Professor S. T. Wara and Dr. A. H. Adebayo.

My heartfelt gratitude goes to my Supervisor, Dr. O. O. Ojuri for promoting “this product” and for his invaluable contributions, support, kindness, patience, and understanding. My co-supervisor, Dr. A. S. Ogbiye, deserve outstanding commendations for his fatherly support, time, prayers and advice.

Many thanks to Dr. D. O. Olukanni (HoD, Civil Engineering) for his advice and support towards the completion of my Ph.D programme, and to all Faculty and Staff of Civil Engineering Department, Covenant University for their support and encouragement. I, particularly, appreciate the contributions of Professor J. Akinmusuru, Dr. D. O. Omole, Dr. A. N. Ede, Dr. B. U. Ngene (Outstanding Postgraduate Coordinator), Engr. J. K. Jolayemi, Mr. G. A. Adeyemi, Mr. B. Durodola, Mr. A. O. Adeyemi and Mr. N. Akhiregbu.

The Commonwealth Scholarship Commission in the United Kingdom provided me the opportunity to undertake one-year Split-Site Ph.D programme at the University of the West of England (UWE), Bristol, United Kingdom (UK). I am grateful to Professor C. A. Booth, my host Supervisor at UWE, for his guidance, friendliness, support and leadership. The Volkswagen Foundation provided me a travel grant that facilitated the presentation of part of my research work at the Engineering and Life Conference held in Hannover, Germany.

The scholarly contributions of my Ph.D defence external examiner (Professor Emmanuel A. Okunade) and external assessors are invaluable and well appreciated. I also express my appreciation to my internal assessor - Professor James A. Omoleye and my examiners from the proposal stage to Ph.D Oral defence: Dr. Uwalomwa Uwuigbe,

Dr. Oluseyi O. Ajayi, and Dr. Oyinkepreye D. Orodu. May God satisfy all your heart desires, according to His perfect will.

Many thanks to my great mother, Mrs. Beatrice Akinwumi, for her sacrificial contribution to my basic and undergraduate education – which is the foundation on which my postgraduate education stands. My in-laws and my younger brother, Dr. Alex Akinwumi, deserves commendation for their support to my family during my one-year Split-site programme. I am grateful to Dr. I. Ayanda, Dr. I. Omuh, Dr. R. Loto and Dr. O. Ajani for their support and encouragement throughout this study.

My sincere gratitude goes to my supportive wife of priceless value and best friend, Hannah Akinwumi. Thank you for your immense sacrifice, prayers and understanding, especially when I was away in the UK for the Split-site programme. To my children - Anna, Samuel and Elijah – thank you for sparing me part of the time we should have used to play together.

I would also like to say a big thank you to all those, whose names I may have unintentionally omitted. God bless you all.

TABLE OF CONTENTS

ACCEPTANCE	iii
DECLARATION	iv
CERTIFICATION	v
DEDICATION	vi
ACKNOWLEDGEMENTS	vii
LIST OF TABLES	xiii
LIST OF PLATES	xv
LIST OF FIGURES	xvi
LIST OF ABBREVIATIONS AND ACRONYMS	xix
ABSTRACT	xxi
CHAPTER ONE	1
INTRODUCTION	1
1.1 Background to the study	1
1.2 Statement of the problem	2
1.3 Aim and objectives	3
1.4 Scope of the study	3
1.5 Justification for the study	4
1.6 Structure of thesis	5
1.7 Chapter summary	7
CHAPTER TWO	8
LITERATURE REVIEW	8
2.1 Introduction	8
2.2 Waste disposal and landfill	8
2.2.1 Landfill	11
2.2.2 Landfill design, structure and management	15
2.3 Heavy metals	18

2.3.1 Heavy metal pollution	19
2.3.2 Effects of heavy metal pollution on human health	20
2.3.3 Reducing or removing heavy metals	21
2.4 Biosorption	22
2.5 Adsorption	23
2.6 Sorption of heavy metals using agricultural waste products	28
2.6.1 Rice husk	28
2.6.2 Waste fruit residue and tree barks	29
2.6.3 Sawdust	30
2.7 Sorption of heavy metals using earth materials	31
2.7.1 Natural zeolite	31
2.7.2 Lava particles	31
2.7.3 Natural soils	31
2.7.4 Bentonite	32
2.8 Clays and clay minerals	33
2.9 Hydraulic conductivity of soils	38
2.10 Landfill liner	38
2.11 Research approach	41
2.12 Chapter summary	42
CHAPTER THREE	43
METHODOLOGY	43
3.1 Introduction	43
3.2 Research design	43
3.2.1 Research question	43
3.2.2 Research approach	44
3.3 Materials and preparation	44
3.3.1 Soil collection, preparation and storage	46

3.3.2 Bentonite	48
3.3.3 Sawdust	48
3.4 Methods	49
3.4.1 Chemical composition of the samples	49
3.4.2 Geotechnical Properties of Samples	50
3.4.3 Hydraulic conductivity	50
3.4.4 Sorption of heavy metals	53
3.5 Data analysis	57
3.6 Chapter summary	57
CHAPTER FOUR	58
RESULTS AND DISCUSSION	58
4.1 Introduction	58
4.2 Chemical and mineralogical composition	58
4.3 Geotechnical properties	62
4.3.1 Sawdust modification of the clay	62
4.3.2 Sawdust modification of the bentonite	73
4.4 Adsorption of lead	82
4.4.1 Adsorption of Pb^{2+} by clay and sawdust-modified-clay	82
4.4.2 Adsorption of Pb^{2+} by bentonite and sawdust-modified-bentonite	94
4.5 Adsorption of cadmium	105
4.5.1 Adsorption of Cd^{2+} by clay and sawdust-modified-clay	105
4.5.2 Adsorption of Cd^{2+} by bentonite and sawdust-modified-bentonite	116
4.6 Adsorption of nickel	127
4.6.1 Adsorption of Ni^{2+} by clay and sawdust-modified-clay	127
4.6.2 Adsorption of Ni^{2+} by bentonite and sawdust-modified-bentonite	138
4.7 Further discussion and comparison of results	149
4.7.1 Adsorption isotherm	155

4.7.2 Adsorption kinetics	158
4.8 Chapter summary	160
CHAPTER FIVE	161
CONCLUSION AND RECOMMENDATIONS	161
5.1 Introduction	161
5.2 Conclusion	161
5.3 Contributions to the body of knowledge	163
5.4 Recommendations	163
5.4.1 Recommendations for landfill liner designers	163
5.4.2 Recommendations for policy-makers	164
5.4.3 Recommendation for future research	164
REFERENCES	165
APPENDICES	184
Appendix A: Natural moisture content	185
Appendix B: Specific gravity	187
Appendix C: Atterberg limits	191
Appendix D: Compaction characteristics	195
Appendix E: Unconfined compressive strength	199
Appendix F: Permeability	201
Appendix G: Adsorption isotherm models	204
Appendix H: Adsorption kinetic models	208

LIST OF TABLES

Table 2.1: Available options for waste disposal on land	10
Table 4.1: Geotechnical properties of the clay	63
Table 4.2: Geotechnical properties of the bentonite	74
Table 4.3: Pb ²⁺ adsorption parameters values for the adsorption isotherms of the clay and sawdust-modified-clay	89
Table 4.4: Kinetic parameters values for the adsorption of Pb ²⁺ by the clay and sawdust-modified-clay	91
Table 4.5: Pb ²⁺ adsorption parameters values for the adsorption isotherms for bentonite and sawdust-modified-bentonite	100
Table 4.6: Kinetic parameters values for the adsorption of Pb ²⁺ onto the Bentonite and sawdust-modified-bentonite	102
Table 4.7: Cd ²⁺ adsorption parameters values for the adsorption isotherms of the clay and sawdust-modified-clay	111
Table 4.8: Kinetic parameters values for the adsorption of Cd ²⁺ by the clay and sawdust-modified-clay	113
Table 4.9: Cd ²⁺ adsorption parameters values for the adsorption isotherms for bentonite and sawdust-modified-bentonite	122
Table 4.10: Kinetic parameters values for the adsorption of Cd ²⁺ by the bentonite and sawdust-modified-bentonite	124
Table 4.11: Ni ²⁺ adsorption parameters values for the adsorption isotherms of the clay and sawdust-modified-clay	133
Table 4.12: Kinetic parameters values for the adsorption of Ni ²⁺ by the clay and sawdust-modified-clay	135
Table 4.13: Ni ²⁺ adsorption parameters values for the adsorption isotherms for bentonite and sawdust-modified-bentonite	144
Table 4.14: Kinetic parameters values for the adsorption of Ni ²⁺ by the bentonite and sawdust-modified-bentonite	146
Table 4.15: Pb, Cd and Ni adsorption capacities of the clay, bentonite and their modification with 8% sawdust	152

Table 4.16: Comparison of metal adsorption capacities of the adsorbents using t-test	154
Table 4.17: Pb ²⁺ adsorption capacities of the clay and sawdust-modified-clay compared with those of similar studies	156
Table 4.18: Adsorption parameters values for the adsorption isotherms	157
Table 4.19: Kinetic parameters values for the adsorption of the metal ions by the adsorbents	159

LIST OF PLATES

Plate 3.1: The tropical clay deposit at the floor of the borrow pit	47
Plate 3.2: The clay samples excavated from the deposit	47

LIST OF FIGURES

Figure 1.1: The thesis structure showing the chapter where the objectives were achieved	6
Figure 2.1: Waste hierarchy designed to minimize waste	9
Figure 2.2: Percentage of population in regions of the world without access to regular collection and sound disposal of solid waste	13
Figure 2.3: Typical engineered landfill	14
Figure 2.4: Difference between absorption and adsorption	24
Figure 2.5: Structure of silica tetrahedron and aluminum octahedron	35
Figure 2.6: Structure of silicate and alumina sheets	36
Figure 2.7: Structure of kaolinite, illite and montmorillonite	37
Figure 3.1: Materials collection, preparation, laboratory analysis and data analysis	45
Figure 3.2: Geotechnical characterization of clay and bentonite with repeated measurements to increase scientific validity of results	52
Figure 3.3: Sampling for batch adsorption tests	54
Figure 4.1: Oxides of the: (a) clay, and (b) bentonite	59
Figure 4.2: X-ray diffraction pattern of the clay	61
Figure 4.3: Particle size distribution of the clay	63
Figure 4.4: Variation of specific gravity of the clay with sawdust	65
Figure 4.5: Variation of Atterberg limits of the clay with sawdust	66
Figure 4.6: Variation of compaction characteristics of the clay with sawdust	68
Figure 4.7: Variation of UCS of the clay with sawdust	69
Figure 4.8: Variation of permeability of the clay with sawdust	71
Figure 4.9: SEM morphology of the clay: (a) without sawdust; (b) with 8% sawdust	72
Figure 4.10: Variation of specific gravity of the bentonite with sawdust	74
Figure 4.11: Variation of Atterberg limits of the bentonite with sawdust	76

Figure 4.12: Variation of compaction characteristics of the bentonite with sawdust	77
Figure 4.13: Variation of UCS of the bentonite with sawdust	79
Figure 4.14: Variation of permeability of the bentonite with sawdust	80
Figure 4.15: SEM morphology of the: (a) unmodified bentonite; and (b) 8% sawdust-modified-bentonite	81
Figure 4.16: Pb adsorption with contact time for varying initial Pb^{2+} concentrations for the clay	84
Figure 4.17: Pb adsorption with contact time for varying initial Pb^{2+} concentrations for the sawdust-modified-clay	85
Figure 4.18: Effect of initial Pb^{2+} concentration on the Pb^{2+} uptake by the clay and sawdust-clay mixture	87
Figure 4.19: Weber and Morris model for adsorption of Pb^{2+} by: (a) clay without sawdust; (b) sawdust-modified-clay	93
Figure 4.20: Pb adsorption with contact time for varying initial Pb^{2+} concentrations for the bentonite	95
Figure 4.21: Pb adsorption with contact time for varying initial Pb^{2+} concentrations for the sawdust-modified-bentonite	96
Figure 4.22: Effect of initial Pb^{2+} concentration on the Pb^{2+} uptake by the bentonite and sawdust-modified-bentonite	98
Figure 4.23: Weber and Morris model for adsorption of Pb^{2+} by the: (a) bentonite; and (b) sawdust-modified-bentonite	104
Figure 4.24: Cd^{2+} adsorption with contact time for varying initial Cd^{2+} concentrations for the clay	106
Figure 4.25: Cd adsorption with contact time for varying initial Cd^{2+} Concentrations for the sawdust-modified-clay	107
Figure 4.26: Effect of initial Cd^{2+} concentration on the Cd^{2+} uptake by the clay and sawdust-modified-clay	109
Figure 4.27: Weber and Morris model for adsorption of Cd^{2+} onto: (a) clay without sawdust; (b) clay with sawdust	115
Figure 4.28: Cd adsorption with contact time for varying initial Cd^{2+} concentrations for the bentonite	117

Figure 4.29: Cd adsorption with contact time for varying initial Cd ²⁺ concentrations for the sawdust-modified-bentonite	118
Figure 4.30: Effect of initial Cd ²⁺ concentration on the Cd ²⁺ uptake by the bentonite and sawdust-modified-bentonite	120
Figure 4.31: Weber and Morris model for adsorption of Cd ²⁺ by the: (a) bentonite; (b) sawdust-modified-bentonite	126
Figure 4.32: Ni ²⁺ adsorption with contact time for varying initial Ni ²⁺ concentrations for the clay	128
Figure 4.33: Ni adsorption with contact time for varying initial Ni ²⁺ concentrations for the sawdust-modified-clay	129
Figure 4.34: Effect of initial Ni ²⁺ concentration on the Ni ²⁺ uptake by the clay and sawdust-modified-clay	131
Figure 4.35: Weber and Morris model for adsorption of Ni ²⁺ by the: (a) clay without sawdust; (b) clay with sawdust	137
Figure 4.36: Ni adsorption with contact time for varying initial Ni ²⁺ concentrations for the bentonite	139
Figure 4.37: Ni adsorption with contact time for varying initial Ni ²⁺ concentrations for the sawdust-modified-bentonite	140
Figure 4.38: Effect of initial Ni ²⁺ concentration on the Ni ²⁺ uptake by the bentonite and sawdust-modified-bentonite	142
Figure 4.39: Weber and Morris model for adsorption of Ni ²⁺ onto: (a) bentonite; (b) bentonite with sawdust	148
Figure 4.40: Recommended composite liner comprising sawdust-modified-clay	151

LIST OF ABBREVIATIONS AND ACRONYMS

AAS:	Atomic Absorption Spectrometer
As:	Arsenic
BS:	British Standards
BSI:	British Standard Institution
Cd:	Cadmium
CH:	Clay of high plasticity
CL:	Clay of low plasticity
Co:	Cobalt
Cr:	Chromium
Cu:	Copper
Fe:	Iron
FEPA:	Federal Environmental Protection Agency
MDUW:	Maximum Dry Unit Weight
ML:	Silt of low plasticity
Mn:	Manganese
Mo:	Molybdenum
Ni:	Nickel
OMC:	Optimum Moisture Content
Pb:	Lead
SC:	Sandy clay
SEM:	Scanning Electron Microscopy
SM:	Sandy silt

UCS: Unconfined Compressive Strength

USCS: Unified Soil Classification System

US EPA: United States Environmental Protection Agency

WHO: World Health Organisation

XRD: X-ray diffractometer

XRF: X-ray fluorescence spectroscopy

Zn: Zinc

ABSTRACT

Access to groundwater, a major source of direct drinking water in many developing countries, should not be assumed as access to safe drinking water. There is a need to prevent or minimize the contamination of groundwater, especially arising from solid waste disposal. This research work investigated the suitability of using clay and bentonite modified with sawdust as landfill liner materials for minimizing the migration of Pb^{2+} , Cd^{2+} and Ni^{2+} in order to protect the environment and public health. Series of laboratory tests were carried out to determine the chemical and mineralogical composition, microstructural analysis of the clay and bentonite in order to characterize the samples. The effects of adding varying percentages of sawdust to the clay and bentonite on their geotechnical properties were determined. The removal of each of Pb^{2+} , Cd^{2+} and Ni^{2+} by the clay, bentonite, sawdust-modified-clay and sawdust-modified-bentonite was investigated using the batch equilibrium adsorption technique for varying initial metal ion concentrations and contact times, while the pH, adsorbent dosage and temperature were kept constant. Results obtained show that the application of up to 8% sawdust to the clay satisfies standard geotechnical properties requirements for use as clay landfill liner, whereas the bentonite and its modification with sawdust did not. Each of the sawdust-modified-clay and sawdust-modified-bentonite removed more Pb^{2+} , Cd^{2+} and Ni^{2+} than the clay and bentonite without sawdust, respectively. The Dubinin-Radushkevich model was found to be the best adsorption isotherm that described the Pb^{2+} , Cd^{2+} and Ni^{2+} adsorption by the sawdust-modified-clay, while the pseudo-second-order kinetic model best described the rate of adsorption of these metal ions by the sawdust-modified-clay. The adsorption by the modified clay can be described as physical adsorption due to weak van der Waals forces. The order of removal of the metals by the clay and sawdust-modified-clay followed a trend of $Pb^{2+} > Cd^{2+} > Ni^{2+}$, while that of bentonite and sawdust-modified-bentonite followed a trend of $Pb^{2+} > Ni^{2+} > Cd^{2+}$. The clay and sawdust-modified-clay removed Pb^{2+} and Cd^{2+} better than the bentonite and sawdust-modified-bentonite, respectively, while the bentonite removed Ni^{2+} better than the clay. Clay modified with sawdust was found suitable and recommended for use as a landfill liner material in a composite lining system, thereby providing a low-cost and sustainable approach to improving the capacity of the clay to minimize the migration of Pb^{2+} , Cd^{2+} and Ni^{2+} from landfills, and protecting the environment (particularly groundwater resources) and public health.

Keywords: Adsorption; Environment; Groundwater pollution; Heavy metals; Sustainability; Waste management