KTH Sustainable Development,
Environmental Science and Engineering

Equilibrium and Kinetic Batch Studies of Cadmium and Lead sorption using Low Cost Biosorbents

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Dedication

To my sister and best friend who passed on during the course of these studies; Mrs Jessica Jaafa. Baaba Jessica you were a real big sister who showed me love and care. You inspired me to strive hard and achieve the best in life. The memory of your relationship remains fresh in my mind all the time. *I beseech the Almighty to rest thy soul in eternal peace.*

Summary

The trace metals cadmium and lead are contaminants that have detrimental health effects on life support systems when chronic exposure to minute quantities in environmental matrices occurs. They adsorb onto soil particles and soil organic matter which increases their retention and reduces their transmission to the soil water. When the soil is overladen or when the soil pH is lowered, trace metals vertical mobility increases and contamination of groundwater occurs through the soil solution. Conventional remediation techniques are available for reducing trace metal contaminants in effluents, wastewater, leachates, surface runoff, surface water and groundwater to allowable levels and to ensure adherence to water quality standards. The conventional remediation techniques have high installation and operational costs besides sludge disposal hazards and non-selectivity for trace metals whereas biosorption studies have shown biosorbents to be effective remediation alternatives for trace metals in minute concentrations. Studies were done to characterize and evaluate the efficiency besides the effectiveness of application of local biosorbents in remediation of selected trace metals in contaminated water. The agricultural wastes; *Albizia coriaria, Erythrina abyssinica, Coffea canephora, Cyperus papyrus* and *Musa spp.* were selected for preparation of biosorbents. Chemical treatment of biosorbents was done using sodium hydroxide and hydrogen peroxide. The characterisation of biosorbents was done using ICP-MS for inorganic contents and XRD for the surface structural constituents. The contaminated water was prepared by diluting AAS standard solutions of cadmium and lead containing 1000 mg/L to required concentrations using distilled deionized water. Equilibrium and kinetic batch studies were done to evaluate biosorbent remediation of aqueous cadmium and lead. The treated water was analysed for DOC and residual trace metal ions using the TOC analyser and ICP-MS respectively. The experimental data were fitted to kinetic models and equilibrium isotherm models. Results in these studies showed that sodium hydroxide treatment enhanced sorption intensity of the biosorbents better than peroxide treatment. A pseudo-second-order kinetic model and the Langmuir isotherm provided good fits to the biosorption data. The underlying reaction mechanism was mainly chemisorption and was potentially monolayer. The studied materials were promising candidates for the biosorption of aqueous cadmium and lead in single component solutions but preferential sorption of Pb^{2+} ions during competitive biosorption from mixed metal solutions indicated high affinity for Pb^{2+} ions and weaker selectivity for Cd^{2+} ions in binary component media. Additional thermodynamic and column studies to determine the most appropriate operational conditions should be the focus of further research. Furthermore speciation studies of treated water will be done using Visual MINTEQ in order to determine the distribution of metal ions in the organic and inorganic phases of the aqueous media and to evaluate the quantities of trace metals that may pause danger to environmental health.

Acknowledgements

Deus gratias ago tibi, quia mihi contulisti tibi hoc donum.

Benedicat te Deus in aeternum.

x

List of papers appended

This thesis is based on the following papers referred to as Articles I to III:

I.   G. K. Bakyayita, A. C. Norrström., M. Nalubega & R. N. Kulabako, 2014. Kinetic studies of Cd (II) and Pb (II) ions biosorption from aqueous media using untreated and chemically treated biosorbents. *Journal of Water Science and Technology (In production DOI: 10.21.2166/wst.2014.147)*

II.   Bakyayita, G., Nalubega, M., Norrström, A. & Kulabako, R., 2014. Single and binary biosorption kinetics for cadmium (II) and lead (II) ions from aqueous media using Coffea canephora, Cyperus papyrus and Musa spp. *(Manuscript).*

III.   Bakyayita, G., Kulabako, R., Nalubega, M. & Norrström, A., 2014. Equilibrium batch studies for biosorption of Cd (II) and Pb (II) ions from single-and binary-component aqueous media *(Manuscript).*

These papers are appended at the end of this thesis.

Author's contributions

Article I: The author was the principal author, did planning and design of the experiments, most of the experimental work and analyses.

Article II: The author was the principal author, did planning and design of the experiments, most of the experimental work and analyses.

Article III: The author was the principal author, did planning and design of the experiments, most of the experimental work and analyses.

TABLE OF CONTENTS

Abbreviations and symbols

AAS	-	Atomic absorption spectrometry
EPA	-	Environmental Protection Agency
DOC	-	Dissolved organic carbon
ICP-MS	-	Inductively coupled plasma-mass spectrometry
ICP-OES	-	Inductively coupled plasma-optical emission spectrometry
rpm	-	revolutions per minute
SOGs	-	Surface oxygen groups
TIC	-	Total inorganic carbon
TOC	-	Total organic carbon
WHO	-	World Health Organisation
XRD	-	X-ray diffraction

Abstract

Agricultural wastes; *Albizia coriaria, Coffea canephora, Cyperus papyrus, Erythrina abyssinica* and *Musa spp* were evaluated for uptake of aqueous Cd^{2+} and Pb^{2+} ions in single- and binary-component solutions. Untreated, base-treated and peroxide-treated biomasses were employed in batch studies. The optimal conditions for Cd^{2+} and Pb^{2+} ions biosorption were pH 3.5 – 5 for contact time 3.0 – 3.5 hours and biosorbent dosage 10 – 12.5 g/L. Base-treated biosorbents showed a 10 – 17 % sorption enhancement for Cd^{2+} ions and a 1.6 – 2.3 % uptake reduction for Pb^{2+} ions. The sorption capacities for Cd^{2+} and Pb^{2+} ions for base-treated biosorbents were between 1.738 and 1.760 mg g^{-1} compared to 1.415 – 1.539 mg g^{-1} for untreated materials. The maximum biosorption of peroxide treated materials in single component media was between 0.819 and 1.595 mg/g for Pb^{2+} ions and between 0.044 and 1.343 mg/g for Cd^{2+} ions while in binary component media it was between 0.472 and 1.303 mg/g for Pb^{2+} ions and between 0.008 and 0.195 mg/g for Cd^{2+} ions. The pseudo-second order kinetic model suitably fitted the Cd^{2+} and Pb^{2+} ions biosorption data with regression coefficients (R^2); 0.892 – 1.000 for peroxide-treated materials and 0.9784 – 0.9999 for base-treated biosorbents which implied that the biosorption was mainly a chemisorption process. The base treated biosorbents had better sorption performance for Cd^{2+} ions than peroxide treated materials and untreated biomass whereas the order for Pb^{2+} ions biosorption was untreated > base treated > peroxide treated materials. All materials showed superior selectivity for Pb^{2+} ions biosorption in comparison to that of Cd^{2+} ions in single- and binary-component media. *A. coriaria* performed best of the base treated biosorbents while *C. canephora* performed best amongst peroxide treated materials for Cd^{2+} and Pb^{2+} ions biosorption in single-and binary-component media. In the competitive biosorption, Cd^{2+} ions showed higher synergistic effects than Pb^{2+} ions although Pb^{2+} ions were preferentially sequestered even when the Cd^{2+}:Pb^{2+} ions ratio was increased through 3:2, 2:1, 3:1 and 5:1. Of the three isotherm models evaluated against the experimental data, the Langmuir model generally fitted the sorption data for both metals. Regression coefficients for the Langmuir model were; 0.983 ≤ R^2 ≥ 1.000 for single-component and 0.939 ≤ R^2 ≥ 1.000 for binary-component solutions which revealed that the biosorption was potentially monolayer. The biosorption equilibrium coefficient K_c values and change in Gibbs' free energy ΔG^0 values showed that Pb^{2+} ions biosorption was more thermodynamically favoured than that of Cd^{2+} ions in single-component and binary-component media. The materials studied displayed potential for use as biosorbents for remediation of aqueous Cd^{2+} and Pb^{2+} ions.

Key words: biosorbents, cadmium, chemisorption, isotherms, kinetics, lead

INTRODUCTION

The increased urbanization, industrialisation, socio-economic and demographic developments in the developing countries have augmented anthropogenic contamination of the environment with trace metals which has had consequential negative impacts on environmental health. Trace metals have been released excessively onto soil, water and air superseding their natural remediation from various matrices by wetlands, plants and soils which has resulted into a major global environmental concern. Of all environmental matrices receiving trace metal contaminants, water is very sensitive since the global availability of usable freshwater is just 200,000 km^3. Moreover water quality is very difficult and costly to reverse to pristine and usable conditions when it deteriorates (Article II).

Trace metals and their health effects

The anthropogenic sources of trace metal contaminants include industrial wastes, wastewater, surface runoff, municipal and domestic waste that accumulate due to lack of proper handling, disposal and recycling systems let alone the inappropriate remediation methods used. Trace metal contaminants are divided into two groups; the essential metals have known biological roles while the non-essential metals have known toxicity to life processes. Trace metals such as cadmium, lead, mercury, copper and zinc are regarded as serious pollutants of aquatic ecosystems due to their environmental persistence, toxicity and ability to be incorporated into food chains (Kishe & Machiwa, 2003).

In this study, the non-essential trace metals; cadmium and lead that are listed amongst the hazardous metals were studied. Cadmium is a hazardous trace metal that threatens toxicity to life support systems and poses detrimental health effects after chronic exposure to low levels in the environment. The notable health risks of chronic or acute exposure to cadmium include; interference with regulation of zinc and copper in the body, growth retardation, bone deformation, testicular atrophy, hypertension and cancer (Krishnani & Ayyapan, 2006). On the other hand, lead shows toxicity effects to both plants and animals. Lead contamination is of great concern since even when the blood lead levels are below 80 µg dL^{-1} above which clinical symptoms of lead toxicity are manifested; it may cause mental impairment in children (Bearer, 2000). Lead toxicity has been linked to effects such as nervous system disorders (Needleman, 1991), anaemia, loss of appetite, high blood pressure, convulsions (Krishnani & Ayyapan, 2006), disorders in bone metabolism and cardiovascular disease.

Remediation of trace metals

Conventional methods for remediation of trace metals contaminated water include chemical precipitation, ion exchange, electrodialysis, solvent extraction, adsorption, membrane separation and reverse osmosis (Leppert, 1990; Yang & Lin, 1998). Due to issues regarding conventional remediation methods such as high installation and operation costs, inefficiency and non-selective sequestration of trace metals in minute concentrations, alternative low cost remediation methods have been extensively studied in recent decades. Due to their abundance in nature biosorbents have been studied as low-cost sorbent materials for removal of trace metal contaminants from aqueous media. Biosorbents have shown high efficiency in sorption of trace metals with minimal chemical besides biological contamination, can be regenerated and have high desorption capacities (Guo, et al., 2008; Pagnanelli, et al., 2003; Conrad, et al., 2007; Patnukao, et al., 2008) moreover they are abundant in nature. The lignocellulosic biosorbents' sorption efficiency and effectiveness has been attributed to various functional groups in the structural components that are active sites for trace metal ions adsorption as argued by Maranon and Demirbas (1992). Lignocellulosic materials are very porous and have high free surface volume that allows accessibility (Rowell, 2006) of aqueous solutions to the biosorbent cell wall components.

Biosorption studies

In the trace metals biosorption studies, biosorbent materials have been used in both modified and unmodified forms. Unmodified biosorbents that have been studied include among others; leaves (Babarinde, et al., 2006; Hanafiah, et al., 2007; King, et al., 2006; Sawalha, et al., 2007; Kumar & Gayathri, 2009), husks and hulls (Bhattacharya, et al., 2006; Johnson, et al., 2002; Tarley, et al., 2004; Ahalya, et al., 2006), peels (Amarasinghe & Williams, 2007; Feng, et al., 2011; Foo, et al., 2011; Kaewsam, et al., 2008), barks (Horsfall Jr, et al., 2006; Masri, et al., 1974) and sawdust (Bulut & Tez, 2003; Taty-Costodes, et al.,

2003). In several studies involving unmodified biosorbents, both good adsorptive capacities and trace metal recoveries through desorption studies have been reported in literature. These characteristics give biosorbent remediation techniques an edge over conventional remediation techniques where spent adsorption materials' disposal poses environmental challenges. In other studies biosorbents have been modified using base solutions (Kumar & Bandyopadhyay, 2006; Memon, et al., 2007; Min, et al., 2004) oxidizing agents (Ganji, et al., 2005; Horsfall Jr. & Spiff, 2005) and, organic and mineral acids (Wong, et al., 2003; Özer & Pirincci, 2006; Taty-Costodes, et al., 2003; Bulut & Tez, 2003; Li, et al., 2006; Horsfall Jr, et al., 2006) to enhance adsorption capacities for trace metal ions as well as to reduce soluble organics transfer to the liquid phase. Different modification chemical and physical methods are known to improve the sorption properties of the biosorbents to varying degrees. In most cases, modified biosorbents perform better than the unmodified materials due to the increased number of metal ions binding sites; surface oxygen groups (Chen & Wu, 2004; Zhao, et al., 2005), improved surface and ion exchange properties.

Biosorbents of plant origin tend to release soluble organics which impacts on the remediated water quality when unmodified biosorbents are employed to remediate contaminated aqueous media. Soluble organic matter has both advantages and disadvantages; they form complexes with metals in the liquid phase which are less toxic than the free ions but increase the mobility of metals in the environment. In spite of the importance of dissolved organics in biosorption, only few studies have considered their effects in the liquid phase although Gaballah, et al., 1997 and Bailey, et al., 1999 suggested an interaction of soluble organics and metal ions. Studies that include the release and effects of soluble organics in treated aqueous media are limited. The soluble organics are extractable with chemicals such as hot water, sodium hydroxide; diethyl ether and ethanol (Browning, 1967; Rowell, 2006). The polar solvents (water, ethanol) dissolve polar substances from the biosorbents such as the phenolics and tannins whereas the non-polar solvents such as diethyl ether dissolve the non-polar substances such as fats and waxes.

Objectives

The main objective of this study was to characterize and evaluate the potential of low-cost agricultural wastes; *Albizia coriaria, Coffea canephora, Cyperus papyrus, Erythrina abyssinica* and *Musa spp* as filter media in removing Cd $^{2+}$ and Pb $^{2+}$ ions from contaminated aqueous media.

The specific objectives of the study were to;

i.   Identify and select agricultural waste materials for preparation of biosorbents to remove trace metal ions from contaminated water,

ii.   Characterize biosorbent filter media in order to determine the constituent organic and inorganic species responsible for biosorption of trace metal ions,

iii. Evaluate the biosorption potential for aqueous Cd $^{2+}$ and Pb $^{2+}$ ions under varying contact time, pH, in single metal and multi-metal aqueous media and

iv.   to analyse the biosorption efficiency through speciation studies on treated water.

METHODS

The choice of biosorbents

Waste plant materials that normally have little or no reuse are peels, husks, cuttings and barks which accumulate as an urban waste burden after the useful products such as timber, food and herbal medicine have been removed. Although waste plant materials are quite varied in chemical structure, they have attracted a lot of research for application as low cost biosorbents for remediation of trace metals in contaminated aqueous media.

| *C. papyrus* | *C. canephora* | *A. coriaria* | *E. abyssinica* | *Musa spp* |
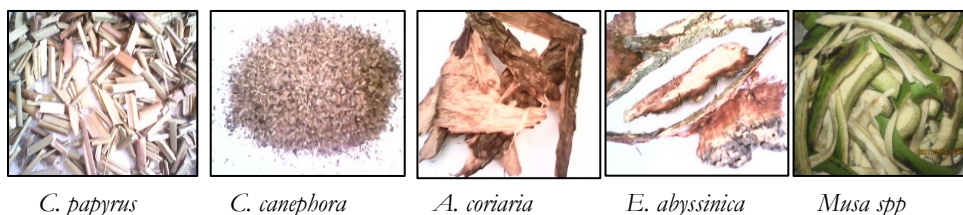
Figure 1 *The plant materials used in these studies to prepare biosorbents*

Plant materials; peels of *Musa spp* (cooking bananas), *Cyperus papyrus* cuttings, husks of *Coffea canephora*, the barks of *Erythrina abyssinica* and *Albizia coriaria* shown in Fig. 1 were sampled from a rural farming district in Uganda and used in this study to prepare biosorbents.

In 2011 Uganda was ranked as the second largest producer of bananas in the world with 11.1 million tonnes (Wikipedia contributors, 2014). Uganda is not amongst the reknowned exporters because in most parts of the country, bananas are an important staple food. The bananas cultivated in Uganda are the East African highland bananas *(matooke),* the cooking bananas which are scientifically referred to as *Musa spp*. When banana fruit matures, it is harvested before rippening and the banana fingures are peeled and cooked for food; *Matooke*. The banana peels are used as fresh animal feeds or as compost manure in farms although they have little suitable reuse in urban centres where they form part of the urban waste burden for municipal authorities.

For the period 2012 – 2014, Uganda was ranked as the second producing country of *Coffea canephora* in the world with 294,000 tonnes of *Coffea canephora* exports (International Coffee Organization, 2014) and it is the country's biggest agricultural export. Dry *C. canephora* is partially processed before the coffee beans are exported. Husks of *C. canephora* are common by-products of coffee processing industries in the country. The husks are recycled as poultry farmhouse fills, as raw materials for compost manure and as fuel for firing clay works kilns. The industrial and agricultural consumption of *C. canephora* husks by reapplication does not surpass its production, hence the waste burden.

On the other hand, *C. papyrus* is a wetland plant with tall stems commonly found in most swamps in Uganda which is used in the local craft industry for making mats, carpets, sanitary towels, shutters and shelters although the stem-cuttings by-products have no reuse.

E. abyssinica and *A. coriaria* are common tropical tree species that are grown for fuel and herbal medicine. When *E. abyssinica* and *A. coriaria* trees are harvested for wood and timber, waste bark materials whose extracts by local herbalists are used as local dermatological medications have little reuse elsewhere.

The waste plant materials were, therefore, chosen for study as biosorbents because of their abundance, low cost and limited reapplication in industry in the country.

Preparation of reagents and biosorbates

All the chemicals used in this study were of analytical reagent grade and obtained from J.T. Baker H, Deventer, Holland. Contaminated aqueous media (biosorbates) were prepared using water purified by reverse osmosis and standard solutions of lead and cadmium containing 1000 mg L^{-1} of trace metal. The water used to prepare reagents was prepared by the reverse osmosis system (Sartorius Arium 61315, Elga Model, Germany) and purified using the Pure lab Utra, Model: Elga Utra Analytic (UK). The pH meter (Orion model: 210A) was used to measure pH values in the aqueous phase. The initial pH of the contaminated aqueous solution was adjusted to the required value using drops of 0.1 M HCl and 0.1 M NaOH.

The plant materials were thoroughly washed with distilled water to remove particulate matter and dried in an oven (E series: ED – E2 Binder, Germany) at 60°C for 72 hours to a constant weight. The dry biosorbent materials were hammer-milled and sieved to 2 mm. The powder was stored in air-tight self-sealing plastic bags. Each of the biosorbent materials was divided into two portions; one was used in batch studies unmodified while the second was chemically pre-modified.

Chemial treatment methods using hydrogen peroxide (Ganji, et al., 2005,) and sodium hydroxide (Tarley, et al., 2004) were modified and employed. In the first modification, 100 g of the biosorbent was soaked in 0.25 M NaOH for 2 hours and neutralized using 0.25 M HCl to pH 7.0 ± 0.2. The modified portion was generously washed with distilled water, dried in an oven at 105°C for 24 hours and stored dry in sealed plastic bags.

In the second modification, 100 g of each plant material were soaked in a 250 mL of 20 % H_2O_2 solution for 24 hours. The materials were then removed from the peroxide solution and thoroughly washed with distilled deionized water and immersed in 0.25 M NaOH for 2 hours. The biosorbents were removed and excess NaOH was neutralized using 0.25 M HCl to pH 7.0 ± 0.2. The modified biosorbent was generously washed with distilled water and oven dried at 105°C for 48 hours then stored in sealed plastic bags.

Characterisation experiments

In order to determine the component organic molecules and species in the biosorbent structures, X-ray diffraction (XRD) analyses were carried out on untreated dry biosorbent powders sieved to 1 mm. The XRD analyses were carried out using a Siemens D5000 XRD with a copper K_α radiation (λ = 1.5405 Å) operating at a voltage and current power of 35 kV and 40 mA. A diffraction interval between 2θ (10° - 80°) with step increments of 0.01° and a scan speed of 0.5 seconds were used. The phases were identified using DIFFRAC Plus software.

For the total inorganic constituents of the biosorbents, 1 g of the biosorbent material was digested with concentrated HNO_3 at 100°C for 1 hour. The mixture was filtered into 50mL polypropylene sample bottles and made up to the volume with distilled water. The elements were analysed using an ICP-MS.

Biosorption experiments

Kinetic studies were done in two separate sets of closed 50 mL bottles at 24 ± 1°C;

Agitation was done at 60 rpm for 3.5 hours using a rotary shaker and the samples were then centrifuged at 2000 rpm for 25 minutes. A portion of the equilibrated solution was then filtered through 0.45 μm and 0.20 μm sterile non-pyrogenic hydrophilic filters into polypropylene sample bottles to which 0.5 mL HNO_3 was added and trace metal ions analysed using Inductively Coupled Plasma-Mass Spectrometry (ICP-MS). All experiments in the first set were done in replicas for both metal ions and all biosorbents; therefore the results are average values of the replicas.

In the first set, studies were done in triplicate with 10 mg L^{-1} of biosorbent agitated with 50 mL of aqueous solutions containing 20 mg L^{-1} of either Pb^{2+} or Cd^{2+} ions. The pH range was from 2.0 to 9.0 for agitation time, 0.5 – 6.5 hours (Article I).

In the second set, studies were carried out in duplicate with 12.5 g L^{-1} sorbent dose and 20 mL of contaminated solution containing 20 mg L^{-1} of trace metal ions in 50 mL plastic bottles. The pH range was from 2.5 to 6.5 and a biosorbent dose of 12.5g L^{-1} (Article II).

Isotherm studies were done in duplicate in the third set. Studies were carried out with 12.5 g L^{-1} biosorbent dose and 20 mL of synthetic solution containing 20 mg L^{-1} of trace metal ions in 50 mL plastic bottles at 24 ± 2°C. The agitation was done at 60 rpm for 3.5 hours using a rotary shaker. The isotherm studies were done at pH 4.5 for metal ion concentrations in the range of 5 to 100 mg L^{-1}. For studies on co-ion effects of trace metals, experiments were done with increasing mixed metal concentrations in equal proportions of 5 – 100mg L^{-1} and . The effects of increasing the initial concentration of Cd^{2+} ions while maintaining that of Pb^{2+} ions were studied for competitive biosorption. The equilibrated solutions were centrifuged at 2000 rpm for 25 minutes and then filtered through 0.20 μm sterile non-pyrogenic hydrophilic filters into polypropylene bottles with a drop of concentrated HNO_3 as described in our earlier studies (Article III).

Determination of residual metal ions and dissolved organics

The filtrates that were to be analysed for trace metals were acidified using 0.5 mL HNO_3. Residual metal concentrations in the filtrates were determined with Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) (Varian Vista AX model) and Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) (ICAP 6300 Series).

Total Inorganic Carbon (TIC) and Dissolved Organic Carbon (DOC) were determined using a TOC analyser (Shimadzu TOC-5000A). The experiments were done in duplicates unless otherwise stated to ensure that the experimental data had a reproducibility of ±0.5%.

Biosorption intensity and efficiency

The biosorption intensity, q_e (mg g^{-1}) of the biosorbent was determined according to equation (1),

$$q_e = \frac{(C_0 - C_e)V}{m} \qquad (1)$$

The biosorption efficiency, E of the metal ions, it was calculated according to equation (2),

$$E = \frac{C_0 - C_e}{C_0} \times 100\% \qquad (2)$$

where,

C_0 (mg L⁻¹) is the initial metal ion concentration in solution

C_e (mg L⁻¹) is the equilibrium concentration of metal ions in the filtrate

V (L) is the volume of solution agitated

m (g) is the mass of the biosorbent material

Kinetic modelling of biosorption

Experimental data of the time-dependent biosorption of Cd^{2+} and Pb^{2+} were fitted to kinetic models to understand the sorption speed and predict the probable sorption mechanisms. Various kinetic models were studied in order to determine the most suitable kinetic equation whose premises would predict the biosorption mechanisms for Cd^{2+} and Pb^{2+} ions. The pseudo-first-order, pseudo-second-order and diffusion-chemisorption models were applied to the experimental data obtained. The Lagergren (pseudo-first-order) model and the Ho (pseudo-second-order) model are the most widely used models in sorption studies to predict the mechanisms involved in the biosorption processes (Ho & McKay, 1998).

The pseudo-first-order kinetic model (Lagergren, 1898), can be expressed as Eq. (3);

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \qquad (3)$$

where,

q_t (mg/g) is the biosorption intensity at time t

q_e (mg/g) is the biosorption intensity at equilibrium

k_1 (min⁻¹) is the rate constant of the first-order biosorption

Integrating Eq. (3) and applying boundary conditions $q_t = 0$ at $t = 0$, and $q_t = q_t$ at $t = t$, the resultant equation is the linear form of the pseudo-first-order kinetic model expressed as Eq. (4);

$$\ln(q_e - q_t) = \ln q_e - k_1 t \qquad (4)$$

The Ho model (pseudo-second-order kinetic model) was derived (Ho & McKay, 1998) to describe sorption of divalent metal ions onto peat. The Ho model can be expressed as Eq. (5);

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \qquad (5)$$

where, k_2 (g/mg/min) is the pseudo-second-order rate

Integrating Eq. (5) and applying boundary conditions $q_t = 0$ at $t = 0$, and $q_t = q_t$ at $t = t$, the resultant equation, the pseudo-second-order kinetic model can be rearranged as Eq. (6);

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (6)$$

The diffusion-chemisorption model was developed by (Sutherland, 2004) to simulate the adsorption of heavy metals onto heterogeneous media.

A correlation was made where the rate of change of concentration of the solid phase q_t, was equated as a function of the rate of mass transfer of metal ions from the liquid phase to the sorption site K_{DC}.

The diffusion-chemisorption model is expressed as Eq (7);

$$\frac{q_e^2}{(q_e - q_t)} dq_e = nK_{DC} t^{n-1} dt \qquad (7)$$

Which when integrated and boundary conditions $q_t = 0$ at $t = 0$, and $q_t = q_t$ at $t = t$, are applied, with rearrangement of Eq (7) with exponetial factor $n = 0.5$; the linear form of diffusion-chemisorption model will be as expressed in Eq (8):

$$\frac{t^{0.5}}{q_t} = \frac{1}{q_e}(t^{0.5}) + \frac{1}{K_{DC}} \qquad (8)$$

where, K_{DC} (mg/g.min⁰·⁵) is the diffusion-chemisorption constant

Equilibrium isotherm models

The isotherm models that were used to fit data in this study were the three parameter isotherm models; Langmuir, Freundlich and Temkin models, which are commonly used in sorption studies.

The Langmuir isotherm model (Langmuir, 1916) is based on three assumptions; namely biosorption is a monolayer process, all biosorbent sites are similar and can only accommodate one sorbing constituent, and the capacity of a site to be occupied by the sorbate is independent of the nature of occupancy of sites in its vicinity. The linearized form of Langmuir isotherm is represented as follows (9),

$$\frac{C_e}{q_e} = \frac{1}{bq_{max}} + \frac{C_e}{q_{max}} \qquad (9)$$

where,

q_{max} is the monolayer sorption intensity (mg g^{-1}),

b is the biosorption constant (L mg^{-1})

A plot of $^1/_{q_e}$ versus $^1/_{C_e}$ should be a straight line with slope 1/bq$_{max}$ and intercept 1/q$_{max}$ when the biosorption follows the Langmuir equation.

The Freundlich isotherm (Freundlich, 1906) model is an empirical isotherm which suites biosorption onto heterogeneous surfaces. It is based on multilayer biosorption process which implies that the biosorbent surface is heterogeneous and the biosorption is due to non-uniform distribution of heat of sorption. The linearized Freundlich isotherm is described by the following equation (10),

$$ln q_e = ln(A_F) + b_F ln C_e \qquad (10)$$

where,

C_e is equilibrium metal concentration (mg L^{-1}),

A_F and b_F are the isotherm empirical constants

A_F the value of q when ln C_e = 0 for the Freundlich isotherm. The value of 1/b_F has to do with site heterogeneity. A value of 1/b_F greater than unity would indicate heterogeneous site-binding affinity for the trace metal ions by the biosorbent.

The other isotherm model considered in this study was the Temkin model. The derivation of Temkin isotherm assumes that the fall in the heat of sorption is linear rather than logarithmic, as implied in the Freundlich equation (Aharoni & Ungarish, 1977). The linearized form of Temkin isotherm is defined by the equation (11),

$$q_e = \frac{R.T}{b_T} ln(C_e) + \frac{R.T}{b_T} ln(A_T) \qquad (11)$$

where,

T is the temperature (K),

R is the universal gas constant, 8.314 Jmol^{-1},

A_T is the equilibrium constant (L mg^{-1})

b_T is related to heat of biosorption E, (Jmol^{-1})

When a particular equilibrium model fits the sorption data, then the model assumptions, predictions of the biosorption mechanism and the underlying assumptions are dependable for description of the sorbate biosorption reaction, sorbent surface properties and the sorbent-sorbate interactions during the process.

Sorption thermodynamics

To get an insight into the nature of the biosorption processes thermodynamic parameter; change in Gibbs free energy (ΔG^0) is investigated and determined from equation (12):

$$\Delta G^0 = -RT \ln K_c \qquad (12)$$

where,

(ΔG^0) is the change in Gibbs free energy,

T is the temperature (K),

R is the universal gas constant, 8.314 Jmol^{-1}

K_c is the apparent sorption equilibrium constant

The apparent biosorption equilibrium constant, K_c was determined from the slope of the plots of q_e versus C_e. The change in Gibbs free energy (ΔG^0) for Cd^{2+} and Pb^{2+} ions biosorption was determined for different biosorbents. The nature of the value of ΔG^0 is used a criterion for impulsiveness of the reaction process since a negative value of ΔG^0 denotes suddenness of a reaction.

Results and Discussion

Characterisation of biosorbents
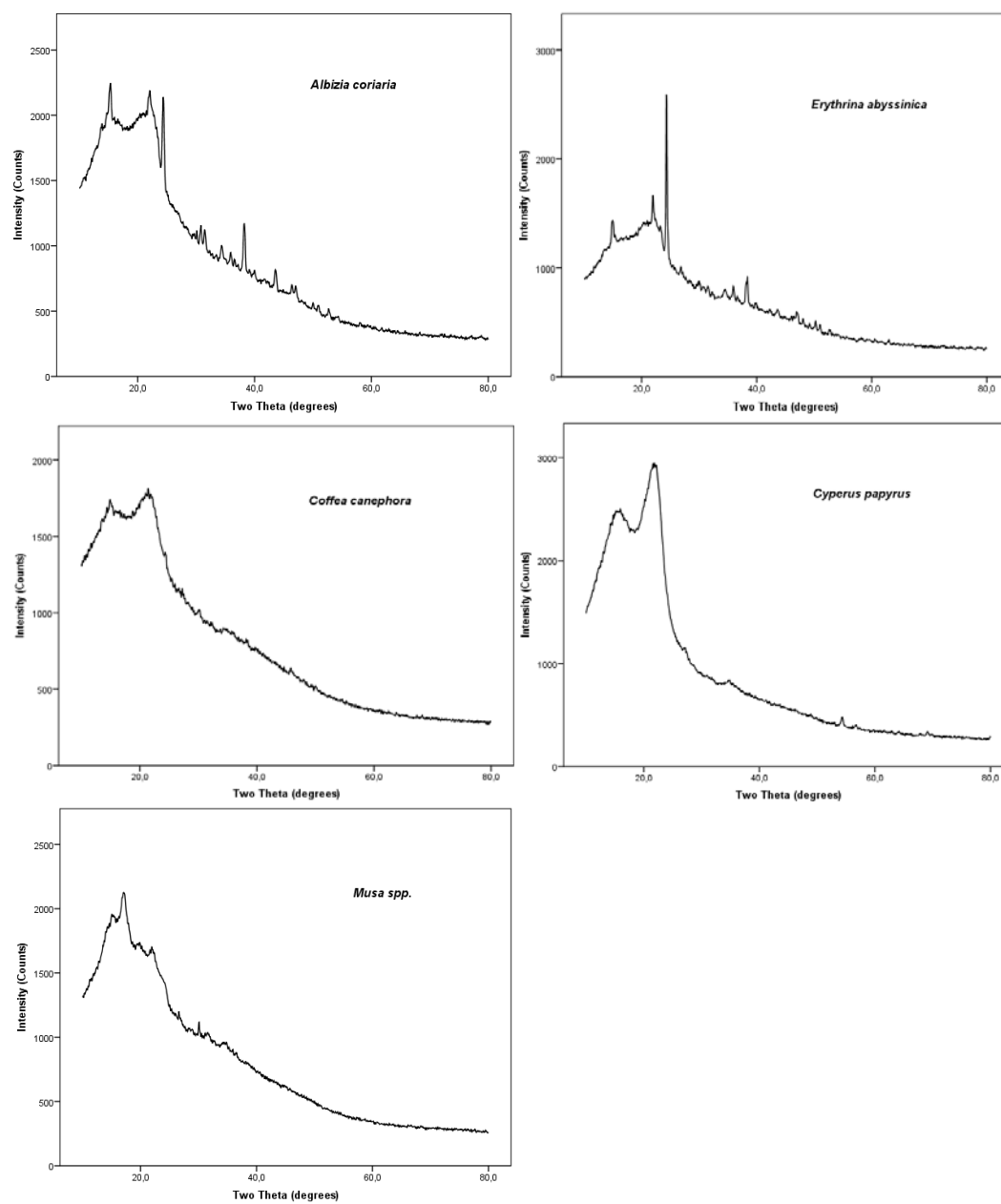
Figure 2 *XRD patterns of raw Albizia coriaria, Erythrina abyssinica, Coffea canephora, Cyperus papyrus and Musa spp. biosorbent powders*

dibenzo-18-crown-6-ether

prednisolone

diglycidyl 4,5-epoxycyclohexane-1,2-dicarboxylate

Pentaerythritol triacrylate

quinquephenyl

1,4 bis (2-phenyl ethenyl)-2,5-dimethylbenzene

cholestan-3-beta-ol

3-betahydroxy-cholestan-6-one
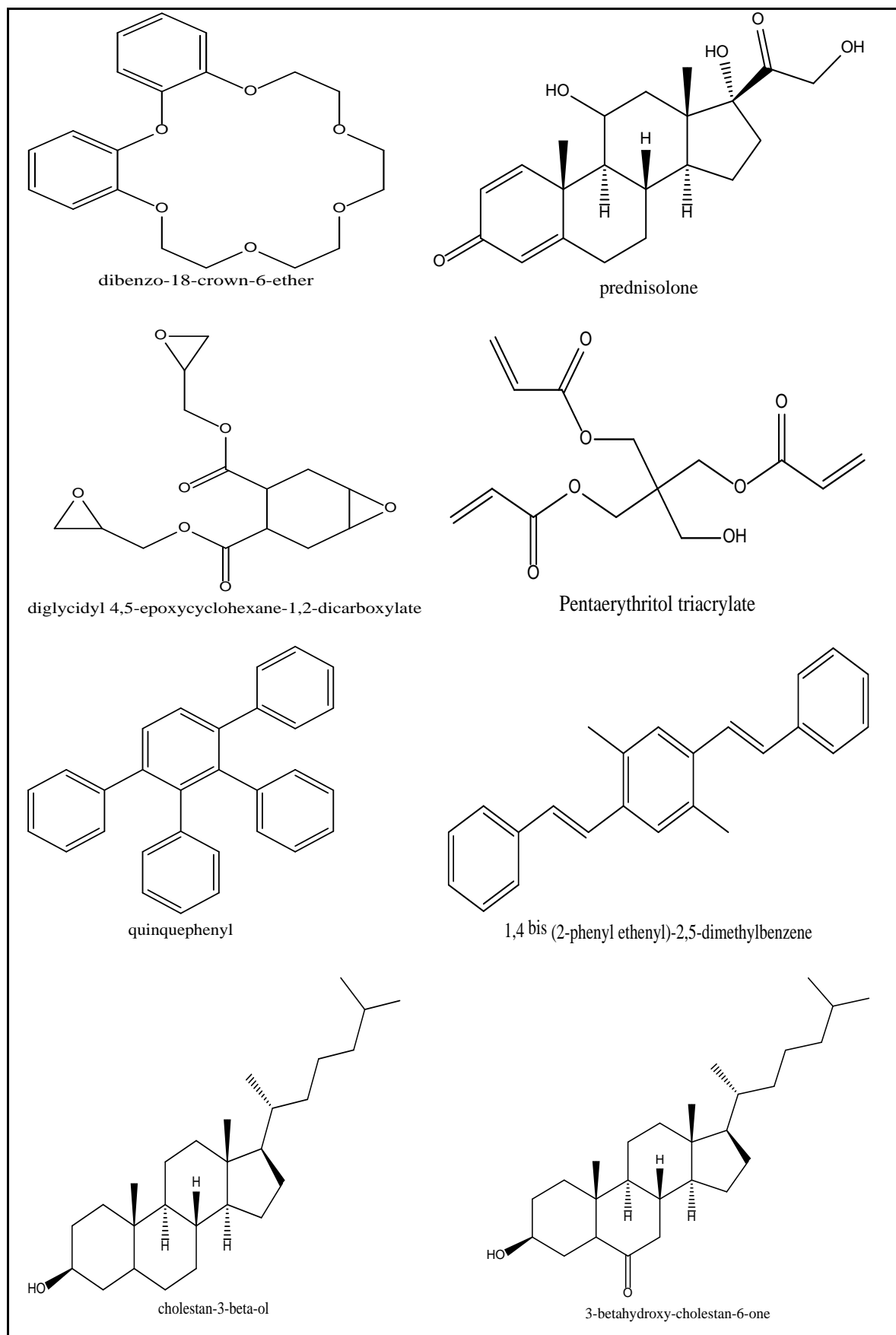
Figure 3 *Chemical structures of selected notable organic species in the biosorbent materials used in the study*

Table 1 *Selected trace metal constituents in samples of the biosorbent materials*

Biosorbents	Main trace metal constituents (μg/g)						
	Mn	Fe	Ni	Cu	Zn	Cd	Pb
A. coriaria	19.2	18.4	6.96	2.85	15.8	0.01	0.56
E. abyssinica	43.0	79.3	4.11	5.12	19.9	0.02	0.97
C. canephora	11.5	4.20	0.92	18.6	5.31	0.02	0.46
C. papyrus	34.6	1.98	0.27	1.26	11.0	0.04	0.18
Musa spp.	11.7	1.53	0.91	2.93	17.8	0.01	1.23

Patterns from the X-ray diffraction (XRD) analyses of untreated dry biosorbent powders of *Albizia coriaria*, *Erythrina abyssinica*, *Coffea canephora*, *Cyperus papyrus and Musa spp.* are presented in Figure 2. The XRD characteristics were used to identify the main organic species in the biosorbent surface structures. The biosorbents were mainly composed of unsaturated compounds and radicals, alcohols, carboxylic acids, carbonyls, phenyls and organometallics besides cellulose and glycerol which were identified with the prominent peaks in the characteristics.

The major organic species in *Albizia coriaria* surface were cyclo hepta kis-ethylene terephthalate, 4-cyno-4'-n nonyloxy biphenyl, penta decylanilide, 3-acetamido-2,3,6-trideoxy-alpha-L-xylohexose, pentaerythriol triacrylate, prednisolone, 5-dehydro episterol and diglycidyl-4,5-epoxycyclohexane. *Erythrina abyssinica* structure contained the following major species; di-p-xylylene, 3'-3"-quaterphenyl, 2',2",4"-quinquephenyl, tri-p-xylylene, 1,1-binaphthyl, cholesterol stearate, 1,4-bis [2-phenylethenyl]-2,5-dimethyl benzene, 1,2-distearoyl-sn-glycerol and egosterol. On the other hand, the structure of *Coffea canephora* had the following major organic species; polystyrene-o-xylene, 1,2-diphenyl cyclohexene, poly(2-methylpentadiene), diethylmagnesium and phenylzinchydride. *Cyperus papyrus* had 4-androstene, poly-p-xylene, polyphenyl acetylene, 1,2-diphenyl cyclohexene, dibenzo-18-crown-6-ether, cis-3-hydroxy-cyclohexane carboxylic acid, 1,2-dipalmitoyl-sn-glycerol and 9,10-dihydroxystearic acid, whereas the key components in *Musa spp.* were poly(4-methyl-1-pentene), tri-p-xylylene, 2-methyl adamantane, 1-adamantyl methanol, cholestan-3-beta-ol, 3-betahydroxy-cholestan-6-one and polstyrene.

Some of the chemical structures of the notable organic species with prominent peaks are shown in Figure 3. It is observed that those organic compounds are electron rich species highly suspected of donating or sharing electrons with metal ions to form metal complexes with the biosorbents surface structures during biosorption. There is another possibilty of leaching of the organic species as dissolved organic matter which may at certain pH levels complex metal ions to form insoluble compounds which renders the metal ions unavailable for biosorption onto the biosorbent surfaces. The functional groups; pi bonds, oxy, hydroxy, carbonyl and carboxylic groups of the organic species in the biosorbent structures are varied and therefore, they form an array of heterogeneous sorption sites for metal ions binding in phases.

The main trace elements that were analyzed in the powdered raw materials are listed in Table 1. The levels varied in the order; Fe > Mn > Zn > Ni > Cu > Pb >> Cd. The biosorbents used in these studies have minute quantities of the trace metals under study and would therefore not contaminate treated water.

Comparative biosorption performance

The biosorption efficiency of untreated and base-treated materials were comparatively studied, the results are presented in Figure 4.
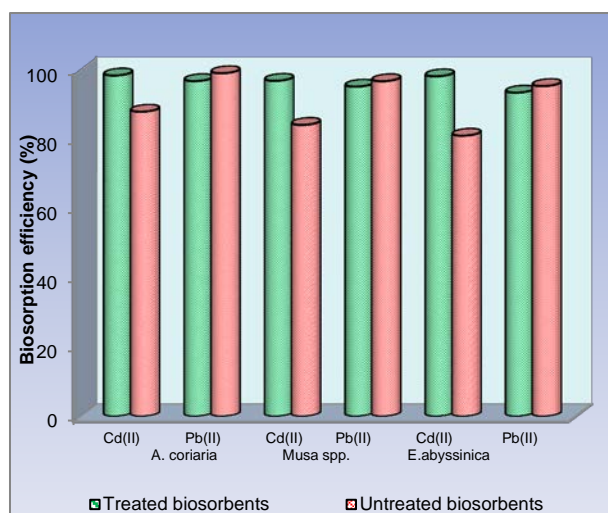
Figure 4 *Effect of chemical treatment on the biosorption efficiencies for Cd²⁺ and Pb²⁺ ions (Article I)*

The results shown in Figure 4, were an average of three replicas with standard between 0.07 and 0.22% for Cd²⁺ ions and 0.06 – 1.03% for Pb²⁺ ions biosorption. All the base-treated biosorbents showed higher sorption efficiencies for Cd²⁺ ions than the untreated biosorbents which were in the order; *E. abyssinica* bark (17.1%) > *Musa spp.* peels (12.7%) > *A. coriaria* bark (10.5%). In several previous studies, it has been reported that chemical treatment of biosorbents improves trace metals biosorption (Wan Ngah & Hanafiah, 2008) although in these studies, a slight reductive effect on Pb (II) ions biosorption in the order; *A. coriaria* bark (2.3%) > *E. abyssinica* bark (1.9%) > *Musa spp.* peels (1.6%) was realised (Article I). The highest Cd²⁺ ions biosorption competences observed were; 98.3%, 98% and 96.7% for treated *A. coriaria, E. abyssinica* and *Musa spp* respectively. Moreover the highest Pb²⁺ ions sorption competences realised were; 98.9%, 96.6% and 95.2% for untreated *A. coriaria, Musa spp.* and *E. abyssinica* respectively. The improvement in metal biosorption for Cd²⁺ was comparable to 2 – 8% reported for alga spirogyra (Bishnoi, et al., 2007) and 10 – 20% improvement reported for waste materials (Chen, et al., 2009; Memon, et al., 2007) and the reduction was similar to that of 5 – 13% for Pb bioremoval by treated cork residues (Mota, et al., 2006). The variation in the biosorption of Cd²⁺ and Pb²⁺ ions observed here may be due to different adsorption mechanisms. Cd²⁺ is well known to exist to a large part in the exchangeable fraction from which explains the biosorption increase after treatment whereas Pb²⁺ is known to bind more strongly to sorbent surfaces and it is therefore expected to be biosorbed through a different adsorption mechanisms.

Organic carbon released and biosorption

Dissolved organics released into treated water were studied for base-treated biosorbents and the results presented in Table 2. The results showed that NaOH treatment of biosorbents considerably reduced extractable organics in the range of 2 – 11 times in both Cd²⁺ and Pb²⁺ ions remediated solutions. It has been suggested in literature that improvement in reduction of extractable organics could further be done by employing thorough washing of biosorbents after chemical treatment. Studies were done to determine the effects of DOC (mg/L) removal on the biosorption efficiency as a function of the pH and the results are shown in Figure 5. The amounts of DOC (mg/L) released by the biosorbents into treated water were not dependent on the initial pH and had no observable effects on the biosorption capacities of the treated biosorbents for Cd²⁺ and Pb²⁺ ions. A comparison of DOC released by untreated and base treated materials showed that it did not vary significantly with increase in pH as well as the increase and decrease in biosorption capacities for Cd²⁺ and Pb²⁺ ions. The results showed that removal of soluble organics from the biosorbents did not have any effects on the biosorption efficiency for the trace metal ions in this study. The plots in Figure 5 indicated that the biosorption intensities of all biosorbents for Cd²⁺ ions and the DOC enrichment of the aqueous solutions coherent whereas the variations in Pb²⁺remediated solutions were illogical.
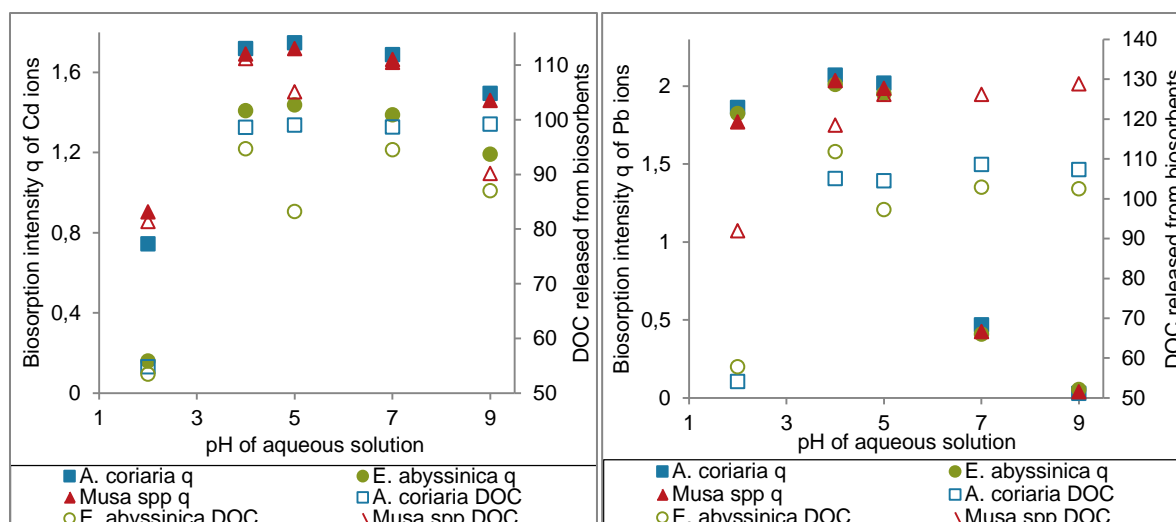
**Figure 5** *Comparison of DOC released (mg/L) with biosorption intensity (mg/g) as a function of the pH*

pH	A. coriaria		Musa spp.		E. abyssinica	
	Treated	Untreated	Treated	Untreated	Treated	Untreated
Solutions from which Cd²⁺ ions were removed (mgL⁻¹)						
2	54.8	697	81.4	438	53.5	580
4	98.6	857	111	470	94.9	732
5	99.0	858	105	470	83.2	714
7	98.7	894	111	257	94.5	709
9	99.2	879	90.2	250	87.0	741
Solutions from which Pb²⁺ ions were removed (mgL⁻¹)						
2	54	599	92	450	58	648
4	105	856	119	455	112	747
5	105	842	126	459	97	712
7	109	879	126	461	103	753
9	107	900	129	477	103	776

Table 2 *Released dissolved organic matter (DOC) (mg/L) in remediated samples at equilibrium for various pH levels*

Figure 6 shows that the variation in Cd²⁺ ions biosorption by *C. canephora* and *Musa spp.* peels as well as the DOC released was expressive over the whole pH range although the trends for Pb²⁺ ions varied regularly for all biosorbents. The peak Cd²⁺ ions biosorption for *C. canephora* was 1.343 mg g⁻¹, 0.462 mg g⁻¹ for *Musa spp.* peels and 0.139 mg g⁻¹ for *C. papyrus* at pH 3.5. Although the variation in released DOC was small, the lowest levels were at pH 5.5 for all the biosorbents. The biosorption for *C. canephora* shows that the material was near saturation of the active sites since the sorption capacity was nearly the same over the pH range from 3.5 to 6.5. The trend is slightly different with the *Musa spp.* peels and *C. papyrus* although they show initial high biosorption which reduces with increase in pH. The results of Cd²⁺ ions biosorption indicated that for the conditions of the study, the optimal pH was 3.5. The Pb²⁺ ions biosorption intensity peaks were 1.595 mg g⁻¹ at pH 2.5 for *C. papyrus*, 1.517 mg g⁻¹ at pH 5.5 for *C. canephora* and 1.427 mg g⁻¹ at pH 2.5 for *Musa spp.* peels.
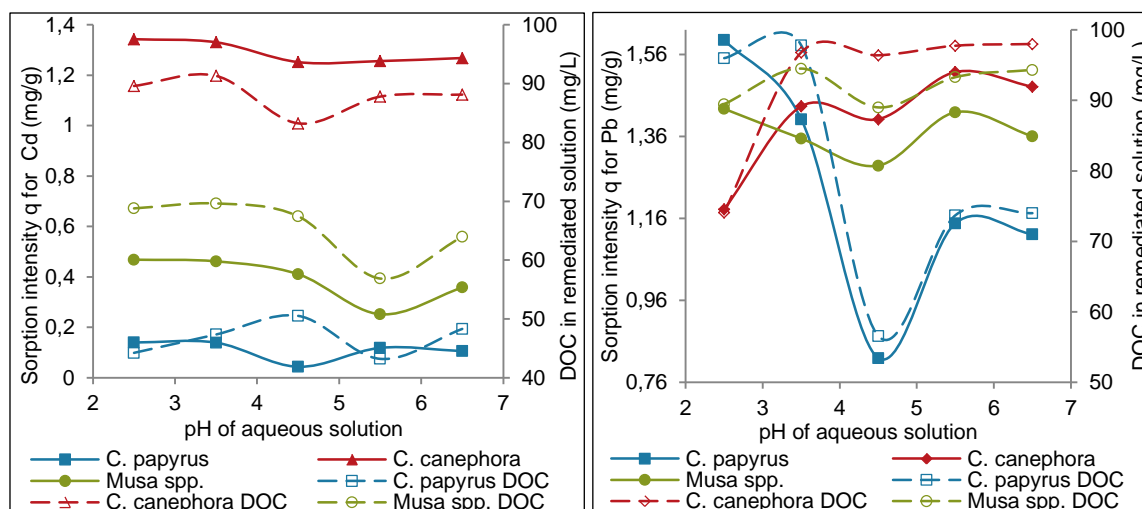
Figure 6 *Comparison of Cd²⁺ and Pb²⁺ ions sorption intensity and DOC as a function of the solution pH of the aqueous solution (Article II)*

Lead is known to form precipitates at high pH levels and exists as free ions in the pH range under study. Pb²⁺ ions biosorption intensity plot for *C. canephora* increases with increase in availability of the active sites. DOC released by biosorbents was reported to have no effect on the biosorption of trace metal ions although in environmental speciation studies of Pb²⁺ ions, DOC is known to provide adsorption sites and a mechanism of transport in aqueous media. The optimal pH for biosorbents was 3.5 for Cd²⁺ ions and 2.5 – 5.5 for Pb²⁺ ions which coincided with the range that speciation studies predicted occurrence of free metal ions dominance over H_3O^+ ions (Article II). The sorption performance for Cd²⁺ and Pb²⁺ ions was in the order; *C. canephora > C. papyrus > Musa spp* for sole metal solutions.

Although the Liquid-solid ratio in column studies is very different from the same ratio in batch studies, the results of studies on the effect of DOC released on the biosorption of trace metals were consistent with reports by Nehrenheim, (2008) and Kalmykova et al. (2009) that indicated that DOC had only a minor effect on metal adsorption and metal transport in column studies.

Effect of agitation time on biosorption

For untreated and base-treated biosorbents, the effect of agitation time on the biosorption of trace metal ions was studied and the results presented in Figure 7 for Cd²⁺ and Pb²⁺ ions biosorption. The biosorption intensities of both treated and untreated biosorbents increased gradually for Cd²⁺ to peak values at equilibrium time (3.5h) before declining for agitation time >3.5h. The biosorption intensities of Cd²⁺ were similar for base-treated and untreated materials although the treated biosorbents presented higher values.

On the other hand, the biosorption intensities for Pb²⁺ ions (Figure 7) onto both treated and untreated biosorbents showed a marked difference with that of Cd²⁺ ions since the increase in biosorption intensities with agitation time was near polynomial with peak biosorption capacities at 3.5 hours. The peak values for Cd²⁺ biosorption using untreated biomass were 1.538 mg g⁻¹ for *A. coriaria*, 1.414 mg g⁻¹ for *E. abyssinica* and 1.467 mg g⁻¹ for *Musa spp* in 3.5 hours. Moreover the peak biosorption for Cd²⁺ ions using base treated materials were 1.760 mg g⁻¹ for *A. coriaria*, 1.753 mg g⁻¹ for *E. abyssinica* and 1.737 mg g⁻¹ for *Musa spp* in 3.5 hours. The treated materials showed improved performance in sequestering the aqueous Cd²⁺ ions. For Pb²⁺ ions biosorption, the plots were near even throughout the study time. Nevertheless, the peak intensity values for aqueous Pb²⁺ ions using untreated biomass were 1.372 mg g⁻¹ for *A. coriaria*, 1.326 mg g⁻¹ for *E. abyssinica* and 1.350 mg g⁻¹ for *Musa spp* while for the base treated materials, the peak intensity values occurred at 1.347 mg g⁻¹ for *A. coriaria*, 1.325 mg g⁻¹ for *E. abyssinica* and 1.320 mg g⁻¹ for *Musa spp* in 3.5 hours.
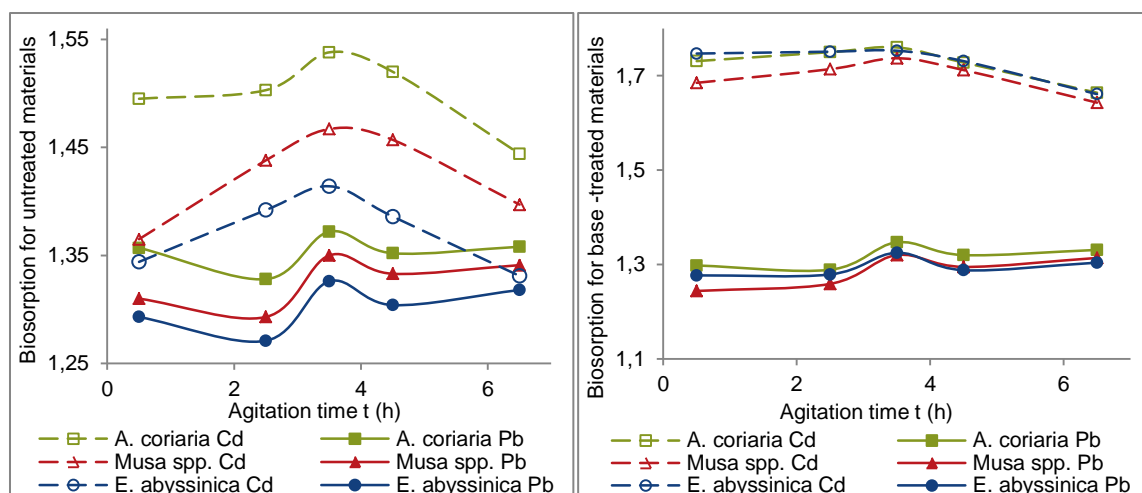
Figure 7 *Biosorption intensities of Cd²⁺ and Pb²⁺ ions (mg/g) onto untreated and base treated biosorbents as a function of the agitation time (Article I)*
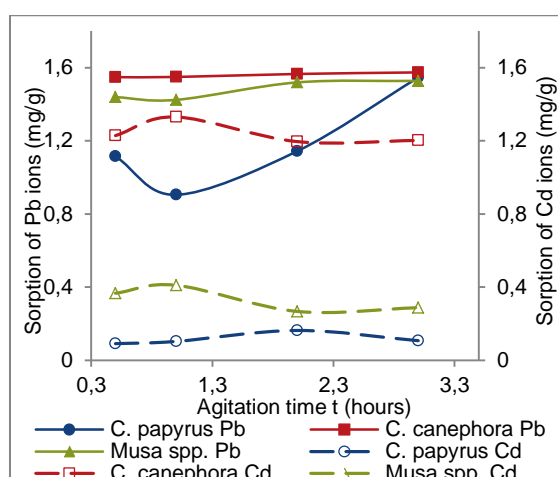
Figure 8 *Biosorption of Cd²⁺ and Pb²⁺ ions from single-component solutions using peroxide treated biosorbents as a function of the agitation time (Article II)*

The results showed that biosorption intensities for Cd²⁺ and Pb²⁺ ions were in the order; *A. coriaria > Musa spp. > E. abyssinica* for untreated materials and *A. coriaria > E. abyssinica > Musa spp.* for base-treated biosorbents. The optimum agitation time was determined as 3.5 hours for Cd²⁺ and Pb²⁺ ions biosorption onto untreated and base treated materials at $24 \pm 1°C$ for 10 mg L⁻¹ biosorbent dosage (Article I).

The characteristic plots of biosorption intensities for Cd²⁺ and Pb²⁺ ions from single-component solutions using peroxide treated biosorbents are shown in Figure 8. The peak values for Cd²⁺ ions biosorption were 1.33 mg g⁻¹ for *C. canephora* and 0.411 mg g⁻¹ for *Musa spp.* peels in 1 hour, then 0.164 mg g⁻¹ for *C. papyrus* in 2 hours. For Pb²⁺ions biosorption, the plots for *Musa spp.* and *C. canephora* are near even throughout the study time. The plots for *C. papyrus* showed steady increase in biosorption from 1 to 3 hours. The peak Pb²⁺ions biosorption values were 1.574 mg g⁻¹ for *C. canephora*, 1.546 mg g⁻¹ for *C. papyrus* and 1.528 mg g⁻¹ for *Musa spp.* in 3 hours. Studies showed that for the biosorbents studied, and under the experimental conditions, the highest biosorption capacities for Cd²⁺ and Pb²⁺ ions were in the order of *C. canephora > Musa spp. > C. papyrus*. The optimum agitation time was determined as 3.0 hours for Cd²⁺ and Pb²⁺ ions biosorption onto peroxide treated materials at $24 \pm 1°C$ for 12.5 mg L⁻¹ biosorbent dosage. These results were consistent with those in literature where optimum agitation time for Cd²⁺ and Pb²⁺ ions biosorption was reported as 2.0 – 4.0 hours (Özer, 2006; Özer & Pirincci, 2006) (Article II). On the other hand, comparative analysis of the biosorption efficiencies of base treated and peroxide treated biomass indicated that base treated materials had higher trace metals sequestering performance than the peroxide treated materials.

Effect of pH on biosorption

The biosorption of trace metal ions from aqueous media by biosorbents is pH-dependent and determination of the optimal pH in biosorption studies is important. The effect of the initial pH of the aqueous solution on the biosorption intensities of untreated and base treated biosorbents were studied then compared for Cd^{2+} and Pb^{2+} ions for initial trace metal ion concentration of 20 mg L^{-1} and agitation time 3.5 hours. The results for Cd^{2+} and Pb^{2+} ions biosorption onto biosorbents for pH range 2.0 – 9.0 are shown in Figure 9. Both base treated and untreated biosorbents showed sharp increases in biosorption intensities for Cd^{2+} ions from pH 2.0 to pH 4.3 followed by a gradual decrease in biosorption occurred with increase in initial pH of aqueous media. The base treated biosorbents had better biosorption intensities for Cd^{2+} ions than the untreated materials at all pH levels which was in the order; *A. coriaria > E. abyssinica > Musa spp.* The Pb^{2+} ions biosorption slightly increased for treated biosorbents between pH 2.0 and 4.0, otherwise there was a decline in biosorption intensities of all biosorbents for Pb^{2+} ions to minima at pH 9 (Article I). Results from different sorption studies are difficult to compare due to variations in experimental conditions, nevertheless the results of the present studies concur with results from earlier studies elsewhere where it was reported that the optimal pH for biosorption for trace metals by other biosorbents as 4.0 – 5.0 (Kaewsam, et al., 2008; Dekhil, et al., 2011). The biosorption intensities were indicative of ionic competition for biosorption sites on biosorbents with the predominant ions; H_3O^+ ions at pH levels lower than 3.5, the trace metal cations at the optimal pH (4.2 – 4.7) and the OH^- ions at pH levels than 5.0. The data suggested the optimal pH range for biosorption of trace metal ions; Cd^{2+} and Pb^{2+} to be 4.2 – 4.7 over which the metal cations had the highest interaction and binding with the biosorbents structural molecules. At low pH levels the H_3O^+ ions shield Cd^{2+} from the negatively charged biosorption sites although due to pH dependent dissociation of organic matter, there aren't many negatively charged sites. In other studies by Patnukao, et al., 2008 and Sari & Tuzen, 2009 clarified that at pH levels higher than 5.0, Cd^{2+} and Pb^{2+} ions complex with OH^- to form soluble hydroxylated species of the metal ions (Patnukao, et al., 2008; Sari & Tuzen, 2009).

Comparative and competitive biosorption of aqueous Cd^{2+} and Pb^{2+} ions

The plots in Figure 10 showed that Cd^{2+} ions biosorption intensity in single-component solutions was in the ranges of 0.045 – 1.343 mg g^{-1} and 0.008 – 0.195 mg g^{-1} in binary-component solutions. The Cd^{2+} ions biosorption suppression was most pronounced in *C. canephora* and least in *C. papyrus* during competitive biosorption. For Pb^{2+} ions, the ranges of biosorption intensities were between 0.819 – 1.595 mg g^{-1} in single-component solutions and 0.472 – 1.303 mg g^{-1} in multi-component solutions. The results implied that there was a much weaker competition for biosorption sites for Cd^{2+} ions multi-component solutions than that for Pb^{2+} ions under similar conditions in binary component solutions.

On the other hand, the plots in Figure 11, showed similar trends of biosorption intensity of the biosorbents for the metal ions in sole metal solutions but with lower values in multi-component solutions. The Cd^{2+} ions biosorption was spasmodic compared to that of Pb^{2+} ions biosorption which was near linear. For all biosorbents, there was preferential Pb^{2+} ions sorption to that of Cd^{2+} ions. The Pb^{2+} ions adsorption was higher (0.472 – 1.303 mg g^{-1}) than that for Cd^{2+} ions (0.008 – 0.195 mg g^{-1}) in multi-component solutions. From the results of biosorption of metal ions from multi-component solutions, the performance of the biosorbents was in the order of *C. canephora > Musa spp. > C. papyrus (Article II)*. For both metal ions, the biosorption was relatively low compared to that in sole metal solutions as shown in the comparative study results in Figure 10. These results were in line with the observations by Khani (2013) in which stated that the uptake of both cadmium and lead in the presence of each other decreased and that the decrease in Cd^{2+} ions sorption was high in binary solution with respect to that of Pb^{2+} ions.

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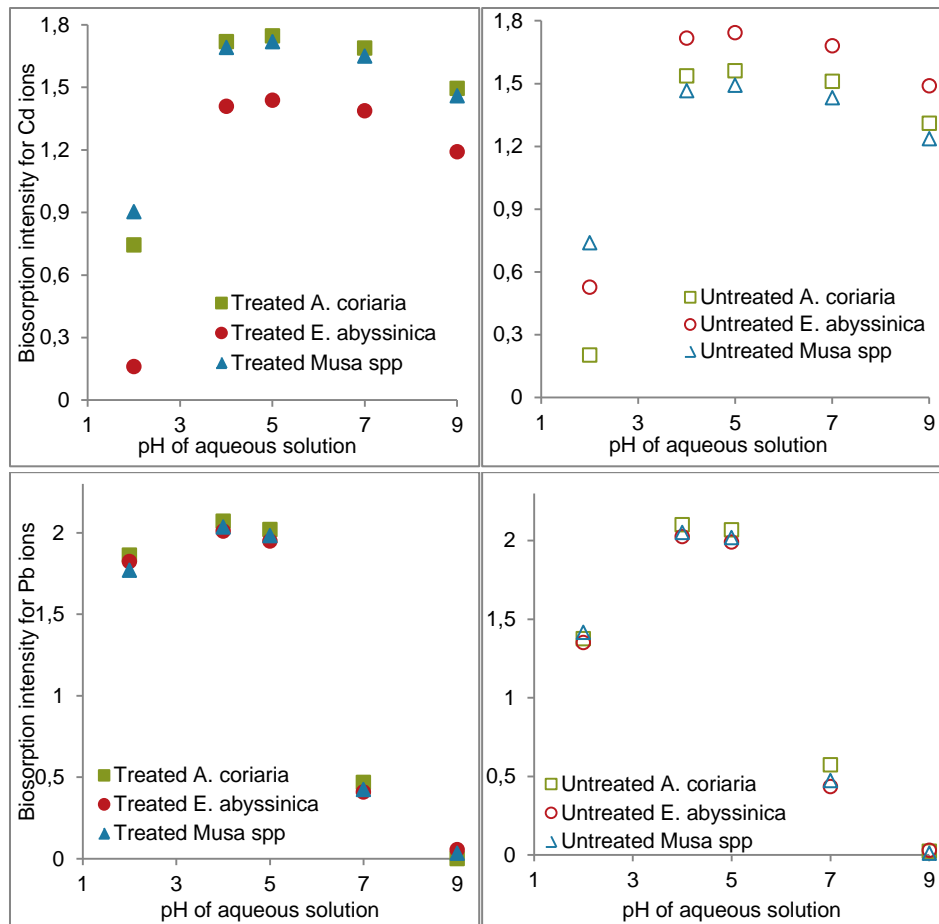
Figure 9 *Variation of biosorption intensities q (mg/g) for Cd^{2+} and Pb^{2+} ions with initial pH for untreated and base treated biosorbents (Article I)*
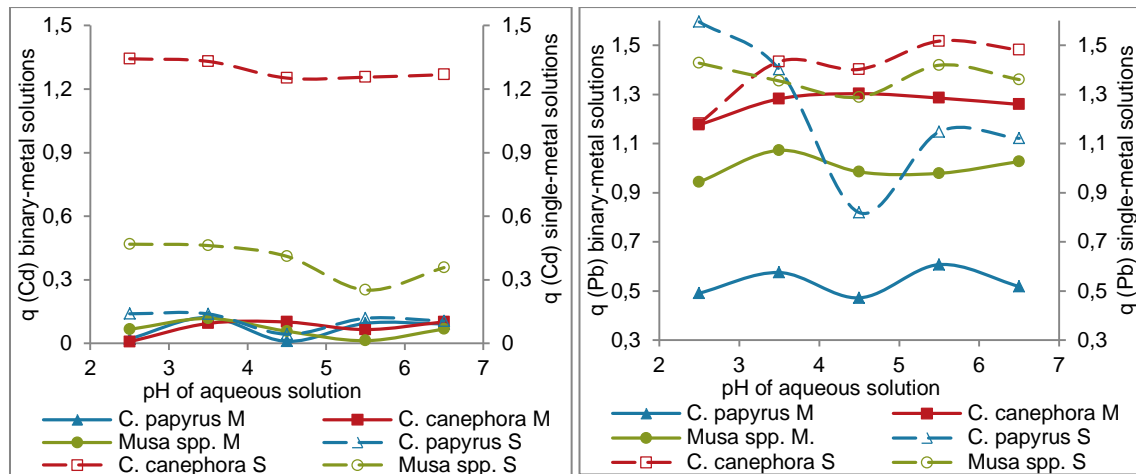
Figure 10 *Comparative plots for biosorption intensities of Cd^{2+} and Pb^{2+} ions from (S) single- and (M) binary-component solutions as a function of the solution pH (Article II)*
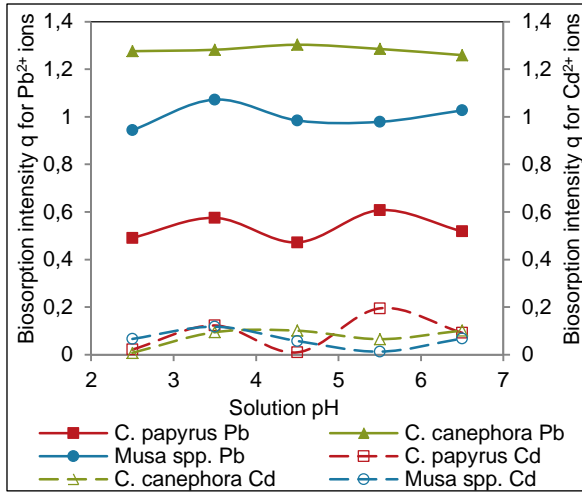
Figure 11 *Variation of the competitive biosorption of Cd $^{2+}$ and Pb $^{2+}$ ions with pH from binary-component solutions using peroxide treated biomass (Article II)*

Co-ion effect in binary solutions

The effects of ionic interactions on the Cd^{2+} and Pb^{2+} ions biosorption processes were predicted using the ratio of the sorption intensity for one metal ion in the mixture, q_{mix} to the sorption of intensity of the same metal ion when it is alone in solution, q_s, such that;

$\frac{q_{mix}}{q_s} > 1$, adsorption is promoted by the presence of other metal ions,

$\frac{q_{mix}}{q_s} = 1$, no observable net interaction effects,

$\frac{q_{mix}}{q_s} < 1$, adsorption is suppressed by the presence of other metal ions (Tan, et al., 1985).

In Table 3 the results of co-ion effects analysis for all biosorbents studied are presented, the ratios were in the range of 0.048 – 0.800 for Cd^{2+} ions biosorption and 0.361 – 0.929 for Pb^{2+} ions biosorption which implied that biosorption for either metal ions was suppressed by the presence of other metal ions in the multi-component solutions. Cd^{2+} ions biosorption was more suppressed than Pb^{2+} ions biosorption in multi-component solutions (Article II). These results were consistent with findings by Khani (2013) in which ratios of 0.85 for Cd^{2+} ions and 0.47 for Pb^{2+} ions sorption in binary solutions were reported.

Effect of sorbate dosage and competitive biosorption

The trend in the sorption intensity variation with increasing initial Cd^{2+} ions concentration for untreated and treated biosorbents shown in Figure 12a was disproportionate. Nevertheless results indicated that as the initial concentration of Cd^{2+} ions increased from 5 to 100 mg L^{-1}, the sorption intensities for all biosorbents increased slightly to peak values at initial Cd^{2+} ions concentration of 10 mg L^{-1}.

The sorption intensities then dropped exponentially to minimum values for initial Cd^{2+} ions concentration of 100 mg L^{-1}. The base treated biosorbents showed better sorption performance at initial concentration lower than 100 mg L^{-1} otherwise the untreated biosorbents showed better sorption intensities for Cd^{2+} ions in the higher concentration solutions. The sorption intensities for Cd^{2+} ions were in the order of *A. coriaria > Musa spp > E. abyssinica* for treated biosorbents and *Musa spp > A. coriaria > E. abyssinica* for the untreated materials.

The variation of sorption intensity with increasing initial Pb^{2+} ions concentration for untreated and treated biosorbents shown in Figure 12b was systematic and linear. It was observed that as the initial Pb^{2+} ions concentration increased from 5 to 100 mg L^{-1}, the sorption intensities for all biosorbents increased substantially to peak values at initial Pb^{2+} ions concentration of 100 mg L^{-1}. The base treated biosorbents showed slightly better sorption intensities for Pb^{2+} ions than the untreated materials. All the biosorbents studied showed very good sorption intensities for Pb^{2+} ions however; the general performance was in the order: *A. coriaria $\geq$ Musa spp $\geq$ E. abyssinica*. The sorption intensities for Pb^{2+} ions for all biosorbents consistently increased with the initial Pb^{2+} ions concentration.

Table 3 *Co-ionic effects on the sorption process in binary-component solutions at 297K (Article II)*

Sorption capacity ratio q_{mix}/q_s for peroxide treated biosorbents						
	C. canephora		*C. papyrus*		*Musa spp.*	
pH	Cd^{2+}	Pb^{2+}	Cd^{2+}	Pb^{2+}	Cd^{2+}	Pb^{2+}
2.5	0.006	0.995	0.154	0.308	0.141	0.661
3.5	0.071	0.894	0.882	0.410	0.255	0.792
4.5	0.081	0.929	0.225	0.576	0.141	0.764
5.5	0.052	0.847	0.800	0.529	0.051	0.690
6.5	0.080	0.850	0.870	0.462	0.190	0.755
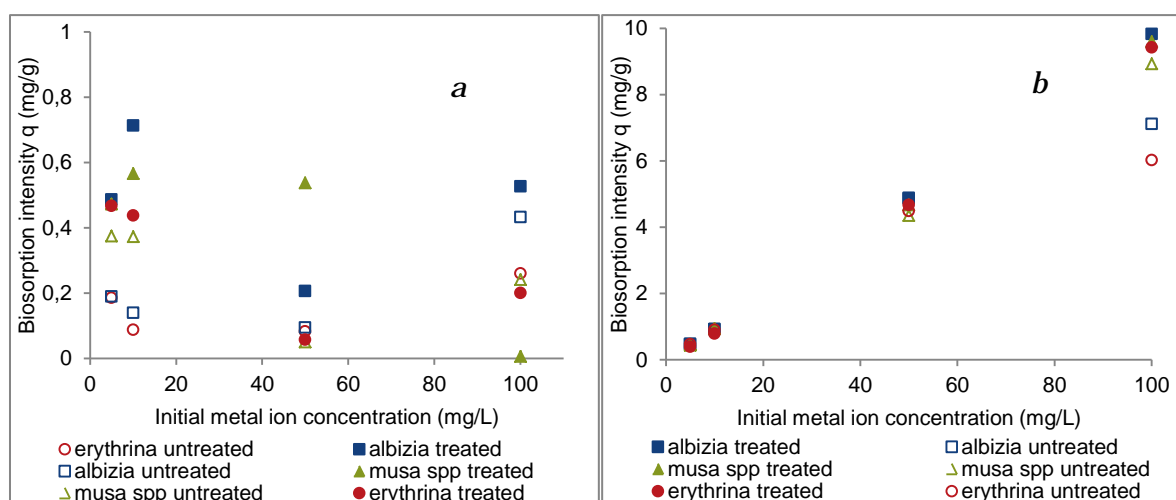
Figure 12 *Sorption intensities q (mg/g) of untreated and base treated biosorbents for Cd^{2+} (a) and Pb^{2+} ions (b) as a function of the initial metal ions concentration (Article III)*

The nature of metal ions sorption in single component solutions differs from that in binary component solutions due to the sorbate-sorbate and sorbate-sorbent interactions. However, plots in Figure 12 *a* and *b* showed that the variations of sorption intensities with increasing initial Pb^{2+} ions concentration were comparable and increased gradually to near level from 50 – 100 mg L^{-1} in both single – and binary – component solutions. The trend of sorption intensities for Cd^{2+} ions were uncharacteristic and analogous for both single – and binary – component solutions except for *C. canephora* that was curvilinear in single – component solutions. The nature of metal ions sorption in single component solutions differs from that in binary component solutions due to the sorbate-sorbate and sorbate-sorbent interactions. However, plots in Figure 13 *a* and *b* showed that the variations of sorption capacities with increasing initial Pb^{2+} ions concentration were comparable and increased gradually to near level from 50 – 100 mg L^{-1} in both single – and binary – component solutions. The trend of sorption intensities for Cd^{2+} ions were uncharacteristic and analogous for both single – and binary – component solutions except for *C. canephora* that was curvilinear in single – component solutions. The sorption intensities for both metal ions were in the order: *C. canephora > Musa spp > C. papyrus*. (Article III)

From the comparative plots of sorption intensities with initial metal ions concentration in Figure 13, it was evident that increasing the initial metal ions concentration under the experimental conditions positively influenced sorption of Pb^{2+} ions although no significant effect on the Cd^{2+} ions sorption was observed between single – and binary – component solutions. The results for binary-component solutions showed that the biosorbents had stronger physical affinity for Pb^{2+} ions than Cd^{2+} ions due to the difference in their ionic radii; Pb^{2+} (1.19Å) and Cd^{2+} (0.97Å) in addition to the hydrated ionic radii; Pb^{2+} (4.61Å) and Cd^{2+} (4.01Å). All the peroxide treated biosorbents showed lower sorption intensities for Cd^{2+}

ions in single- and binary-component solutions than the base treated materials though the performance was in the order: *C. canephora ≥ Musa spp ≥ C. papyrus*. For all biosorbents, there was preferential Pb²⁺ ions sorption to that of Cd²⁺ ions although the biosorption of all metal ions from binary-component solutions was suppressed when compared to the single-component solutions which were similar to findings by other scholars (Khani, 2013) (Article III).

The co-ion effect in binary component solutions with constant initial Pb²⁺ ions concentration (20 mg L⁻¹) and varying Cd²⁺ ions concentration was studied and results presented in Figure 14. The plots of percentage biosorption of Pb²⁺ ions for all the biosorbents showed linear decline with increasing initial Cd²⁺ ions concentration in binary–component solutions. The biosorbents' sorption performance for Pb²⁺ ions biosorption was in the order; *C. canephora > C. papyrus >> Musa spp*. The Cd²⁺ ions biosorption gradually increased for *C. papyrus* although it was spasmodic for *C. canephora* and uniform for *Musa spp*. The biosorbents' performance for Cd²⁺ ions biosorption was in the order of *Musa spp. > C. canephora > C. papyrus*. The Cd²⁺ ions biosorption does not surpass that of Pb²⁺ ions even when the ratio of Cd²⁺:Pb²⁺ ions was increased through 3:2, 2:1, 3:1 and 5:1. There was preferential biosorption of Pb²⁺ ions for all the biosorbents even when its initial concentration was very low in binary – component solutions (Article III).
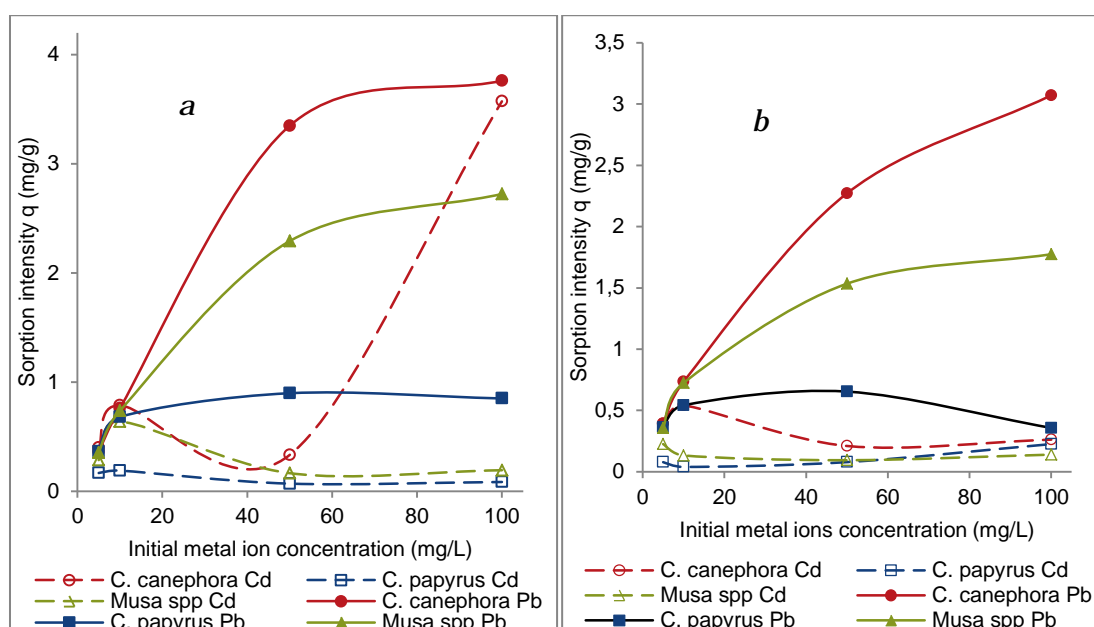
Figure 13 *Sorption intensities q (mg/g) of peroxide treated biosorbents for Cd²⁺ and Pb²⁺ ions as a function of the initial metal ions concentration in single-component (a) and binary-component solutions (b) (Article III).*
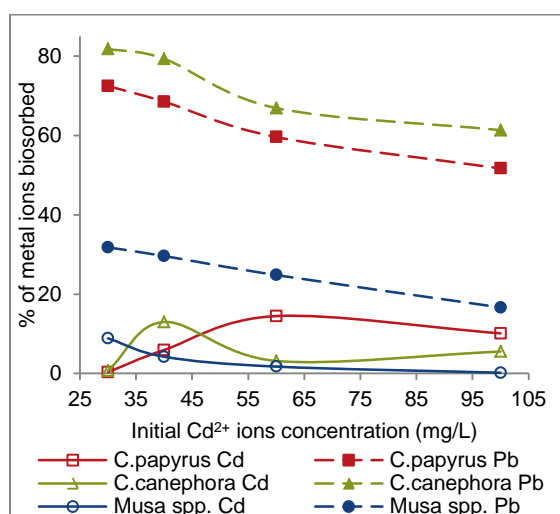
Figure 14 *Percentage Cd²⁺ and Pb²⁺ ions biosorbed as a function of increasing initial Cd²⁺ ions concentration in binary-component solutions (Article III)*
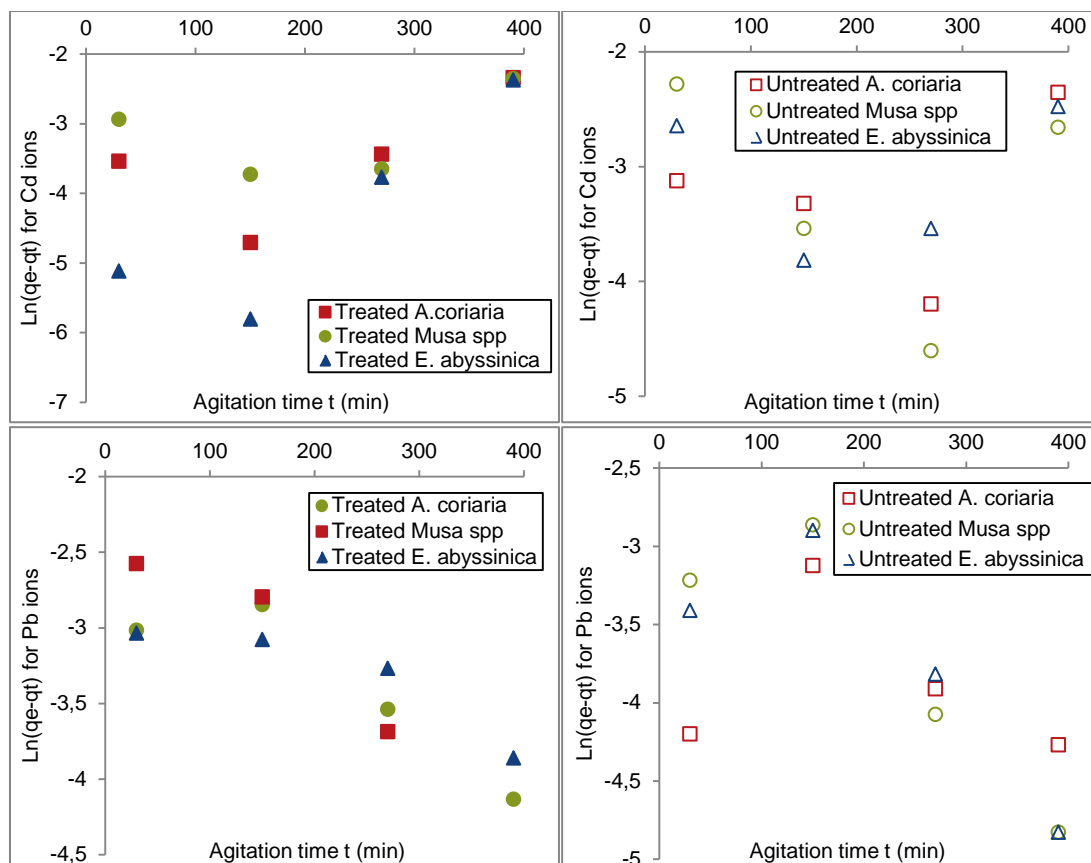
Figure 15 *Pseudo-first-order kinetics for biosorption of Cd^2 and Pb^2 ions onto unntreated and base treated biosorbents (Article I)*

The competing effect of Pb^{2+} ions on Cd^{2+} ions was high and these results imply that Cd^{2+} and Pb^{2+} ions have different affinities to the biosorbents' surfaces and differ in binding strength; therefore, their sorption was governed by disparate sorption mechanisms.

Ions with greater hydrated ionic radii will be far away from the sorbent surface and will experience weaker binding forces to the sorption sites, which implies that Cd^{2+} ions selectivity for sorption in binary-component solutions was weaker than that of Pb^{2+} ions. The trends in biosorption of Cd^{2+} and Pb^{2+} ions from binary metal systems reported here were in agreement with those reported elsewhere in literature (Khani, 2013).

Biosorption kinetic studies

In Figure 15, the plots indicated that the Pseudo-first-order model did not fit all the experimental data for Cd^{2+} ions although part of the data for Pb^{2+} ions sorption gave good regression coefficient (R^2) values; 0.8183 – 0.9084. The Lagergren model could not explain the Cd^{2+} ions sorption mechanisms but could describe Pb^{2+} ions sorption for short durations. The plots in Figure 16, show the Ho model kinetics for untreated and base-treated bisorbents which gave very satisfactory fits for both Cd^{2+} and Pb^{2+} biosorption data for all biosorbents with regression coefficient (R^2) values; 0.9978 – 0.9999 for Cd^{2+} ions and 0.9995 – 0.9998 for Pb^{2+} ions.

The Ho model parameters for all the biosorbents were a very good representaion of the sorption process. Here the q_e values were; 1.334 – 1.728 mg g^{-1} for Cd^{2+} ions and 1.306 – 1.360 mg g^{-1} for Pb^{2+} ions. Since the Ho model fits all the Cd^{2+} and Pb^{2+} ions experimental data, the biosorption mechanism predicted was chemisorption as reported in previous studies (Kalmykova, 2009; Dekhil, et al., 2011; Sari & Tuzen, 2009; Bulut & Tez, 2003).

The plots in Figure 15 suggested that the biosorption behaviour could be attributed to the time of agitation over which modelling was done since it applies well to short periods up to 30 minutes otherwise

the results indicate that the biosorption mechanisms for Cd^{2+} and Pb^{2+} ions do not follow the pseudo first-order model. The plots in Figure 16 and the parameters in Table 5 for the Pseudo-second-order model showed that it provided very satisfactory fits for both Cd^{2+} and Pb^{2+} ions biosorption data for untreated and base treated biosorbents. It was observed that the second-order model provided very satisfactory fits for the biosorption data for both Cd^{2+} and Pb^{2+} ions for untreated and treated biosorbents than the first-order kinetic model. The regression coefficient (R^2) values for the second-order kinetic model were in the range of 0.9978 to 0.9999. The principle on which the pseudo-second order model was established was that when it fits experimental data it deduces chemisorption as the operative reaction mechanism. Ho & McKay, (1998) asserted that the pseudo second order model predicts the kinetic behaviour of biosorption with chemical sorption being the rate controlling step. The results in these studies showed that the second-order kinetic model (Ho model) gave better correlation for Cd^{2+} and Pb^{2+} ions biosorption than the pseudo first-order kinetic model for the biosorption of Cd^{2+} and Pb^{2+} ions onto biosorbents. These findings were in line with sorption studies reviewed by Wan Ngah & Hanafiah, (2008) and the generally held opnion that the biosorption processes follow pseudo second order kinetics.
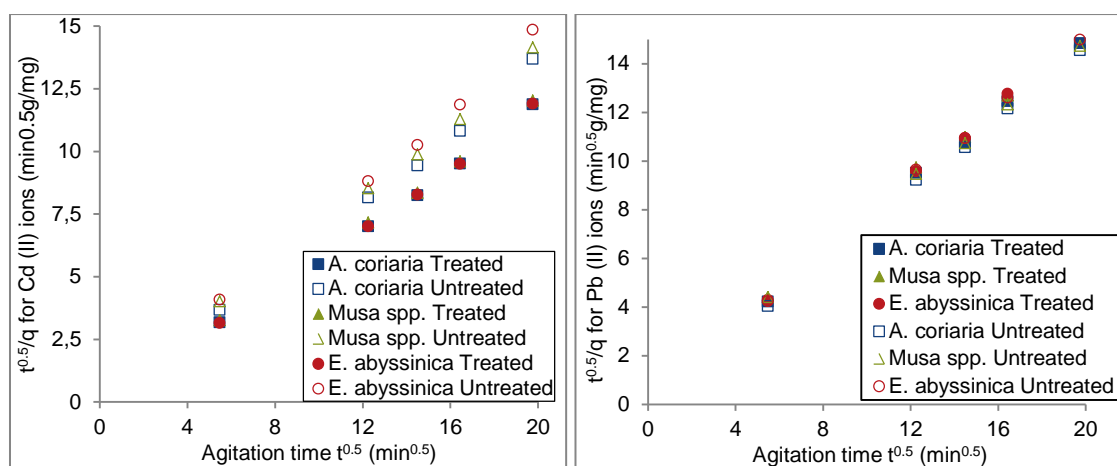
From Figure 17, the diffusion-chemisorption model satisfactorily fits Pb^{2+} and Cd^{2+} ions biosorption data to a very good degree with high regression coefficients, R^2 in the range of $0.995 - 0.999$ for untreated and base treated biosorbents. It was suggested that when the diffusion-chemisorption model fits the experimental data with high precision, it implies that the rate of occupation of sorption sites by the Pb^{2+} and Cd^{2+} ions is not only a function of the unoccupied sites but also the structure of the biosorbent.

The plots in Figure 18*a* and the kinetic model parameters in Table 5, showed that for all peroxide treated biosorbents, the biosorption data were not well represented by the Lagergren model except for *C. papyrus* and *C. canephora* where the regression coefficient, R^2 was >0.93 for agitation time $0 - 1$ hour whereas graphs and the regression coefficient (R^2) values of the Pseudo-second-order model, indicated that it fitted best the experimental biosorption data for both Cd^{2+} and Pb^{2+} ions for all the biosorbents. The regression coefficient (R^2) values for the pseudo second-order kinetic model were close to unity ($0.89 \leq R^2 \geq 1.00$). The plots in Figures 18*b* and the parameters in Table 5 showed that the diffusion-chemisorption model fitted the biosorption data for both *C. canephora* and *Musa spp.* of the data with regression coefficient of values of $0.95 \leq R^2 \geq 1.00$.

From Table 4 and 5, it was observed that the experimental data for Cd^{2+} ions sorption for all biosorbents did not fit the Pseudo-first-order (Lagergren) model although the data for Pb^{2+} ions sorption onto treated biosorbents gave good regression coefficient (R^2) values in the range of $0.818 - 0.908$ for base treated and untreaed materials and $0.713 - 0.973$ for peroxide treated materials. The Lagergren model could describe the Pb^{2+} ions sorption well for up to 30 minutes agitation time implying that the rate of uptake of Pb^{2+} ions is proportional to the number of free sorption sites during this time. All Cd^{2+} ions sorption data did not fit the Lagergren model, therefore, it can not be used to explain the underlying Cd^{2+} ions sorption mechenisms. The pseudo-second-order model regression coefficients were in the range of $0.9978 - 0.9999$ for base treated and untreated biosorbents and $0.892 - 1.000$ for peroxide treated materials which were indicative of very good representaion of the sorption process. Since the biosorption of Cd^{2+} and Pb^{2+} ions follows the Ho model, the reaction mechanism was chemisorption. The fitting of the experimental data to the diffuision-chemisorption model with regression coefficients in the range of $0.996 - 0.999$ for base treated and untreated biosorbents and $0.641 - 0.992$ for peroxide treated materials which revealed a complex process with more than one biosorption mechanism influencing the biosorption reaction. This conformity infers that the rate of occupation of biosorption sites by Pb^{2+} and Cd^{2+} was gorverned mainly by chemisorption although the biosorption process appeared more complex than could be defined by satisfactory fitting to a particular model. The diffusion-chemisorption model fitting of experimental data implies that the rate of occupation of biosorption sites by Pb^{2+} and Cd^{2+} ions is not only a function of unoccupied sites but also the structure of the biosorbent in line with the argument by Sutherland & Venkobachar, (2010).
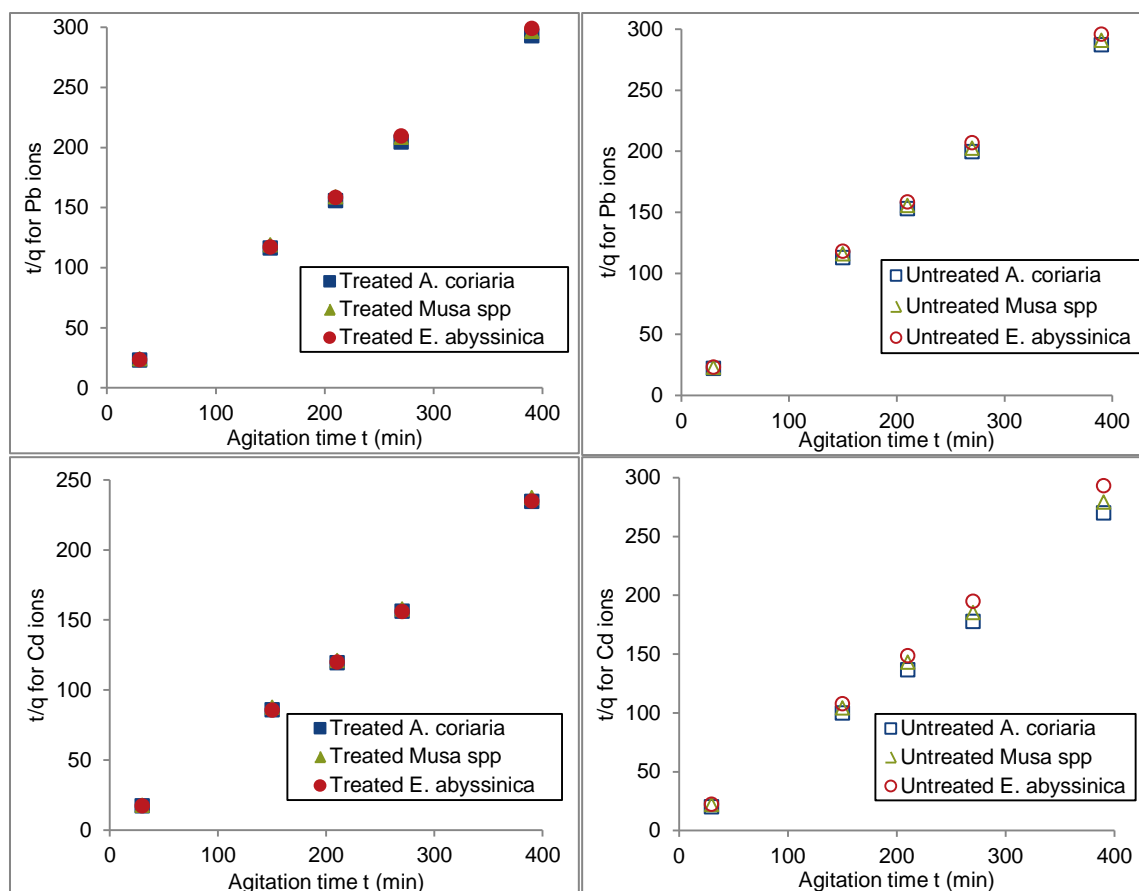
Figure 16 *Second order kinetics for biosorption of Cd^2 and Pb^2 ions onto unntreated and base treated biosorbents (Article I)*

***Figure 17** Diffusion-chemisorption plots for biosorption of Cd^{2+} and Pb^{2+} ions onto unntreated and base treated biosorbents*

Table 4 *Sorption kinetic parameters for the biosorption of Cd²⁺ and Pb²⁺ ions onto base treated biosorbents*

Biosorbents		Pseudo-first-order			Pseudo-second-order			Diffusion-chemisorption		
Biosorption Kinetic Models										
		k_1	q_e	R^2	k_2	q_e	R^2	K_{DC}	q_e	R^2
A. coriaria										
Treated	Cd²⁺	0.245	0.013	0.4223	0.454	1.728	0.9999	3.492	1.660	0.996
	Pb²⁺	0.206	0.068	0.8183	0.393	1.336	0.9996	4.803	1.348	0.999
Untreated	Cd²⁺	0.084	0.030	0.1016	0.118	1.450	0.9978	3.768	1.454	0.995
	Pb²⁺	0.053	0.025	0.0671	0.853	1.360	0.9998	16.393	1.362	0.999
E. abyssinica										
Treated	Cd²⁺	0.038	0.038	0.0217	0.093	1.659	0.9985	3.052	1.651	0.997
	Pb²⁺	0.135	0.058	0.8384	0.752	1.306	0.9996	7.424	1.315	0.999
Untreated	Cd²⁺	0.530	0.002	0.6839	0.137	1.334	0.9982	5.013	1.346	0.995
	Pb²⁺	0.258	0.059	0.6664	0.322	1.323	0.9996	5.043	1.331	0.999
Musa spp.										
Treated	Cd²⁺	0.093	0.030	0.1306	0.112	1.647	0.9984	4.778	1.652	0.996
	Pb²⁺	0.426	0.128	0.9084	0.207	1.323	0.9995	2.504	1.346	0.998
Untreated	Cd²⁺	0.110	0.056	0.0751	0.210	1.408	0.9984	35.84	1.434	0.996
	Pb²⁺	0.251	0.049	0.9802	0.307	1.348	0.9996	2.062	1.389	0.999
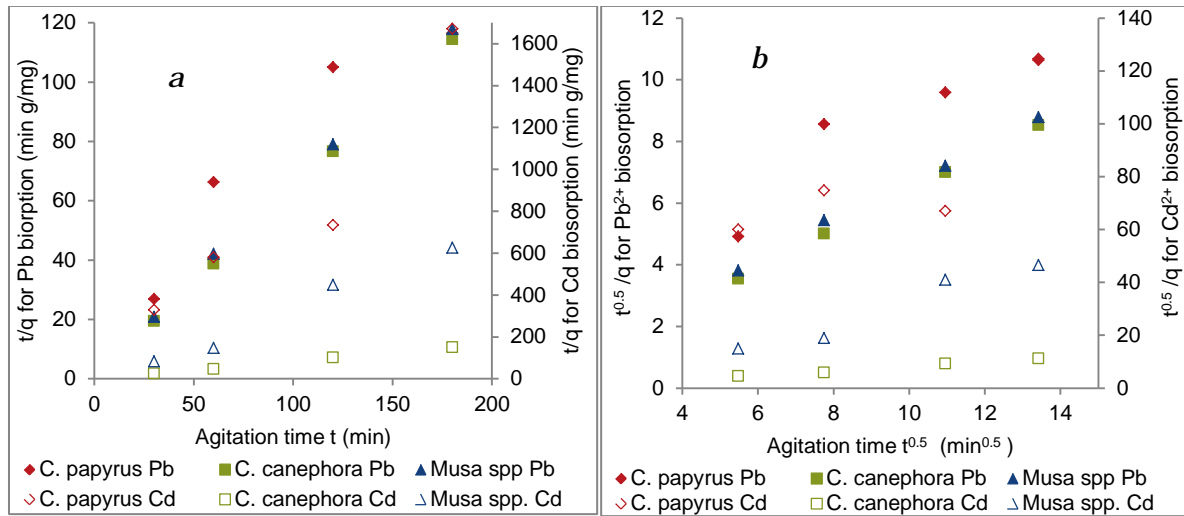
Figure 18 *Pseudo-second-order fits (a) and Diffusion-chemisorption fits (b) for Cd²⁺ and Pb²⁺ ions biosorption data for single-component solutions*

Table 5 *Sorption kinetic parameters for the biosorption Cd^{2+} and Pb^{2+} ions onto peroxide treated biosorbents*

Biosorption Kinetic Models									
Biosorbents		Pseudo-first-order model			Pseudo-second-order model			Diffusion-chemisorption model		
		k_1	q_e	R^2	k_2	q_e	R^2	K_{DC}	q_e	R^2
Coffea canephora	Cd^{2+}	0.003	0.20	0.134	0.25	1.18	0.999	1.83	1.15	0.992
	Pb^{2+}	0.005	0.06	0.973	0.67	1.58	1.000	8.24	1.60	1.000
Cyperus papyrus	Cd^{2+}	0.013	0.18	0.946	4.22	0.12	0.892	0.05	0.15	0.641
	Pb^{2+}	0.016	1.34	0.713	0.02	1.73	0.894	0.45	1.52	0.861
Musa spp.	Cd^{2+}	0.010	0.05	0.465	0.31	0.26	0.984	0.09	0.23	0.950
	Pb^{2+}	0.010	0.19	0.877	0.17	1.56	1.000	1.92	1.62	0.988

Equilibrium studies

Biosorption data for untreated and base treated biosorbents was fitted to the Freundlich, Langmuir and Temkin isotherm models and the resultant model parameters determined are presented in Table 6. The correlation coefficients (R^2) for the models were used to determine the model that best fitted the experimental data. The overall fitting of the isotherm models for Cd^{2+} ions biosorption data followed the order; Langmuir ($0.993 \leq R^2 \geq 1.000$), Freundlich ($0.431 \leq R^2 \geq 0.993$) and Temkin ($0.425 \leq R^2 \geq 0.966$). The general isotherm model fitting for Pb^{2+} ions biosorption data followed the order; Freundlich ($0.731 \leq R^2 \geq 0.987$), Temkin ($0.757 \leq R^2 \geq 0.944$) and Langmuir ($0.400 \leq R^2 \geq 0.993$). The Temkin and Freundlich models fitted Pb^{2+} ions biosorption data for both treated and untreated biosorbents better than they did for Cd^{2+} ions biosorption data. The values of the Langmuir and Freundlich parameters showed that the models explained the sorption by untreated biosorbents better than they did for base treated biosorbents. (Article III)

For the Langmuir isotherm, the *b* values for Pb^{2+} ions sorption were superior to those of Cd^{2+} ions which signified that the biosorbents had higher affinity for Pb^{2+} ions than Cd^{2+} ions. The b_F values were less than unity for all biosorbents except for Pb^{2+} ions biosorption onto treated materials. Freundlich isotherm fitted Pb^{2+} ions biosorption data for treated biosorbents although the high b_F values indicated unfavourable biosorption.

The values of Temkin isotherm parameters A_T and b_T (Table 6) were high and in the same range as those reported by Otun, et al., (2006) for the adsorption of Pb^{2+}, Ni^{2+} and Cd^{2+} ions onto powdered egg shells. The values of A_T and b_T implied that the biosorption intensities for Cd^{2+} and Pb^{2+} ions were high for all biosorbents studied and that the sorption processes were complex in nature (Article III). The regression coefficient, R^2 values for Temkin model fitting of Pb^{2+} ions biosorption suggested that it could describe the sorption processes onto untreated and treated biosorbents.

On the other hand, fitting of biosorption data for Cd^{2+} and Pb^{2+} ions by peroxide treated biosorbents from single – and binary – component solutions to the Freundlich, Langmuir and Temkin sorption isotherms was done to determine the isotherm model parameters presented in Table 7. The correlation coefficients (R^2) for the models were used to determine the best fitting model. The overall fitting of the isotherm models for Cd^{2+} ions biosorption data followed the order; Langmuir ($0.951 \leq R^2 \geq 1.000$), Temkin ($0.492 \leq R^2 \geq 0.951$) and Freundlich ($0.363 \leq R^2 \geq 0.882$). The isotherm model fitting for Pb^{2+} ions biosorption data followed the order; Langmuir ($0.990 \leq R^2 \geq 1.000$), Temkin ($0.831 \leq R^2 \geq 0.993$) and Freundlich ($0.769 \leq R^2 \geq 0.954$). The three models tested fit Pb^{2+} ions biosorption data better than the Cd^{2+} ions biosorption data for both single- and binary-component solutions. For the Langmuir sorption isotherm, the *b* values for the sorption data of the peroxide treated biosorbents implied high affinity for Cd^{2+} and Pb^{2+} ions. For the Freundlich sorption isotherm, the high b_F values for sorption of Cd^{2+} and Pb^{2+} ions onto peroxide-treated biosorbents indicated that these sorbents have heterogeneous site binding affinities while the values of A_T and b_T in the Temkin sorption isotherm were high and implied higher sorption capacities for Cd^{2+} and Pb^{2+} ions especially in binary-component solutions. To a good extent Temkin isotherm fits sorption data for Cd^{2+} and Pb^{2+} ions in binary-component solutions (Article III).

Table 6 *Sorption isotherm parameters for biosorption of Cd^{2+} and Pb^{2+} ions onto untreated and base-treated biosorbents*

Sorption Isotherm Models										
Biosorbents		Langmuir			Freundlich			Temkin		
		b	q_{max}	R^2	b_F	a_F	R^2	b_T	A_T	R^2
A. coriaria										
Treated	Cd^{2+}	1.362	0.148	0.998	0.141	0.477	0.431	2.74E4	5.0E3	0.425
	Pb^{2+}	2.176	1.196	0.667	1.742	3.062	0.905	5.05E2	2.718	0.757
Untreated	Cd^{2+}	2.278	0.040	0.999	0.249	0.247	0.993	7.35E4	7.4E2	0.966
	Pb^{2+}	3.401	2.343	0.979	0.537	1.540	0.736	1.76E3	6.810	0.830
E. abyssinica										
Treated	Cd^{2+}	2.470	0.022	0.993	0.397	0.413	0.706	3.17E4	2.8E2	0.740
	Pb^{2+}	3.889	0.222	0.766	2.091	0.274	0.910	4.27E2	1.309	0.874
Untreated	Cd^{2+}	1.279	0.063	1.000	0.268	0.212	0.688	7.24E4	3.7E2	0.669
	Pb^{2+}	4.721	1.433	0.993	0.571	0.994	0.899	1.92E3	3.460	0.944
Musa spp.										
Treated	Cd^{2+}	0.089	6.006	1.000	0.026	0.506	0.527	1.86E5	4E16	0.506
	Pb^{2+}	7.985	0.963	0.400	1.272	1.293	0.934	6.89E2	2.051	0.829
Untreated	Cd^{2+}	3.163	0.015	0.993	0.588	0.733	0.831	4.38E3	2.557	0.811
	Pb^{2+}	13.49	1.287	0.607	0.808	1.154	0.987	1.14E3	2.711	0.860

Table 7 *Sorption isotherm parameters for biosorption of Cd^{2+} and Pb^{2+} ions using peroxide-treated biosorbents*

Single component solutions										
Biosorbents		Langmuir			Freundlich			Temkin		
		b	q_{max}	R^2	b_F	a_F	R^2	b_T	A_T	R^2
C. canephora	Cd^{2+}	0.078	4.285	1.000	0.228	0.455	0.363	6.3E3	6.0E1	0.492
	Pb^{2+}	2.880	1.381	0.997	0.459	0.803	0.850	3.4E3	5.232	0.934
C. papyrus	Cd^{2+}	0.623	0.131	0.983	0.266	0.254	0.780	7.7E4	9.9E2	0.780
	Pb^{2+}	0.019	45.46	0.999	0.142	0.503	0.769	2.9E4	4.9E2	0.831
Musa spp.	Cd^{2+}	0.566	0.334	0.993	0.216	0.463	0.600	2.0E4	3.0E2	0.951
	Pb^{2+}	3.661	0.780	0.998	0.350	0.705	0.803	5.1E3	4.663	0.992
Binary component solutions (C₀ Cd²⁺ = C₀Pb²⁺)										
C. canephora	Cd^{2+}	1.133	0.224	0.983	0.383	1.215	0.882	1.36E4	2.6E2	0.925
	Pb^{2+}	4.806	0.673	0.990	0.408	0.614	0.954	4.62E3	4.222	0.993
C. papyrus	Cd^{2+}	5.575	0.016	0.951	0.691	0.008	0.886	3.54E4	6.967	0.728
	Pb^{2+}	0.550	1.203	1.000	0.129	0.422	0.916	3.85E4	8.2E2	0.953
Musa spp.	Cd^{2+}	4.038	0.033	0.939	0.154	0.218	0.540	1.000	6.9E3	0.589
	Pb^{2+}	2.666	0.679	0.997	0.283	0.554	0.905	9.3E3	1.1E1	0.982

Although different isotherm models fit the experimental biosorption data with varying degrees of correlation coefficients, the Langmuir model generally presented the best fits for the Cd^{2+} and Pb^{2+} ions sorption data for all biosorbents. The fitting of experimental data to Freundlich and Langmuir isotherm models suggested that the biosorption process was a monolayer capacitive sorption process in which heterogeneous surface conditions co-existed.

Biosorption thermodynamics

Biosorption thermodynamics were studied for Cd^{2+} and Pb^{2+} ions biosorption onto all biosorbents; treated and untreated in single- and binary component solutions, and the values of the thermodynamic parameters are presented in Table 8 and 9. The apparent biosorption equilibrium constant, K_c values for Pb^{2+} ions were far higher than those for Cd^{2+} ions which implied that the remediation of Pb^{2+} ions in contaminated aqueous media using biosorbents would be achieved faster than that for Cd^{2+} ions. The K_c values for Cd^{2+} and Pb^{2+} ions were noticeably different for the untreated and base treated biosorbents although the difference reduced for peroxide treated biosorbents and binary-component solutions. The negative value of ΔG^0 indicated impulsiveness for Pb^{2+} ions biosorption onto base treated biosorbents whereas the Cd^{2+} ions biosorption processes were not. The ΔG^0 values for Pb^{2+} ions sorption onto base treated are more negative than for untreated materials. The ΔG^0 values for Cd^{2+} ions biosorption are positive and the processes were thermodynamically non-spontaneous. For sorption of the Cd^{2+} and Pb^{2+} ions from single-and binary-component solutions, the ΔG^0 values were all positive which showed that the processes were non-impulsive at 297K and in agreement with positive values reported by Azouaou et al., (2010) for cadmium adsorption onto coffee grounds however, Khani (2013) reported increased suddenness of sorption processes for Cd^{2+} and Pb^{2+} ions at higher temperatures by algae. However, a comparison of the ΔG^0 values for Cd^{2+} and Pb^{2+} ions biosorption indicates that the values for Cd^{2+} ions are twice those for Pb^{2+} ions for single- and binary-component solutions indicative of the preference for Pb^{2+} ions sorption in binary solutions even when the ratio of the initial ion concentration of $Cd^{2+}:Pb^{2+}$ was increased in the range 3:2, 2:1, 3:1and 5:1 (Article III). Further studies are required to investigate other thermodynamic parameters such as entropy and enthalpy changes in order to fully understand and determine the nature of the Cd^{2+} and Pb^{2+} ions sorption processes.

Table 8 *Sorption equilibrium constant* K_c *and Gibbs free energy* ΔG^0 *for* Cd^{2+} *and* Pb^{2+} *ions biosorption onto untreated and base treated biosorbents at 297K*

Biosorbents	A. coriaria				E. abyssinica				Musa spp			
Treatment	NaOH		None		NaOH		None		NaOH		None	
Metal ions	Cd^{2+}	Pb^{2+}	Cd^{2+}	Pb^{2+}	Cd^{2+}	Pb^{2+}	Cd^{2+}	Pb^{2+}	Cd^{2+}	Pb^{2+}	Cd^{2+}	Pb^{2+}
K_c (x10^{-3})	8.2	6707	1.7	3946	3.1	2076	1.5	861	4.9	2187	1.9	775
ΔG^0 (kJ/mol)	11.86	-4.70	15.75	-3.39	14.26	-1.80	16.06	0.37	13.13	-1.93	15.47	0.63

Table 9 *Sorption equilibrium constant* K_c *and Gibbs free energy* ΔG^0 *for* Cd^{2+} *and* Pb^{2+} *ions biosorption onto peroxide treated biosorbents from single-and binary-component aqueous media at 297K*

Composition of the aqueous solution							
Biosorbents		Single-component		Binary-component ($C_0 Cd^{2+} = C_0 Pb^{2+}$)		Binary-component (increasing $C_0 Cd^{2+}$)	
	Metal ions	K_c (x10^{-2})	ΔG^0 (kJ/mol)	K_c (x10^{-3})	ΔG^0 (kJ/mol)	K_c (x10^{-2})	ΔG^0 (kJ/mol)
C. canephora	Cd^{2+}	4.51	7.652	5.40	12.89	0.66	11.14
	Pb^{2+}	36.4	2.497	41.6	7.851	8.00	5.468
C. papyrus	Cd^{2+}	0.24	14.90	1.70	15.75	1.10	12.40
	Pb^{2+}	1.00	11.35	5.30	12.94	10.9	6.237
Musa spp.	Cd^{2+}	0.63	12.51	2.10	15.23	0.29	14.43
	Pb^{2+}	8.45	6.102	33.1	8.416	5.68	7.082

Conclusions and implications

Chemical treatment reduced dissolved organics released to trace metal treated water and the dissolved organics were found to have no effect on Cd^{2+} and Pb^{2+} ions biosorption. Base treatment of biosorbents enhanced Cd^{2+} ions removal but exhibited reductive effects on Pb^{2+} ions biosorption efficiencies. Base treated materials archieved higher sorption capacities (1.325 – 1.753 mg g^{-1}) than peroxide treated biosorbents (1.202 – 1.528 mg g^{-1}). The base treated materials achieved maximum biosoprtion intensities at pH 4 for Pb^{2+} ions(2.036 – 2.071 mg g^{-1}) and at pH 5 for Cd^{2+} ions (1.438 – 1.747 mg g^{-1}) whereas the peroxide treated materials exhibited maximum sorption intensities of (1.148 – 1.517 mg g^{-1}) for Pb^{2+} ions at pH 5.5 and (0.139 – 1.331 mg g^{-1}) for Cd^{2+} ions at pH 3.5 in 3.5 hours of contact time at 24 ± 1°C. The biosorption data was adequately described by the Ho model with regression coefficient (R^2) values; 0.9978 – 0.9999 for Cd^{2+} ions and 0.9995 – 0.9998 for Pb^{2+} ions, and the fitting of the diffusion-chemisorption model indicated that the sorption process was complex with diffusion and chemisorption reaction mechanisms gorverning the process. The base treated biosorbents were more appropriate for Cd^{2+} ions removal whereas the untreated materials were more suitable for Pb^{2+} ions sorption. Cd^{2+} and Pb^{2+} ions biosorption from binary component solutions was supressed although the synergistic effects were great for Cd^{2+} than Pb^{2+} ions. Pb^{2+} ions biosorption was more favoured with better values of Gibbs free energy than Cd^{2+} ions. Geenerally all the sorption equilibrium models studied showed fitting of experimental data to some extent but the Langmuir model offered the best fits and described best the Cd^{2+} and Pb^{2+} ions biosorption from aqueous media. Biosorption is feasible and the plant wastes; *A. coriaria, C. canephora, C. papyrus, E. abyssinica* and *Musa spp* were found to be potential biosorbents for removal of aqueous Cd^{2+} and Pb^{2+} ions in minute concentrations (≤20 mg L^{-1}) from aqueous media although Pb^{2+} ions were preferentially sequestered in multi-component solutions. The presence of Pb^{2+} ions had great synergistic effects on the biosorption of aqueous Cd^{2+} ions.

Implications

The environmental implication of this study is that waste biomass was found to be reusable with the biosorption technique being a low cost alternative remediation method for removing trace metal ions from contaminated aqueous media. On the other hand the waste biomass disposal burden will be minimised with reapplication. The socio-economic implication of these studies is that the vulnerability of children and women due to exposure to trace metal contaminats in contaminated water can be reduced through the application of biosorbents to remove the contaminants.

Areas for further research

Future research on thermodynamics is recommended to understand the sorption mechanism and design filter media using the biosorbents in this study. Column studies using environmental samples of contaminated water should be undertaken to understand the chemical interactions of different ions during biosorption. Speciation studies of the treated solutions will be carried out to evaluate the sorption performance of the materials in decontaminating aqueous media to WHO acceptable water quality standards. Desorption studies need be undertaken to determine the sustainability of the biosorption technique in full scale applications.

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APPENDINCES

I.   G. K. Bakyayita, A. C. Norrström., M. Nalubega & R. N. Kulabako, 2014 (*In press*). Kinetic studies of Cd (II) and Pb (II) ions biosorption from aqueous media using untreated and chemically treated biosorbents. *Journal of Water Science and Technology (In production DOI: 10.21.2166/wst.2014.147)*

II.   Bakyayita, G., Nalubega, M., Norrström, A. & Kulabako, R., 2014. Single and binary biosorption kinetics for cadmium (II) and lead (II) ions from aqueous media using Coffea canephora, Cyperus papyrus and Musa spp. *(Manuscript)*.

III.   Bakyayita, G., Kulabako, R., Nalubega, M. & Norrström, A., 2014. Equilibrium batch studies for biosorption of Cd (II) and Pb (II) ions from single-and binary-component aqueous media *(Manuscript)*.