Research Article

Competitive and Noncompetitive Batch Sorption Studies of Aqueous Cd(II) and Pb(II) Uptake onto *Coffea canephora* Husks, *Cyperus papyrus* Stems, and *Musa* spp. Peels

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Coffea canephora, *Cyperus papyrus,* and *Musa* spp. were studied for competitive and noncompetitive removal of aqueous Cd^{2+} and Pb^{2+}. The optimal conditions were pH 4.5 and agitation time 3.0 hours. Biomass constituent ions showed no interference effects whereas cation exchange capacity values corresponded to the sorption efficiencies. XRD spectroscopy revealed surface oxygen and nitrogen groups that provide binding sites for metal ions. The maximum sorption efficiency ranges for metal ions in noncompetitive media were 95.2–98.7% for *C. canephora*, 42.0–91.3% for *C. papyrus,* and 79.9–92.2% for *Musa* spp. and in competitive sorption 90.8–98.0% for *C. canephora*, 19.5–90.4% for *C. papyrus,* and 56.4–89.3% for *Musa* spp. The Pb^{2+} ions uptake was superior to that of Cd^{2+} ions in competitive and noncompetitive media. In competitive sorption synergistic effects were higher for Cd^{2+} than Pb^{2+} ions. The pseudo-second-order kinetic model fitted experimental data with $0.917 \leq R^2 \geq 1.000$ for Pb^{2+} ions and $0.711 \leq R^2 \geq 0.999$ for Cd^{2+} ions. The Langmuir model fitted noncompetitive sorption data with $0.769 \leq R^2 \geq 0.999$; moreover the Freundlich model fitted competitive sorption data with $0.867 \leq R^2 \geq 0.989$. Noncompetitive sorption was monolayer chemisorption whereas competitive sorption exhibited heterogeneous sorption mechanisms.

1. Introduction

The present-day socioeconomic and industrial growths together with world demographic trends continuously dispense toxic trace metal contaminants into the environment. The pollution of the aqueous environmental resources subsequently affects life processes. Although existing conventional remediation techniques have been employed to remove metal ions, reversing freshwater quality to pristine and usable conditions when it deteriorates remains an intricate challenge. In addition, the revelation of detrimental health effects in humans occurs after acute exposure to high levels or chronic consumption of low concentrations of toxic trace metals. Plants usually adapt to toxic trace metals in polluted environments with little or no observable effects on growth and plant health presented but ordinarily animals express notable detrimental health effects after exposure to toxic trace elements. Detailed discussions of health effects of exposure to toxic trace metals have been done by Chang et al. [1] and Krishnani and Ayyappan [2], including kidney dysfunction, growth retardation, bone deformation, testicular atrophy, hypertension, nervous system disorders, anaemia, hypertension, brain damage, and liver and kidney disease as well as cancer among other ailments. Amongst the toxic trace metals in industrial, domestic, and municipal wastewaters, lead and cadmium have been studied for possible removal using low cost biosorbents.

Water provides an avenue for transport and distribution of aqueous metal contaminants in the environment; therefore, the removal of toxic trace metals from wastewater,

surface water, and groundwater ensures definite quality of the meagre water resources. Several physical and chemical conventional remediation techniques have been used for removal of trace metals from contaminated environmental matrices for many decades. In their reports, Namasivayam and Ranganathan [3] and Volesky [4] have discussed several conventional techniques of removal of metal ions from the water environment including chemical precipitation, adsorption, evaporation, electrochemical treatment, solvent extraction, membrane separation, reverse osmosis, and ion exchange. The conventional techniques are inadequate in removing metal ions in minute concentrations; moreover they are expensive to install and operate besides generating hazardous sludge. Therefore, in recent decades researchers have intensively studied low cost alternative methods of removal of trace metals from aqueous media using natural materials which are biodegradable, renewable, and environmental friendly. Among the promising techniques of removal of trace metals, Guo et al. [5] and Patnukao et al. [6] reported metal sorption onto biomasses to have substantial capacities for metal ions removal from aqueous media with good recoveries and regeneration of biosorbents in noncompetitive media. Sorption techniques that have been studied using biosorbents are ultimately meant for decontamination of polluted natural water in which toxic trace metal ions exist in association with inorganic and organic species which show synergistic effects on each other during sorption processes. Similarly Kapoor et al. [7] and Chen et al. [8] reported lower sorption capacities for metal ions in competitive sorption studies than those for metal ions in noncompetitive sorption studies. Continuous complex chemical interactions of inorganics, organics, and particulate matter under varying conditions of pH, metal concentration, and organic matter content implore sorption studies for competitive and noncompetitive media in order to explicate sorption performance in natural systems.

Biosorbents have been used in both modified and unmodified forms. Chemical modifications of biosorbents have been done using base solutions and oxidizing agents, as well as organic and mineral acids, to reduce soluble organics and enhance sorption performance [9]. The report by Horsfall Jr. et al. [10] indicated that when cassava tuber bark was treated using nitric acid the sorption intensity for Cd^{2+} ions improved from 2.7 to 11.5 mg/g. Ye et al. [11] reported that metal ions uptake onto rice husk was enhanced by treatment with sodium hydroxide from 63.4 to 293.3 mg/g for Cd^{2+} ions and 63.4 to 293.3 mg/g for Pb^{2+} ions whereas Feng et al. [12] indicated that methyl acetate treatment of orange peels increased Cd^{2+} ions uptake from 74 to 126 mg/g. In another study, Bakyayita et al. [9] reported enhancement in sorption intensities for sodium hydroxide treated biosorbents for Cd^{2+} ions onto *Albizia coriaria* from 1.56 to 1.75 mg/g and *Musa* spp. peels from 1.49 to 1.74 mg/g. Bakyayita et al. [9] also reported reduction in uptake of Cd^{2+} ions from 1.74 to 1.44 mg/g for *Erythrina abyssinica,* and for Pb^{2+} ions from 1.99 to 1.95 mg/g for *Erythrina abyssinica*, from 2.07 to 2.02 mg/g for *Albizia coriaria*, and from 2.02 to 1.98 mg/g for *Musa* spp. for sodium hydroxide treated biosorbents.

Chemical modifiers that have been used in several sorption studies include sodium hydroxide, calcium hydroxide, sodium carbonate, hydrochloric acid, nitric acid, sulphuric acid, tartaric acid, citric acid, propanoic acid, ethylenediamine, formaldehyde, and methanol as well as hydrogen peroxide to transform the chemical and physical properties of the biosorbents. In the review of modifications of materials in several studies, Rivera-Utrilla et al. [13] observed that oxidation of biosorbents increased the concentration of acid oxygen groups on the activated carbon surfaces resulting in increased polarity and decreased pH of the point of zero charge. Using bases such as NaOH and $Ca(OH)_2$ in modifications is known to convert ester groups to carboxyl groups. Wan Ngah and Hanafiah [14] averred that sodium hydroxide treatment causes swelling and increase in internal surface area, decrease in the degree of polymerization, decrease in crystallinity, and separation of structural linkages between carbohydrates and lignin. Biosorbent modifications using oxidizing agents such as H_2O_2 were reported by Qiao et al. [15] to have altered the surface chemistry of activated carbon from coconut shell by introduction of surface oxygen groups such as carboxyl, ketone, and ether groups.

The aim of this study was to investigate the efficacy of low cost plant waste materials in removing trace metals from contaminated water through the evaluation of the kinetics and the equilibrium isotherms of the competitive and noncompetitive sorption of Cd^{2+} and Pb^{2+} ions under batch conditions with the intention of scaling up conditions to fit water treatment plants. The biosorbents investigated were *Musa* spp. (cooking banana peels), *Coffea canephora* (coffee husks), and *Cyperus papyrus* (papyrus stems). The cooking banana peels are normally removed from the cooking banana just before they are steamed for food and they are salvaged as fodder for domestic animals; however, the coffee husks are recycled as a bedding material in poultry houses, as a source of energy in firing bricks and tiles in kilns, and as manure in plantations whereas the papyrus stem cuttings have no reuse. The main reason for the choice of *Musa* spp. peels, *C. canephora* husks, and *C. papyrus* stems was that their annual production rate in Uganda supersedes the demand for their reuse thence the waste burden in municipalities.

The total ionic content, dissolved organic carbon (DOC), cation exchange capacity (CEC), and pH of the biomass were evaluated and compared to the sorption efficiencies and capacities. Conversely, the evaluation of the effects of solution pH, agitation time, initial metal ions concentration, and competition on the sorption of Cd^{2+} and Pb^{2+} ions was studied and the experimental data was fitted to kinetic and equilibrium isotherm models to assess the biosorbents' performance and predict the sorption dynamics and mechanisms.

The specific objectives were to analyze and evaluate the total cationic content, dissolved organic carbon (DOC), and the cation exchange capacity (CEC) of the biomass and compare them to the sorption efficacies.

2. Materials and Methods

2.1. Preparation of Biosorbents. The cooking banana peels were obtained from roadside urban markets where cooking

bananas were peeled before steaming whereas the coffee husks were acquired from coffee processing industries in farming districts of Luweero and Nakaseke while the papyrus stem cuttings were collected from local Ugandan craftsmen in Wakiso as by-products. The plant materials were further prepared in the laboratory at Makerere University to a diameter of 2 mm according to the previous method described by Bakyayita et al. [9]. For chemical treatment, 100 g of each plant material was soaked in 250 mL of 20% H_2O_2 solution for 24 hours. The biomass was then removed from the peroxide solution and thoroughly washed with distilled deionized water before being immersed in 0.25 M NaOH for 2 hours. The NaOH was decanted and the biosorbents were neutralized using 0.25 M HCl to pH 7.0 ± 0.2. The modified biosorbents were copiously washed with distilled water and oven-dried at 105°C for 48 hours to a constant mass and stored in sealed plastic bags.

2.2. Preparation of Reagents and Biosorbates. The chemicals used were analytical grade reagents from J. T. Baker H, Deventer, Holland. Standard lead and cadmium solutions for atomic absorption spectrometry containing 1,000 mgL^{-1} were diluted to required concentrations using distilled deionized water. The noncompetitive media were prepared by diluting known portions of the standard metal solutions to the required concentration, and for competitive media mixtures of the known standard metal solutions were made up to the appropriate volume of spiked solutions using distilled deionized water. 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 prior to agitation of the mixture.

2.3. Determination of pH of the Biomass. One gram of biomass was mixed with 20 mL of distilled deionized water and shaken in a closed centrifuge bottle for 25 minutes. The bottle and contents were centrifuged at 200 rpm for 15 minutes after which 15 mL of the clear supernatant was transferred to a sample bottle and the pH was determined using a pH/ION meter model pHM95 with sensitivity 97.9%.

2.4. Measurement of Cation Exchange Capacity. For each 1.5 g of biomass placed in a plastic bottle, 100 ml of 0.1 M BaCl$_2$ was added before being capped. The bottles were shaken with a rotary shaker for 6 hours and clear extracts were filtered into clean bottles using coarse filters. To 15 mL of sample solutions, 35 mL of distilled water was added and the exchangeable acidity measured using an autotitrator by successively adding 0.01 M NaOH until pH 7.0 was attained. Another 20 mL of sample was filtered through 0.45 μm filters for metal ions analyses. The experiments were done in triplicate and the mean values were used to calculate the cation exchange capacity (CEC).

2.5. X-Ray Diffraction (XRD) Analysis. The identification of chemical composition and crystallographic structures of surface chemical species in untreated biosorbents was achieved by X-ray diffraction analysis. The biomass samples were crushed in a ceramic mortar to fine powder of diameter ≤ 1 mm and consolidated into aluminum holders. The samples were scanned at 35 kV and 40 mA from 10° to 80° of the diffraction interval with a step size of 0.01° and scan duration of 0.5 seconds for exposure time 2θ of 30 minutes for each sample. The diffraction patterns were analyzed using the DIFFRAC Plus software and plotted using Microsoft Excel.

2.6. Nitric Acid Digestion. Nitric acid digestion procedure was used to prepare biomass for total metal constituents analysis. One gram of dry biomass was placed in a 250 mL digestion tube and 10 mL of concentrated HNO_3 acid was added. The mixture was heated at 100°C for 2 hours and then treated with hydrogen peroxide. After digestion the clear supernatant was diluted using distilled deionized water to 50 mL. The solution was filtered through 0.20 μm sterile nonpyrogenic hydrophilic filters into plastic sample bottles and analyzed for metal ions using an Inductively Coupled Plasma-Mass Spectrometry (ICP-MS).

2.7. Sorption Experiments. Kinetic studies for metal ions sorption were carried out in duplicate with 12.5 g/L sorbent dose in 20 mL of synthetic solution containing 20 mg/L of trace metal ions during agitation time, 1–3 hours. The sorption studies were carried out at 24 ± 2°C and agitation was done at 60 rpm for 3.5 hours using a rotary shaker. For the assessment of pH dependence, sorption experiments were done at pH 2.5–6.5 because, at pH ≤ 2.0, H_3O^+ ions prevail in the aqueous solutions and compete for sorption sites on the biosorbent surfaces with the metal ions whereas, at pH ≥ 6.5, the metallic ions under study tend to form a number of hydroxyl complexes which render the accessibility of the biosorbent sorption sites difficult due to the large size of the species. The time dependence experiments were done in 0.5–6.5 hours for metal ion concentration of 20 mg/L for biosorbent dosage of 12.5 g/L. The metal sorption equilibrium experiments were done at the optimal pH 4.5 for initial metal ion concentrations in the range of 5–100 mg/L. The competitive sorption studies were done with increasing mixed metal concentrations in equal proportions of 5–100 mg/L. The equilibrated solutions were centrifuged at 2000 rpm for 20 minutes and then filtered. Sorption studies were carried out with biosorbent dosage of 12.5 g/L and 20 mL of spiked solutions containing 20 mgL^{-1} of trace metal ions in 50 mL plastic bottles at 24 ± 2°C.

2.8. Measurement of Residual Metal Contents and Dissolved Organic Carbon. The filtrates that were to be analyzed using Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) for trace metals were preserved using 0.2 mL of concentrated HNO_3. The samples for analysis of dissolved organic carbon (DOC) were refrigerated until analyses were done using a TOC machine (Shimadzu TOC-5000A Model). All the measurements were done in triplicate to ensure that the experimental data had a reproducibility of ±0.5%.

2.9. *Data Analysis.* The amount of metal ions that was taken up by the *C. canephora*, *Musa* spp., and *C. papyrus* per gram of biomass, q_e, was calculated from

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

However, the sorption efficiency of the biomass for the metal ions was determined from the expression in

$$E = \frac{(C_0 - C_e)}{C_0} \times 100, \tag{2}$$

where V is the volume of aqueous solution (L), m is the mass of the biomass (g), C_0 is the initial concentration (mg/L), C_e is the equilibrium concentration (mg/L), q_e is the metal ion sorption capacity (mg/g), and E is the metal sorption efficiency.

2.10. *Sorption Kinetics.* The kinetic models are essential in describing the surface properties and predicting the sorption mechanisms. The various premises on which the models were devised predict the particular mechanisms of biosorption when they best fit the experimental data. In order to investigate the kinetics of the sorption processes, the pseudo-second-order kinetic model which is frequently used to predict sorption mechanisms was fitted to the experimental data. The resultant integral of the pseudo-second-order kinetic model [16] that was used can be expressed as

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}, \tag{3}$$

where q_t is the sorption capacity of the biomass at time t, q_e is the sorption capacity of the biomass at equilibrium, and k_2 is the pseudo-second-order rate constant (g/mg/min).

2.11. *Sorption Isotherms.* The sorption isotherms for the uptake of Cd^{2+} and Pb^{2+} ions were studied for initial metal concentrations of 10 to 100 mg/L using biomass dosage of 12.5 g/L for *C. canephora*, *C. papyrus*, and *Musa* spp. at the optimal conditions of pH 4.5, agitation time 3 hours, and temperature $24 \pm 2°C$ in competitive as well as noncompetitive solutions.

2.12. *Langmuir Isotherm.* Langmuir isotherm [17] model is based on three assumptions; namely, metal sorption is a monolayer process, all biosorbent sites are similar and can only accommodate one atom, and the capacity of a site to be occupied by one sorbate atom is independent of the nature of occupancy of sites in its vicinity. The linearized form of Langmuir isotherm shown in (4) was used:

$$\frac{C_e}{q_e} = \frac{1}{b q_{max}} + \frac{C_e}{q_{max}}, \tag{4}$$

where q_{max} is the maximum monolayer sorption capacity of the biosorbent (mg/g) and b is the sorption constant (L/mg).

The Langmuir parameter b is related to the separation factor R_L which is used to predict the affinity between sorbate

and the biomass surface molecules. The Langmuir parameters can be used to predict the affinity between the sorbate and the biosorbent using the dimensionless separation factor R_L outlined in

$$R_L = \frac{1}{(1 + bC_0)}, \tag{5}$$

where b is the constant from Langmuir equation and C_0 is initial trace metal ion concentration. The parameter R_L indicates the shape of the isotherm and nature of the sorption process. According to Horsfall Jr. and Spiff [18] when the $R_L > 1$ it implies that the isotherm is unfavourable; for $R_L = 1$ it shows a linear isotherm, while $R_L = 0$ means that the isotherm is irreversible, and if $0 < R_L < 1$ then the isotherm is favourable.

2.13. *Freundlich Isotherm.* Freundlich isotherm [19] model is an empirical isotherm which suites sorption onto heterogeneous surfaces. It is based on multilayer sorption process that assumes the biosorbent surface to be heterogeneous and the sorption as nonuniform distribution. The linearized Freundlich isotherm that was used is described by

$$\ln q_e = \ln (A_F) + b_F \ln C_e, \tag{6}$$

where A_F and b_F are the Freundlich isotherm empirical constants.

A_F is the maximum sorption capacity for Freundlich isotherm and b_F predicts the suitability of the model for describing the sorption process. If the value of $1/b_F$ is greater than unity, it implies favourable adsorption [20] of the trace metal ions.

3. Results and Discussion

3.1. *Characterisation of Biomass.* Characterisation of biomass was done by measuring the pH besides the levels of K, Ca, Mg, Na, and B which are major elements known to contribute to the cation exchange capacity of a material as well as Mn, Fe, Cu, Al, and Zn which are essential trace metals in addition to the nonessential trace metals, Ni, Cd, and Pb. The results presented in Table 1 showed that the biomass contained higher levels of the major elements but lower levels of essential and nonessential trace elements. The nitric acid digestion was done to determine the total amounts of metal components of the materials and to find if the application of the biosorbents in remediation of trace metals in contaminated water would not compromise the water quality. The levels of cadmium and lead are very trace compared to those of copper, manganese, and calcium. Leaching of major metallic ions such as Ca^{2+} and Mg^{2+} into the solution during remediation would cause synergistic effects on the sorption of Cd^{2+} and Pb^{2+} ions. Al-Ahmary [21] studied retention profiles and reported reduction in sorption capacities of lead and cadmium in the presence of calcium and magnesium ions. However, findings in this study suggest that Ca^{2+} and Mg^{2+} constituent ions of the biomass did not leach to water during the sorption of aqueous metal ions

Table 1: Total levels of cations (μg/g) in the biomass studied.

Cation	C. canephora	C. papyrus	Musa spp.
Mn	11.5	34.6	11.7
Fe	4.2	1.98	1.53
Ni	0.9	0.27	0.91
Cu	18.6	1.26	2.93
Zn	5.3	10.99	17.79
Cd	0.02	0.04	0.01
Pb	0.46	0.18	1.23
Ca	1329	276	198
Mg	420	93.8	278
Na	19.5	413	17.3
K	7724	6025	9030
Al	27.5	2.5	19.3
B	27.5	2.8	14.5

Table 2: Exchangeable acidity (EA) and cation exchange capacity (CEC) of the biomass [22].

Biomass	pH	EA (cmol/kg)	CEC (cmol/kg)
Musa spp.			
Treated	5.49	0.19	53
Untreated	5.22	1.64	142
C. canephora			
Treated	5.41	0.22	95
Untreated	4.91	1.66	91
C. papyrus			
Treated	5.95	0.42	36
Untreated	5.39	0.95	85

in cation exchange and this contributes to the observation that the biomass that contained higher levels of metallic ions showed the highest sorption efficiencies (Figure 2) which indicated occurrence of minimal interference effects of major metallic elements.

From Table 2, the pH of the biomass indicated that the application of the materials in sorption studies would not affect the sorption process since the pH range 4.9–5.9 is that in which metal ions are dominant over hydroxyl ions in solution. There was a reduction in the cation exchange capacities and the total cation exchange capacities of the three biosorbents due to treatment; however the observed values were above 10 cmol/kq which indicated that the materials had a high capacity to hold cations. Untreated materials had a higher potential to hold cations than treated materials. The biomass order from the highest to the lowest negative potential for binding base cations was *Musa* spp. > *C. canephora* > *C. papyrus* for untreated biomass and *C. canephora* > *Musa* spp. > *C. papyrus* for treated materials.

The patterns of the X-ray diffraction analyses of untreated biomass presented in Figure 1 were obtained using the DIFFRAC Plus software and the prominent organic species in the biosorbents' surface structures corresponding to peaks labelled a–i were identified.

The XRD spectral peaks for untreated biosorbents revealed the presence of 2,2-bipyridine, cyclotetradecaheptaene, 2,2′-bis(2-indenyl) biphenyl, and N-ethyltryptamine in *Coffea canephora*; 9-methylfluorene, 4-ethylpyrene, sodium cyanurate, 3-beta-hydroxy-cholestan-6-one in *Musa* spp.; and 2,2′-bis(2-indenyl) biphenyl, N-ethyltryptamine, chalcone oxime, and 1,2-diphenyl cyclohexene in *Cyperus papyrus*. The notable surface organic species were mainly aromatic ringed structures rich in *pi*-electrons as well as surface oxygen and nitrogen containing groups, which form ligands that are capable of forming bonds with metallic ions through complexation during the uptake of Cd^{2+} and Pb^{2+} ions. The uptake of metal ions, therefore, may take place through cation exchange and complexation with biosorbents' surface chemical species.

3.2. Comparison of the Biomass Sorption Efficiencies and DOC Released.

The sorption efficiencies showed in Figures 2 and 3 corresponded to the observation that the metal uptake was expected to be closely related to CEC results. In Figure 2, the biomass sorption efficiencies for the metal ions and the DOC released into the remediated water samples were compared at different pH levels. The sorption efficiencies and DOC released were observed to vary in the same order for *C. canephora* husks, *Musa* spp. peels, and *C. papyrus* stems. The peak Cd^{2+} ions sorption efficiency values were 83.9% for *C. canephora*, 29.3% for *Musa* spp. peels, and 8.7% for *C. papyrus* at pH 2.5, while the peak Pb^{2+} ions sorption efficiencies were 94.3% for *C. canephora* at pH 5.5, 89.2% for *Musa* spp. peels, and 99.7% for *C. papyrus* at pH 2.5. Although the DOC released into remediated water samples was nearly constant with increase in pH, the peak DOC values in Cd^{2+} remediated solutions were 91.3 mg/L for *C. canephora* and 69.6 mg/L for *Musa* spp. peels at pH 3.5 and 48.5 mg/L for *C. papyrus* at pH 4.5, whereas the peak DOC values in Pb^{2+} remediated water were 98.0 mg/L for *C. canephora* at pH 6.5, 94.5 mg/L for *Musa* spp. peels at pH 3.5, and 97.8 mg/L for *C. papyrus* at pH 5.5. For all biosorbents, sorption performance for Cd^{2+} ions was lower than that for Pb^{2+} ions and nearly linear over the pH range 2.5–6.5. The sorption of Cd^{2+} and Pb^{2+} ions in the pH range studied showed that the metal ions were prevailing and preferred over H_3O^+ ions. The optimal pH for the removal of Cd^{2+} and Pb^{2+} ions from aqueous solutions for the biomass studied was between 3.5 and 4.5. The sorption performance for Cd^{2+} ions was in the order *C. canephora* > *Musa* spp. > *C. papyrus*. The sorption performance for Pb^{2+} ions was in the order *C. canephora* > *C. papyrus* > *Musa* spp. for noncompetitive sorption. The conditions in batch studies differ from those in column studies, but, for comparison purposes, the results showed that the effects of DOC on the sorption efficiencies of the materials were in agreement with the reports by Nehrenheim [23] and Kalmykova [24] which indicated that DOC had only minor effects on metal sorption and transport in column studies.

In Figure 3, plots for correlations were done to determine the relationship between sorption intensities and DOC released by the materials during sorption. The coefficient of determination r for Cd^{2+} ions uptake was 0.992 for *Musa* spp.
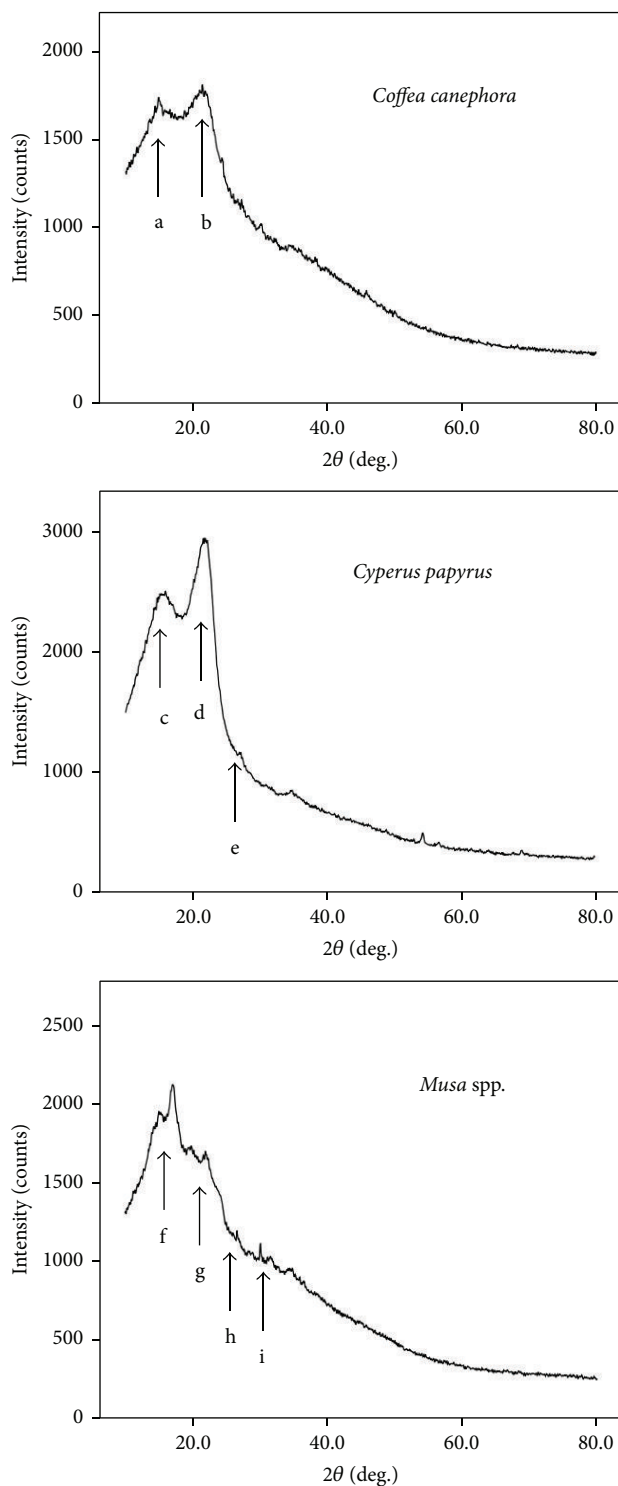
FIGURE 1: XRD Patterns for *Coffea canephora*, *Musa* spp., and *Cyperus papyrus*.

peels and 0.84 for *C. canephora*; moreover the coefficient of determination r for Pb^{2+} ions was 0.959 for *C. canephora* and 0.962 for *C. papyrus*. These coefficients of determination were strong whereas weak coefficients of determination r were observed for Cd^{2+} ions sorption onto *C. papyrus*, 0.553, as well as for Pb^{2+} ions sorption onto *Musa* spp. peels, 0.707. The strong coefficients of determination r values showed that there was an association between the amount of remediated
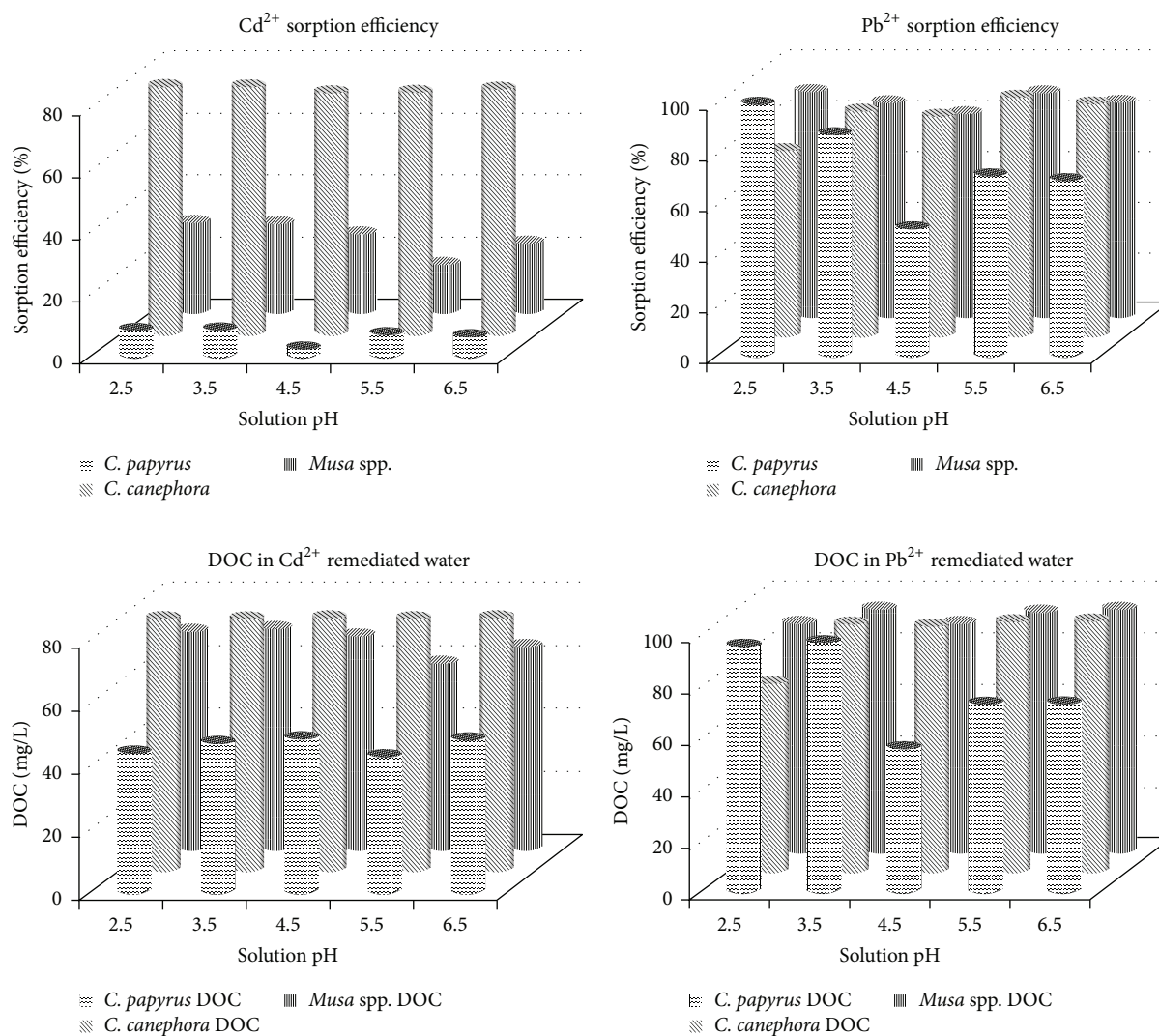
FIGURE 2: Comparison of sorption efficiencies and DOC released as a function of the solution pH for the various biosorbents studied.

metal ions and DOC released from biomass whereas the weak correlations indicated weak relationships.

3.3. Effect of Agitation Time on Metal Ions Sorption Efficiency.

The results for sorption efficiencies as a function of agitation time are presented in Figure 4. In Figure 4(a) the time dependence of the sorption efficiencies for Pb^{2+} ions onto *C. canephora* varied in the order 96.8–98.4%, for *Musa* spp. they were 89–95.5%, and for *C. papyrus* they varied from 69.7 to 84.1% for agitation time 30–180 minutes.

For all biosorbents the maximum sorption efficiencies occurred at agitation time 180 minutes. On the other hand in Figure 4(b), the sorption efficiencies for Cd^{2+} ions onto *C. canephora* were 74.8–83.2%, for *Musa* spp. they were 16.7–25.7%, and for *C. papyrus* theywere 5.7–10.2% for agitation time 30–180 minutes. The sorption efficiencies of the biomass for Cd^{2+} ions were lower than that for Pb^{2+} ions. The maximum sorption efficiency for all biosorbents for Pb^{2+} ions

occurred at an agitation time of 180 minutes and for Cd^{2+} ions it was 60 minutes.

The results also showed that the range between the minimum and maximum sorption efficiencies was very narrow which implied that the sorption process was too fast and was nearly complete with sorption sites fully occupied throughout the duration of the experiment.

The other implication is that Pb^{2+} ions sorption is slower but realizes higher efficiencies than the Cd^{2+} ions sorption most likely due to a difference in the binding mechanism. The highest sorption efficiencies for Cd^{2+} and Pb^{2+} ions were in the order of *C. canephora* > *Musa* spp. > *C. papyrus*.

3.4. Competitive Metal Sorption of Cd^{2+} and Pb^{2+} Ions.

The results of competitive sorption of Cd^{2+} and Pb^{2+} ions from binary component solutions onto *C. canephora* husks, *C. papyrus* stems, and *Musa* spp. peels as a function of

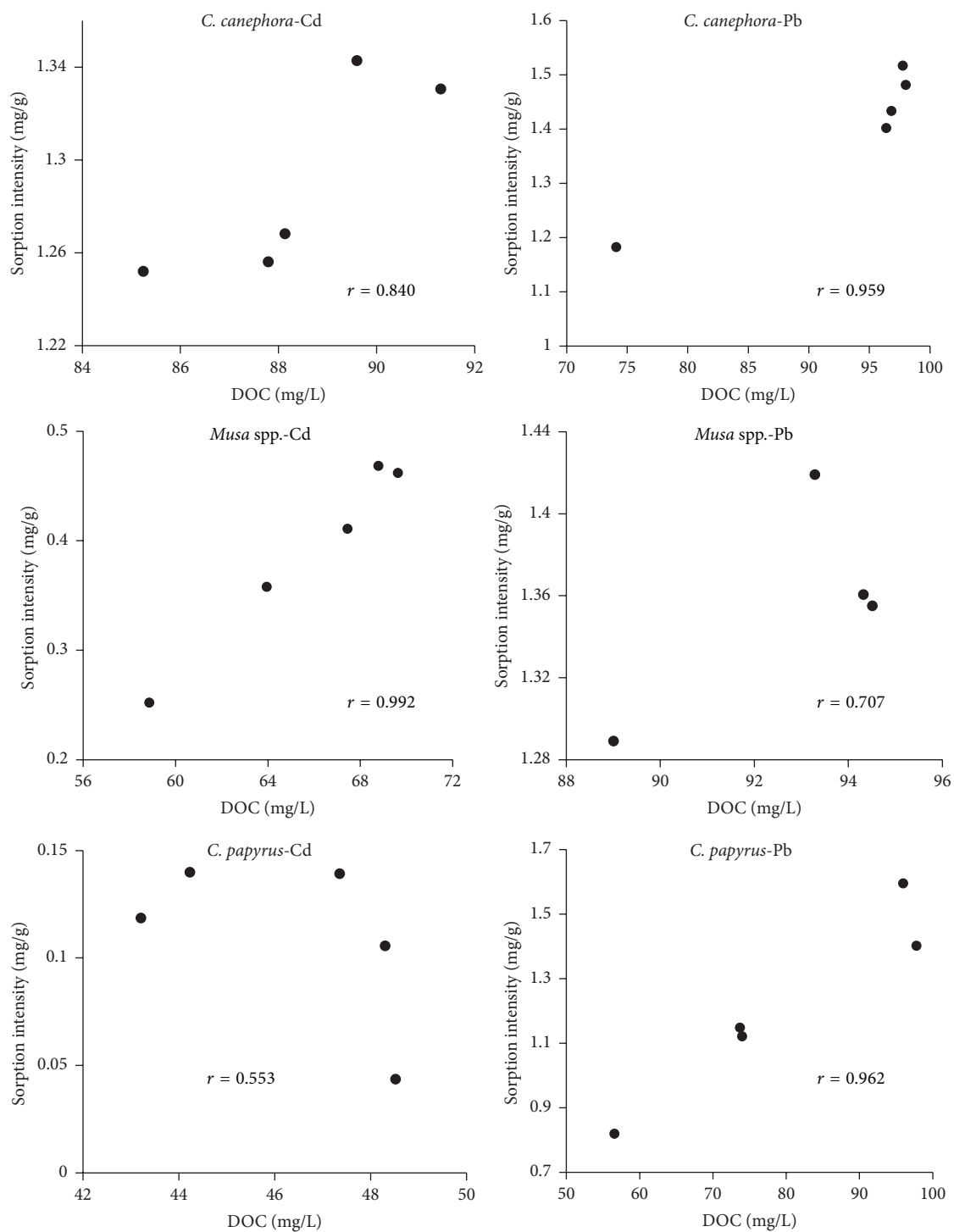Figure 3: Correlation of DOC released into solutions with the sorption intensities of *C. canephora*, *Musa* spp., and *C. papyrus* for Cd^{2+} and Pb^{2+} ions.
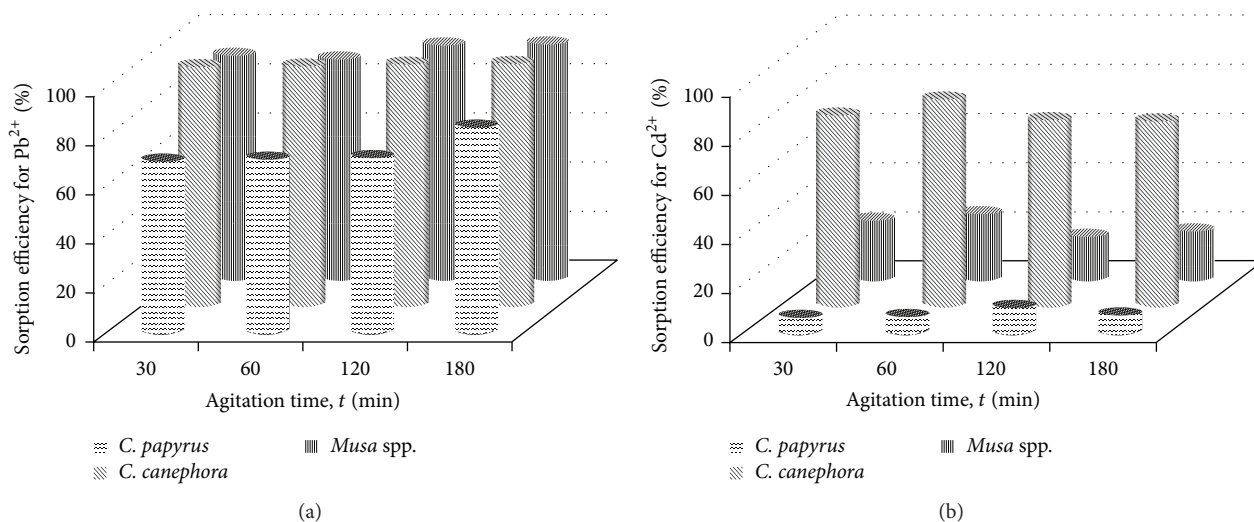
FIGURE 4: Effects of agitation time, t, on noncompetitive sorption efficiencies of *Musa* spp., *C. papyrus*, and *C. canephora* for (a) Pb^{2+} ions and (b) Cd^{2+} ions at pH 4.5, agitation time 1–3 hours, biosorbent dosage 12.5 g/L, and initial metal ion concentration 20 mg/L.
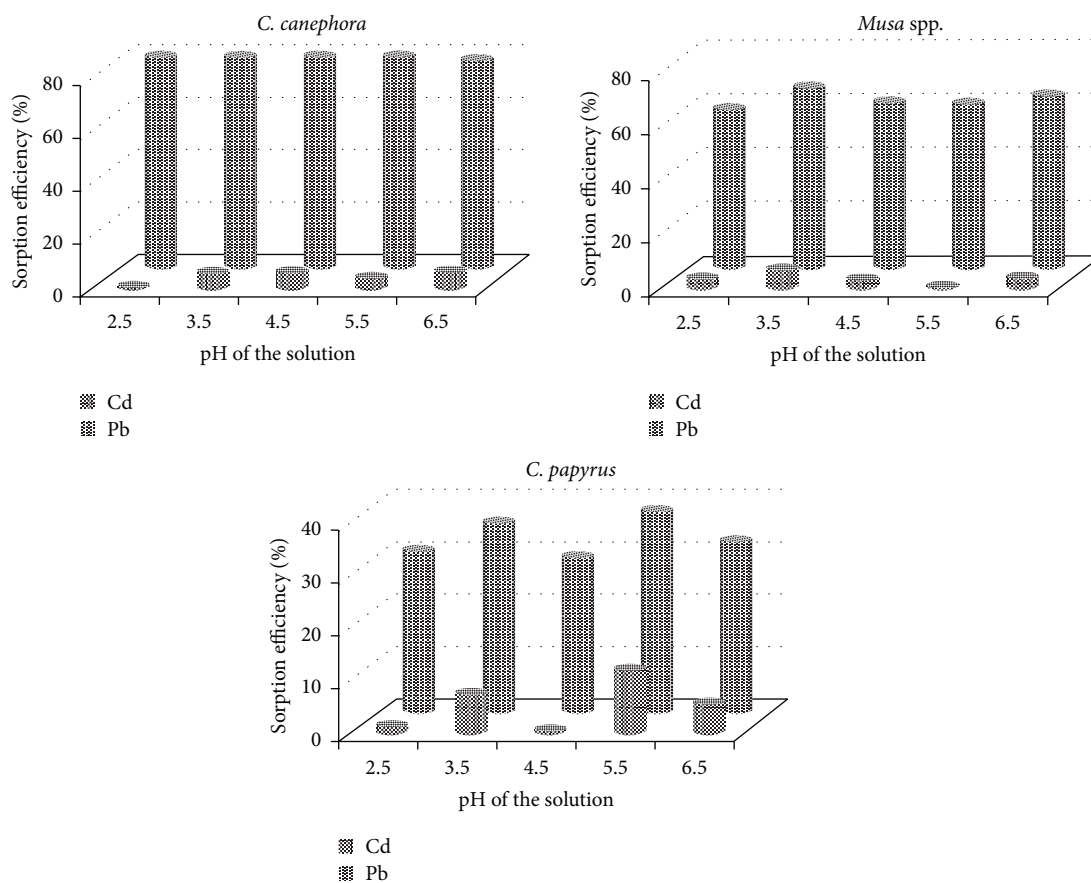

FIGURE 5: Effects of competition on the sorption efficiencies of *C. canephora*, *Musa* spp., and *C. papyrus* for Cd^{2+} and Pb^{2+} ions as a function of the solution pH.
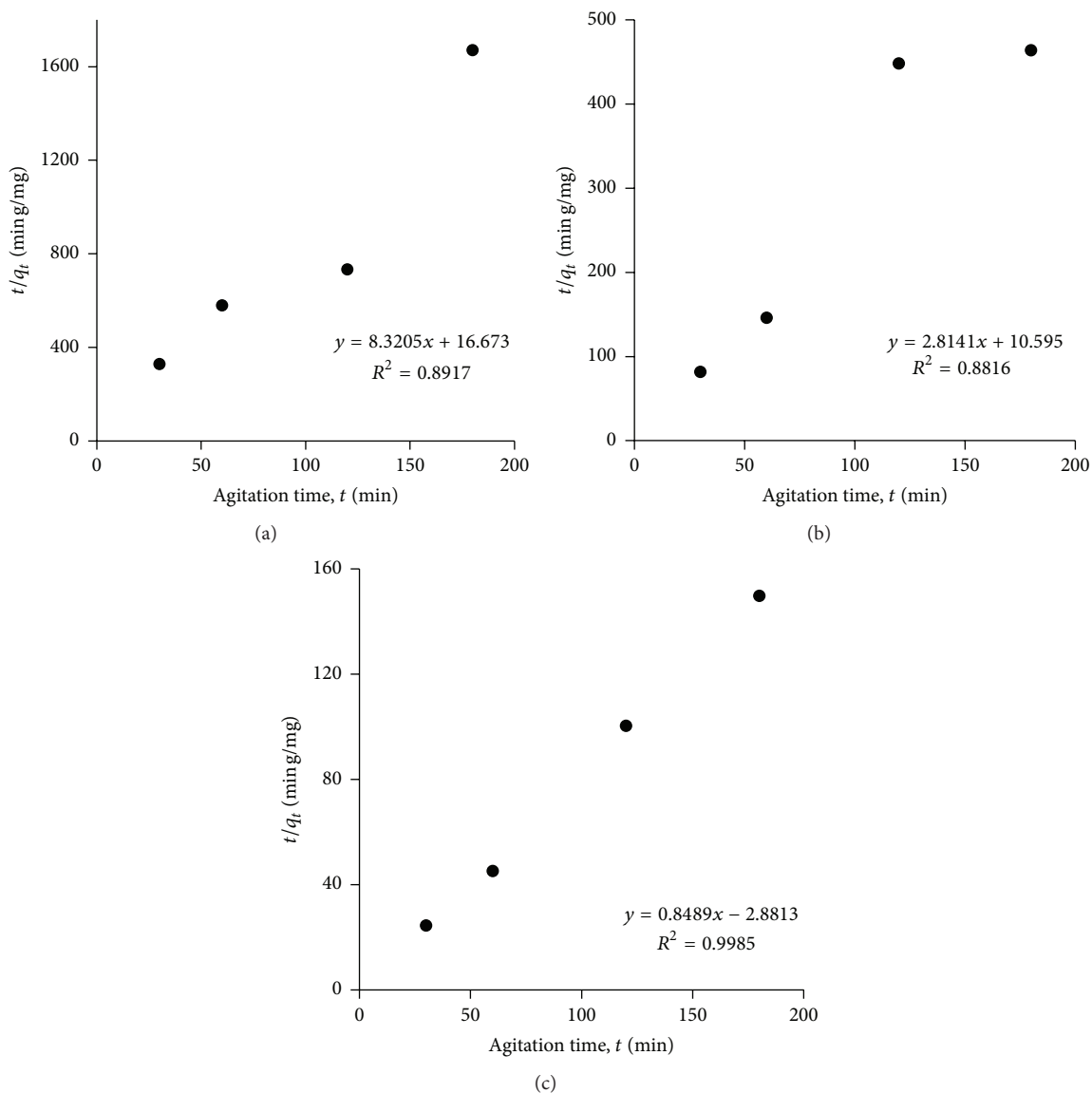
(a)

(b)

(c)

FIGURE 6: Plots of the pseudo-second-order kinetic model for Cd^{2+} ions sorption data of (a) *C. papyrus*, (b) *Musa* spp. peels, and (c) *C. canephora* husks.

the solution pH are shown in Figure 5. The plots in Figure 5 show competitive sorption efficiencies for Cd^{2+} and Pb^{2+} ions in which a small variation is sorption efficiencies was evident which was similar to trends for noncompetitive sorption shown in Figure 2. Sorption efficiencies of biosorbents in competitive media were lower than those in noncompetitive media which indicated coion effects amongst the metal ions studied. The coion effects in competitive sorption processes are due to sorbate-sorbate and sorbate-sorbent interactions as well as the chemistry of the interacting ions. The reduction in Cd^{2+} ions sorption efficiency at pH 4.5 was from 2.7 to 0.62 for *C. papyrus*, 78.25 to 6.30 for *C. canephora*, and 25.68 to 3.61 for *Musa* spp. For Pb^{2+} ions the reduction in sorption efficiency was from 51.20 to 29.51 for *C. papyrus*, 87.63 to 81.44 for *C. canephora*, and 80.56 to 61.54 for *Musa* spp.

The results show that, in competitive sorption, Pb^{2+} ions uptake was preferred to that of Cd^{2+} ions for all biosorbents. Indication of effects of ionic interactions on the sorption process may be represented by the ratio of the competitive sorption intensity for a metallic ion q_{mix} to its noncompetitive sorption intensity q_s such that for

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

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

$q_{mix}/q_s < 1$, adsorption is suppressed by the presence of other metal ions [25].

Table 3 shows that the sorption intensity ratios for Cd^{2+} and Pb^{2+} ions onto *C. canephora*, *Musa* spp., and *C. papyrus* were all below unity over the pH range of the study. This
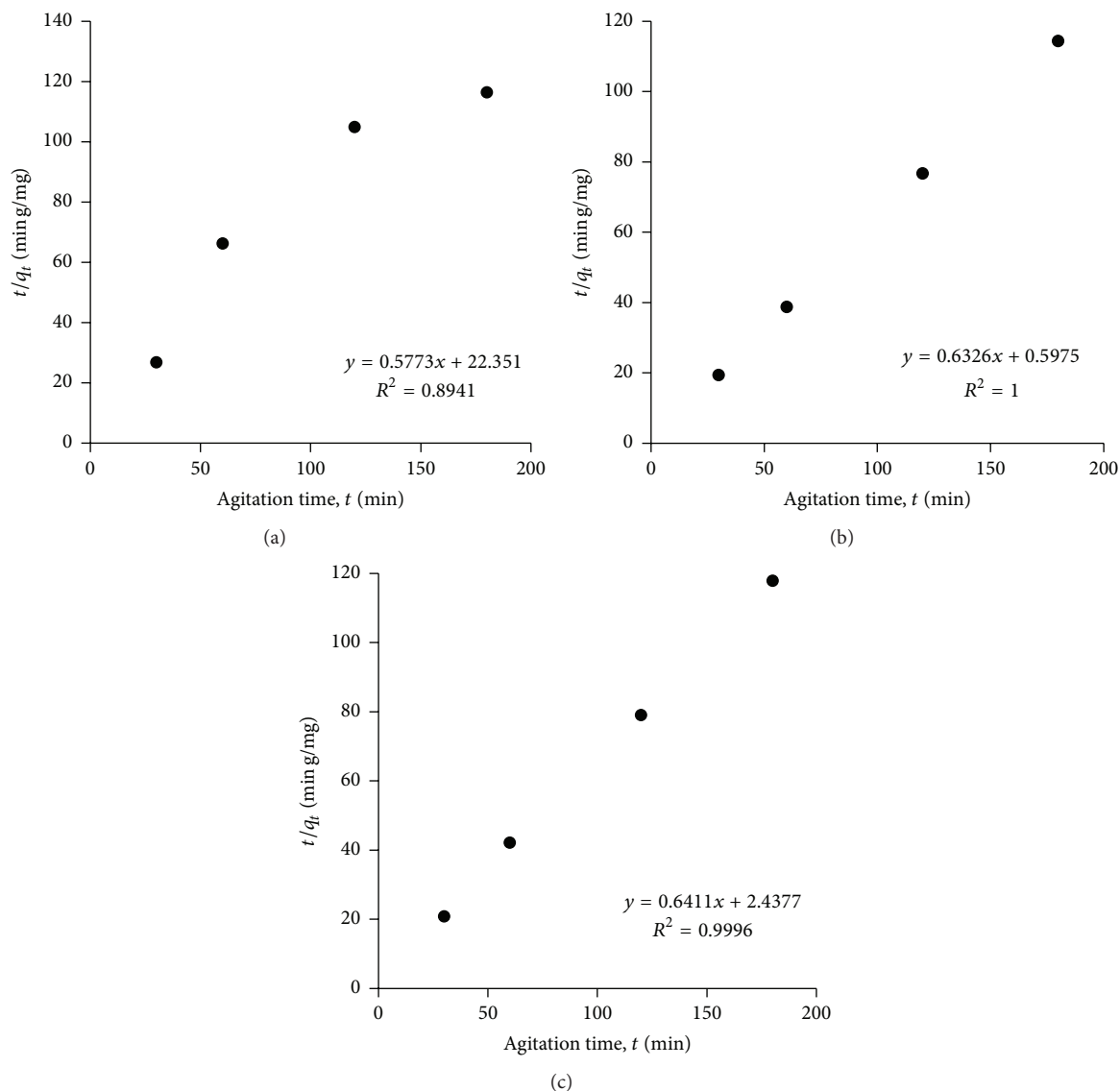
(a)

(b)

(c)

FIGURE 7: Plots of the pseudo-second-order kinetic model for Pb^{2+} ions sorption data of (a) *C. papyrus*, (b) *C. canephora* husks, and (c) *Musa* spp. peels.

TABLE 3: Effects of ionic interactions of competing ions on sorption intensities, q_{mix}/q_s at 297 K.

| | Sorption intensity ratio q_{mix}/q_s for 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	0.41	0.255	0.792
4.5	0.081	0.929	0.225	0.576	0.141	0.764
5.5	0.052	0.847	0.8	0.529	0.051	0.69
6.5	0.08	0.85	0.87	0.462	0.19	0.755

implied that, for both Cd^{2+} and Pb^{2+} ions, sorption onto all the biosorbents was suppressed by the presence of other metal ions in the competitive media. The Cd^{2+} ions sorption

exhibited greater synergistic effects than Pb^{2+} ions with the greatest effects observed in the order *C. canephora* > *Musa* spp. > *C. papyrus*. The synergistic effects may be explained using the chemistry of the metals; cadmium has a lower electronegativity value of 1.69 compared to that of lead of 1.87, and the hydrated ionic radius of Pb^{2+} is 4.61 Å compared to that of Cd^{2+} which is 4.01 Å. The chemistry implies that Pb^{2+} ions were strongly attracted towards the negatively charged surface groups than Cd^{2+} ions; moreover the bonds formed were stronger for Pb^{2+} ions due to the size of the hydrated ionic radius and difference in electronegativity which explains the selectivity and higher affinity for Pb^{2+} ions compared to Cd^{2+} ions in competitive sorption. The differences in hydrated ionic radii and electronegativities of Cd^{2+} and Pb^{2+} ions also explain the difference in binding to sorption sites and suggest disparate sorption mechanisms.

TABLE 4: The co-ionic effects on metal ions uptake efficiencies of biosorbents in competitive sorption studies.

Biosorbent	Ion sorbed	pH	Competing ions and removal efficiency (%)				Reference
			None	Pb	Cd	Cu	
	Pb		3.81	—	2.87	1.83	
Aspergillus niger	Cd	4.0	2.00	0.96	—	0.33	[7]
	Cu		2.09	1.05	1.44	—	
	Cd		86.6	68.5	—	—	
			None	Zn	Cd	Cu	
	Cu		90	87.5	85	—	
Date palm waste	Cd	6.0	57.5	58	—	55	[26]
	Zn		37.5	—	35.5	35	
			None	Pb	Cu	Zn	
Musa sapientum	Cu	6.0	86.8	86.8	—	87.4	[27]
	Zn		84.6	57.9	84.8	—	
			None	Pb	Cd	—	
Coffea canephora	Pb		98.1	—	82.4	—	
	Cd		82.9	18.8	—	—	
Musa spp.	Pb	4.5	95.2	—	70.7	—	This study
	Cd		30.6	16.7	—	—	
Cyperus papyrus	Pb		98.1	—	43.1	—	
	Cd		11.1	7.7	—	—	

On the other hand, the synergistic effects on metal sorption efficiencies indicate how the biosorbents perform in uptake of metal ions when used in remediation of real contaminated natural water from the environment. This study has been compared to other competitive and noncompetitive sorption studies as shown in Table 4.

3.5. Kinetics of Sorption. The t/q_t was plotted against agitation time, t, and straight lines were fitted by regression.

The plots in Figures 6 and 7 represent the sorption kinetics for Cd^{2+} and Pb^{2+} ions onto *C. canephora*, *Musa* spp., and *C. papyrus*. The regression coefficient R^2 values of the pseudo-second-order kinetic model show that it fits the sorption data for both Cd^{2+} and Pb^{2+} ions for all the biosorbents. The regression coefficient (R^2) values were $0.8816 \leq R^2 \geq 0.9985$ for Cd^{2+} ions sorption and $0.8941 \leq R^2 \geq 1.000$ for Pb^{2+} ions. The values of the regression coefficient were high and indicated suitability of the pseudo-second-order model in explaining the sorption dynamics of cadmium and lead uptake onto the biosorbents studied. The parameters of the pseudo-second-order model, k_2, the rate constant, and the sorption capacity, q_e, at equilibrium were determined from the slope and intercept of the plots in Figures 6 and 7. For all materials the k_2 values presented in Table 5 were in the range of 0.015–$0.728 \, min^{-1}$ for Pb^{2+} ions and 0.113–$0.839 \, min^{-1}$ for Cd^{2+} ions, which implies that the rate of uptake of the metal ions was good and in the order of *C. canephora* > *Musa* spp. > *C. papyrus*. The q_e values were 0.120–$1.178 \, mg/g$ for Cd^{2+} ions and 1.560–$1.732 \, mg/g$ for Pb^{2+} ions showing that Pb^{2+}

TABLE 5: The pseudo-second-order model parameters.

Biomass	Metal ion	q_e (mg/g)	k_2 (g/mg/min)	R^2
C. canephora	Cd^{2+}	1.178	0.25	0.9985
	Pb^{2+}	1.581	0.67	1
Musa spp.	Cd^{2+}	0.355	0.747	0.8816
	Pb^{2+}	1.56	0.169	0.9996
C. papyrus	Cd^{2+}	0.12	4.152	0.8917
	Pb^{2+}	1.732	0.015	0.8941

ions were removed from solution more efficiently than Cd^{2+} ions. The application of this model proposed that the kinetic behaviour of sorption process for Cd^{2+} and Pb^{2+} ions onto *C. canephora*, *Musa* spp., and *C. papyrus* is based on chemical interactions between the metal ions and the active sites of the biosorbents' surfaces. The implication is that the rate controlling step in the sorption process involved the divalent Cd^{2+} and Pb^{2+} ions binding onto two monovalent negatively charged sites on the biosorbent surface and the pseudo-second-order model assumes that the rate is proportional to the square of the unoccupied sites. The findings of this study are in agreement with selected sorption studies for metal ions in wastewater reviewed by Wan Ngah and Hanafiah [14] which revealed the pseudo-second-order model as the most followed kinetic model in sorption studies of metal ions removal from contaminated aqueous solutions.
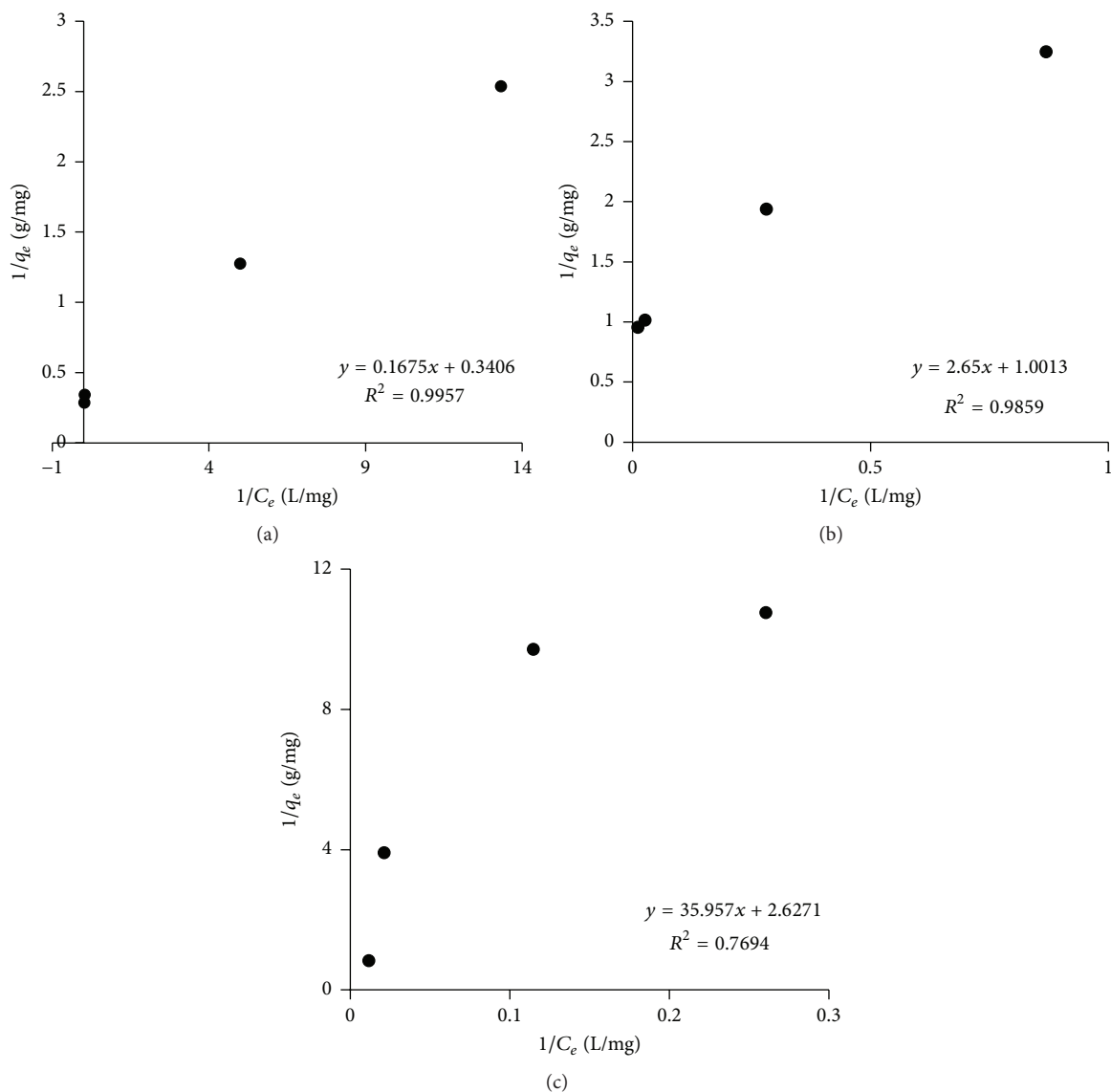
(a)

(b)

(c)

FIGURE 8: Langmuir sorption isotherms of Cd^{2+} ions by *C. canephora* (a), *Musa* spp. (b), and *C. papyrus* (c) in noncompetitive sorption studies.

3.6. Sorption Isotherm Models. The two parameter isotherm models, Langmuir and Freundlich models, were employed in this study. Linear forms of Langmuir and Freundlich models were fitted to the experimental data to determine the corresponding parameters. Figures 8 and 9 show the fitting of Langmuir isotherms to metal uptake data from noncompetitive media whereas Figures 10 and 11 show fitting of Freundlich isotherms to metal sorption data from competitive media. The regression coefficients (R^2) for the models were used to determine the model that gives the best fit. The regression coefficients (R^2) for the Langmuir model for noncompetitive Cd^{2+} ions sorption were $0.769 \leq R^2 \geq 0.996$ from Figures 8 and 9 whereas for competitive Cd^{2+} ions sorption the Freundlich model had better regression coefficients of $0.956 \leq R^2 \geq 0.965$ from Figures 10 and 11.

The q_{max} values for Cd^{2+} ions were between 0.028 and 5.97 mg/g, whereas the b values were between 0.442 and 13.6 which indicated that Cd^{2+} ions sorption was good over the range of initial metal ion concentration studied. When the b values were substituted into (5), R_L values obtained were between 0 and 1. The values of R_L that were determined from parameter b were 0.004–0.289 for *C. canephora*, 0.003–0.070 for *Musa* spp., and 0.001–0.131 for *C. papyrus* which indicated that the Langmuir model was suitable to describe the sorption processes and that the metal uptake followed a monolayer distribution mechanism. For the competitive sorption of cadmium ions, the Freundlich b_F values were between 0.256 and 0.639 and the A_F values were between 0.014 and 0.395 which was indicative of suitability of the model to explain the competitive metal sorption processes for Cd^{2+} ions.
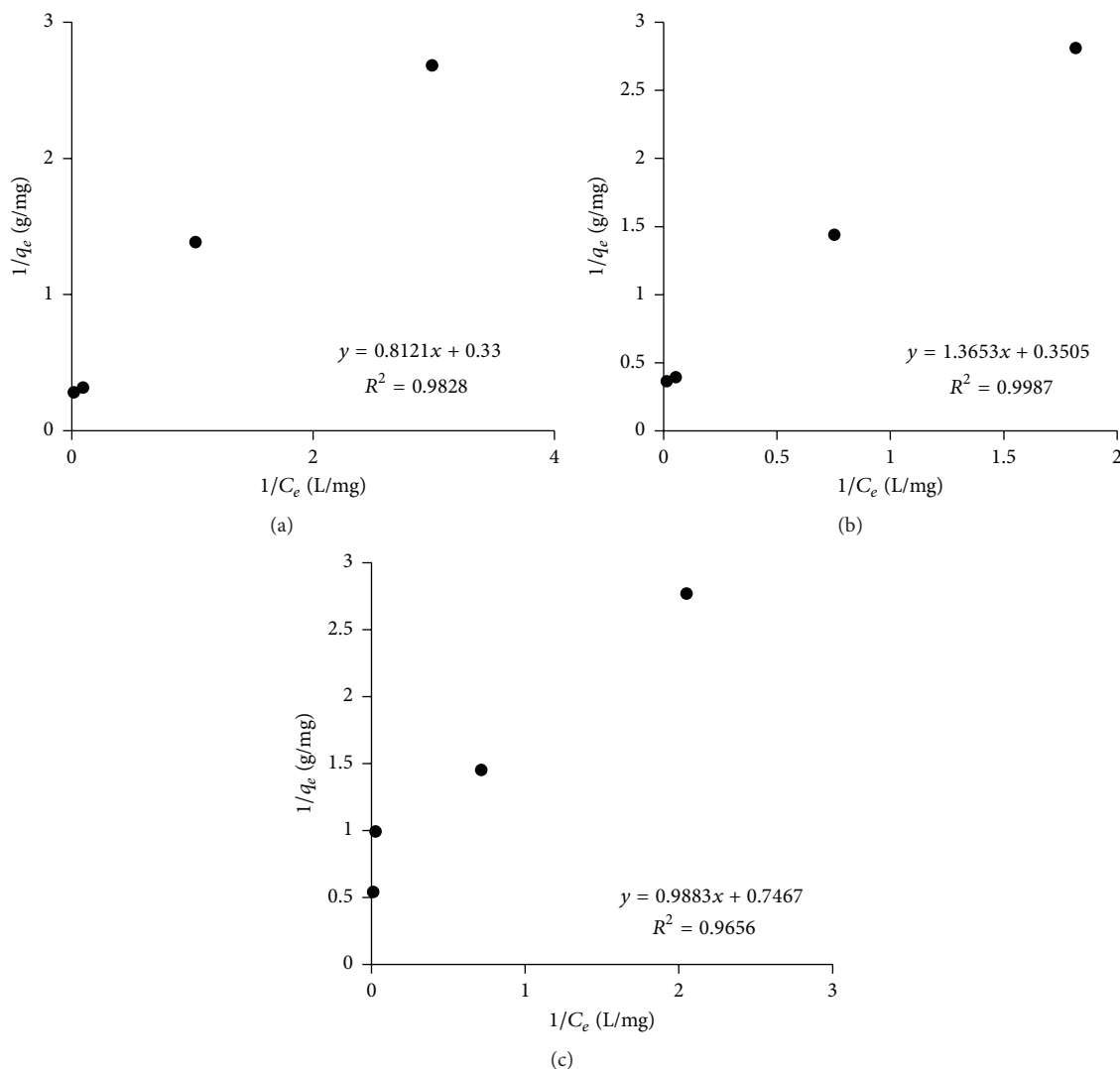
$$y = 0.8121x + 0.33$$
$$R^2 = 0.9828$$

(a)

$$y = 1.3653x + 0.3505$$
$$R^2 = 0.9987$$

(b)

$$y = 0.9883x + 0.7467$$
$$R^2 = 0.9656$$

(c)

FIGURE 9: Langmuir sorption isotherms of Pb^{2+} ions sorption by *C. canephora* (a), *Musa* spp. (b), and *C. papyrus* (c) in noncompetitive sorption studies.

The regression coefficients (R^2) values for the Langmuir model for noncompetitive sorption of Pb^{2+} ions were in the range $0.966 \leq R^2 \geq 0.999$, whereas those for Freundlich model for competitive sorption of Pb^{2+} ions were of the order $0.867 \leq R^2 \geq 0.989$. The q_{max} values for Pb^{2+} ions were between 0.732 and 1.231 mg/g.

The b values were between 1.324 and 3.895 which indicated that Pb^{2+} ions sorption was suitable over the range of initial metal ion concentration studied. For competitive sorption of Pb^{2+} ions sorption the Freundlich b_F values were between 0.174 and 0.507 and the A_F values were between 0.386 and 0.525 which were indicative of suitability of the model to explain the competitive sorption processes Pb^{2+} ions. The values of the Langmuir parameter b that showed high affinity of sorbent surfaces for the metal ions studied and predicted high bond energies when the Langmuir isotherm

describes the noncompetitive sorption processes. The Freundlich parameter b_F values were less than unity which indicated that the biomass had heterogeneous site binding affinities for the metal ions and the sorption processes were favourable.

When a model fits the biosorption data, the equation parameters and the underlying assumptions are dependable for description of the biosorption mechanism and sorbent surface properties besides the sorbent-sorbate interactions in the process. The Langmuir model (Figures 8 and 9) fits data for noncompetitive sorption where the metal ions uptake was a monolayer distribution mechanism and the Freundlich model (Figures 10 and 11) fits the data for competitive uptake of Pb^{2+} and Cd^{2+} ions onto *C. canephora*, *C. papyrus*, and *Musa* spp. biomass where the metal ions followed a heterogeneous distribution mechanism.
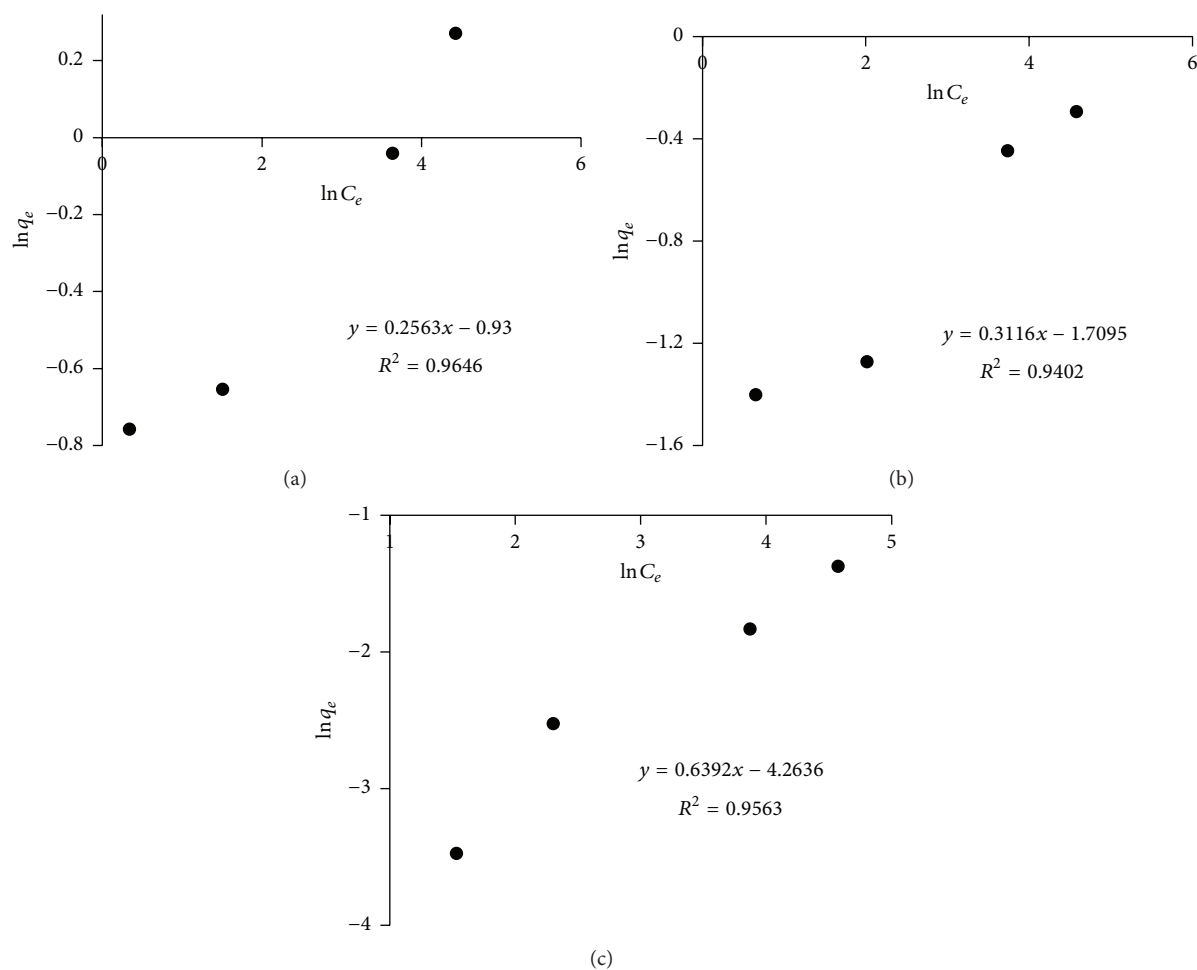
FIGURE 10: Freundlich sorption isotherms of Cd^{2+} ions by *C. canephora* (a), *Musa* spp. (b), and *C. papyrus* (c) in competitive sorption studies.

4. Conclusions

Whereas sorption processes are pH, initial metal concentration, and time dependent, the variation in sorption of Pb^{2+} and Cd^{2+} ions onto *C. canephora*, *C. papyrus*, and *Musa* spp. with the initial metal concentration, time, and pH dependence of sorption was nearly linear. There were strong correlations between the DOC released and the sorption intensities of the materials which suggested that the metal ions removal had a relationship with DOC released for all the biosorbents in this study. The constituent Ca, K, Mg, and Na ions in the materials contribute to cation exchange capacities of the materials and the sorption efficiencies although the toxic trace metals were in small concentrations and would not contaminate the remediated water. Competitive sorption efficiencies of all biosorbents were lower than the noncompetitive sorption efficiencies and indicated synergistic effects on the sorption of both metal ions. Moreover the synergistic effects were ultimate in the order of *C. canephora* > *Musa* spp. > *C. papyrus* for Cd^{2+} ions and least in the order of *C. canephora* > *Musa* spp. > *C. papyrus* for Pb^{2+} ions. The sorption kinetics for both metal ions adequately followed the pseudo-second-order model which predicted chemisorption as the main reaction mechanism of the sorption process. The Langmuir isotherm fitted the noncompetitive sorption data whereas the Freundlich isotherm fitted the competitive sorption data better which inferred that the sorption process was complex and involved several mechanisms. The waste plant materials, *C. canephora*, *C. papyrus*, and *Musa* spp. may be studied further in column studies and pilot scale studies in order to exhaust the conditions under which they may be used to remediate trace metals in contaminated natural aqueous media. Sorption performance was in the order *C. canephora* husks > *Musa* spp. peels > *C. papyrus* stems.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.
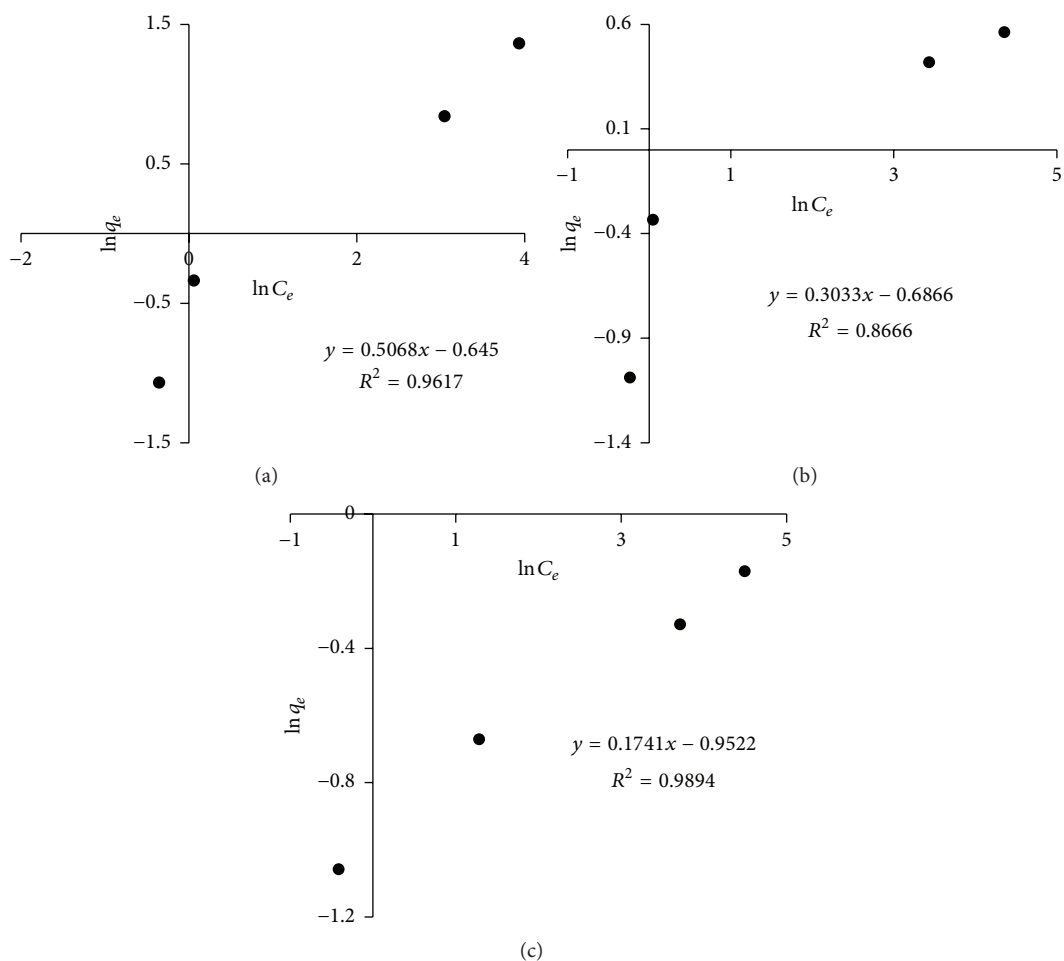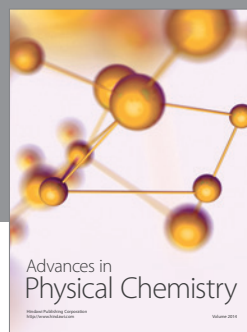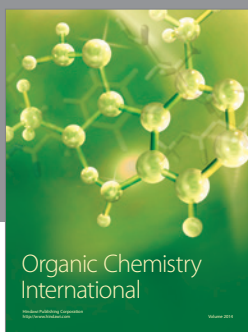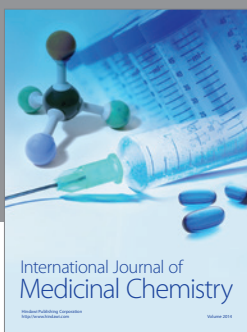
Acknowledgments

(a)

(b)

(c)

FIGURE 11: Freundlich sorption isotherms of Pb^{2+} ions sorption by *C. canephora* (a), *Musa* spp. (b), and *C. papyrus* (c) in competitive sorption studies.

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