

# Kinetic studies of Cd (II) and Pb (II) ions biosorption from aqueous media using untreated and chemically treated biosorbents

G. K. Bakyayita, A. C. Norrström, M. Nalubega and R. N. Kulabako

## ABSTRACT

Untreated and chemically treated *Albizia coriaria*, *Erythrina abyssinica* and *Musa* spp. were studied in batch for uptake of Cd<sup>2+</sup> and Pb<sup>2+</sup> ions at pH 2.0–9.0 and agitation time of 30–390 min. Optimum biosorption conditions were pH 4 for Pb<sup>2+</sup> ions and pH 5 for Cd<sup>2+</sup> ions, contact time was 3.5 hours at 24 ± 1 °C for 10 mg/L biosorbent dosage and initial metal ions concentration of 20 mg/L. Chemical treatment had a 10–17% biosorption efficiency enhancement for Cd<sup>2+</sup> ions and a 1.6–2.3% reduction effect for Pb<sup>2+</sup> ions. The sorption capacities for Cd<sup>2+</sup> and Pb<sup>2+</sup> ions for treated biosorbents were 1.760–1.738 mg g<sup>-1</sup> compared to 1.415–1.539 mg g<sup>-1</sup> for untreated materials. The pseudo second-order model suitably fitted the Cd<sup>2+</sup> and Pb<sup>2+</sup> ions biosorption data with regression coefficients ( $R^2$ ) of 0.9784–0.9999. Fitting of the Ho model to the experimental data showed that the biosorption mechanism for both metal ions studied was mainly a chemisorption process. Therefore, treated *A. coriaria*, *E. abyssinica* and *Musa* spp. were potential biosorbents for remediation of Cd<sup>2+</sup> ions and the untreated materials suitable for removing Pb<sup>2+</sup> ions from contaminated aqueous media.

**Key words** | biosorbents, cadmium, chemical treatment, chemisorption, kinetics, lead

**G. K. Bakyayita** (corresponding author)

**A. C. Norrström**

Department of Sustainable Development,  
Environmental Science and Engineering, Kungliga  
Tekniska Högskolan,  
Brinellvägen 28,  
SE-100 44 Stockholm,  
Sweden  
E-mail: gkba@kth.se

**M. Nalubega**

Water and Sanitation Department,  
African Development Bank,  
Tunis,  
Tunisia

**G. K. Bakyayita**

**R. N. Kulabako**

Department of Civil and Environmental  
Engineering,  
College of Engineering, Design, Art and  
Technology,  
Makerere University,  
Uganda

## INTRODUCTION

Industrialization, urbanization, exploitation of mineral resources and other anthropogenic activities have triggered a rise in trace metal contamination of the environment. The trace metals 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). Chronic exposure to cadmium poses health effects such as kidney dysfunction, growth retardation, bone deformation, testicular atrophy, hypertension and cancer while exposure to lead manifests through nervous system disorders, anaemia, loss of appetite, hypertension, and damage to the brain, liver and kidney (Krishnani & Ayyapan 2006).

There are conventional remediation techniques with high installation and operational costs, 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. Biosorbents that have been studied in both modified and unmodified forms include, among others: leaves, husks and hulls, peels, barks, and sawdust. Biosorbents of plant origin

consist of hemicellulose, lignin, extractives, lipids, proteins and starch (Bailey *et al.* 1999). Biosorbents release soluble organics that are extractable with solvents such as hot water, sodium hydroxide, diethyl ether and ethanol (Rowell 2006) to ensure that the filtrate meets the water quality standards. 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 biosorption performance. Chen and Wu, as well as Zhao *et al.*, attributed the high performance of modified biosorbents to increased binding sites, the surface oxygen groups for metal ions (Chen & Wu 2004; Zhao *et al.* 2005), besides the improved ion exchange properties.

The purpose of this study was to investigate the kinetics of biosorption of Cd and Pb ions from contaminated aqueous media under batch conditions using *Musa* spp. banana peels, the barks of *Erythrina abyssinica* and *Albizia coriaria*. *E. abyssinica* and *A. coriaria* are common tropical tree species that are grown for fuel and herbal medicine, whereas *Musa* spp. are bananas grown for food. When *E. abyssinica* and *A. coriaria* trees are harvested for wood

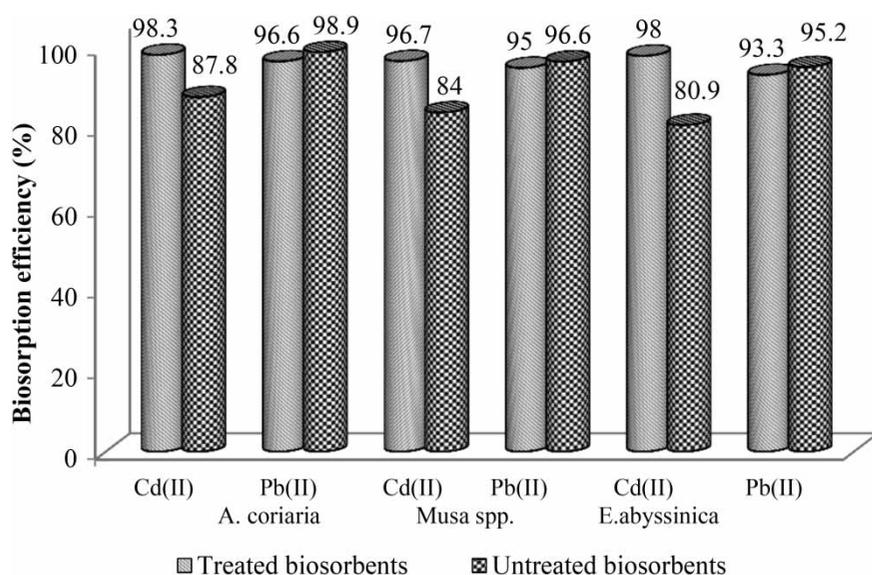


Figure 1 | Effect of chemical treatment on biosorption efficiencies.

and timber, waste bark materials, whose extracts by herbalists are used as local dermatological medications, have little use. Green *Musa* spp. peels are removed from the banana fingers before cooking the food and they form an urban waste burden with minimal potential for reuse.

The effects of initial pH and agitation time on the biosorption performance for Cd (II) and Pb (II) ions were evaluated for untreated and chemically treated biosorbents. The resultant biosorption data for the metal ions were fitted to two kinetic models to evaluate the performance of the biosorbents and predict the underlying biosorption dynamics and mechanisms.

## METHODS

### Preparation of biosorbents

The samples of the tropical plants; *Musa* spp. peels and the barks of *E. abyssinica* and *A. coriaria* were collected from a rural farming district. The plant materials were thoroughly washed with distilled water and dried in an oven (E series: ED – E2 Binder, Germany) at 60 °C for 72 hours to a constant weight. The dry materials were hammer-milled, sieved to 2 mm and stored in air-tight plastic bags. For modification, 100 g of the material was soaked in 0.25 M NaOH for 2 hours and neutralized using 0.25 M HCl. The modified biosorbent was generously washed with distilled water, dried in an oven at 105 °C for 24 hours and stored in plastic bags.

### Preparation of reagents and biosorbates

Cadmium and lead standard solutions for atomic absorption spectrometry containing 1,000 mg L<sup>-1</sup> were diluted using distilled deionized water to required concentrations. The initial pH of the aqueous solutions was adjusted using drops of either 0.1 M HCl or NaOH.

Table 1 | Comparison of biosorbents' performance with other biomasses

Biosorbent	% Biosorption		Reference
	Cd	Pb	
Treated <i>A. coriaria</i>	98.3	96.6	This study
Untreated <i>A. coriaria</i>	87.8	98.9	
Treated <i>Musa</i> spp.	96.7	95	
Untreated <i>Musa</i> spp.	84	96.6	
Treated <i>E. abyssinica</i>	98	93.3	
Untreated <i>E. abyssinica</i>	80.9	95.2	
Rice bran	98.3	99.3	Chen et al. (2009)
Pine sawdust	90.2	95.3	
Sphagnum peat	95.2	99.3	Kalmykova (2009)
Sawdust of <i>Pinus sylvestris</i>	–	98	Taty-Costodes et al. (2003)
Nile rose plant	61.4	98.7	Abdel-Ghani & Elchaghaby (2007)
Marine green macrofungus	98	97	Sari & Tuzen (2009)
Marine green macroalga	91	97	Dekhil et al. (2011)
Cork residues	–	80–93	Mota et al. (2006)

## Biosorption experiments

Biosorption experiments were carried out by agitating 0.5 mg of biosorbent with 50 mL of aqueous solution containing 20 mg L<sup>-1</sup> of either Pb<sup>2+</sup> or Cd<sup>2+</sup> ions in closed bottles. The biosorption studies were done in triplicate at 24 ± 1 °C. Agitation was done at 60 rpm at pH 2.0–9.0 for 0.5–6.5 hours. After agitation, bottles were centrifuged at 2,000 rpm for 25 min. A portion of the equilibrated solution was then filtered through 0.45 µm sterile non-pyrogenic hydrophilic filters into polypropylene sample bottles to

which a drop of concentrated HNO<sub>3</sub> was added and residual trace metal ions analysed using inductively coupled plasma-mass spectrometry.

## Biosorption capacity

The biosorption capacity,  $q_e$  for trace metal ions at equilibrium was calculated according to the following Equation (1)

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

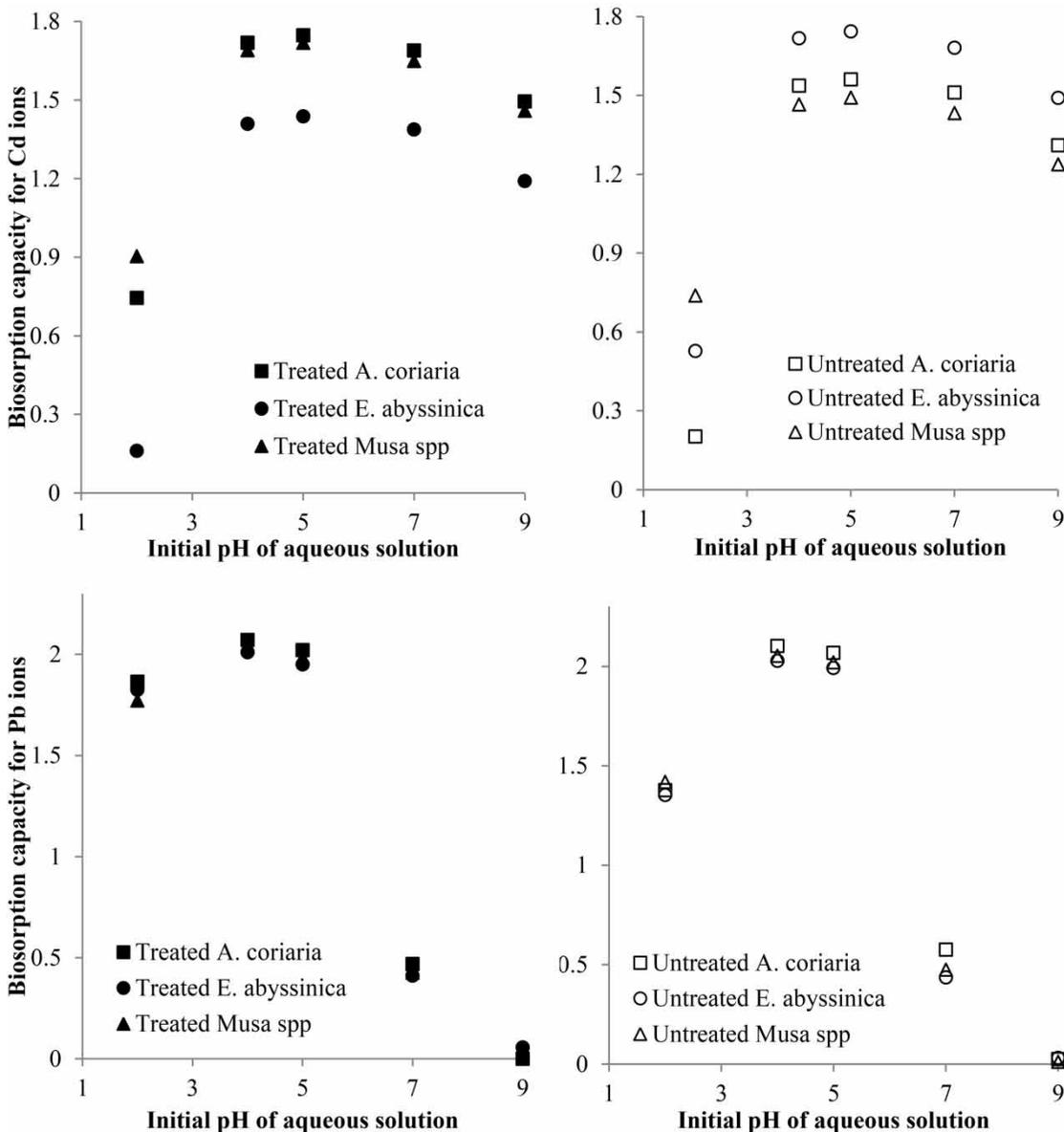


Figure 2 | Variation of biosorption capacities  $q$  (mg/g) for Cd<sup>2+</sup> and Pb<sup>2+</sup> ions with initial pH.

where  $C_0$  is the initial concentration,  $C_e$  is the equilibrium concentration,  $V$  is the volume of solution (L) and  $m$  is the mass of the biosorbent material (g).

### Kinetic modelling of biosorption

The nature of the biosorption processes were analysed using the pseudo first-order (Lagergren 1898) and the pseudo second-order (Ho & McKay 1998) kinetic models. The linear form of the pseudo first-order kinetic model is given by expression (2)

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (2)$$

where  $q_e$  and  $q_t$  (mg/g) are the amounts of the trace metal ions biosorbed at equilibrium and time  $t$  (min) respectively, and  $k_1$  is the rate constant of the equation ( $\text{min}^{-1}$ ). From the plots of  $\ln(q_e - q_t)$  versus  $t$ , the rate constant  $k_1$  can be calculated. The linear form of the pseudo second-order model is defined by Equation (3)

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \left(\frac{1}{q_e}\right)t \quad (3)$$

where  $k_2$  (g/mg min) is the rate constant of the second-order equation,  $q_t$  (mg/g) is the biosorption at time  $t$  (min) and  $q_e$  (mg/g) is the amount of metal ions biosorbed at equilibrium.

## RESULTS AND DISCUSSION

### Effect of chemical treatment on biosorption

The results of the effects of chemical treatment on biosorption efficiency are presented in Figure 1.

The results shown in Figure 1, were an average of three replicas for each biosorbent with standard deviation in the biosorption efficiencies in the ranges of 0.07–0.22% for Cd (II) ions and 0.06–1.03% for Pb (II) ions biosorption. Chemical treatment improved Cd (II) ions biosorption in the order of *E. abyssinica* bark (17.1%) > *Musa* spp. peels (12.7%) > *A. coriaria* bark (10.5%). Reports of several studies reviewed by Wan Ngah and Hanafiah showed that chemical treatment of biosorbents improved biosorption (Wan Ngah & Hanafiah 2008) although in these studies, a slight reductive effect on Pb (II) ions biosorption occurred in the order of *A. coriaria* bark (2.3%) > *E. abyssinica* bark (1.9%) > *Musa* spp. peels (1.6%). The highest  $\text{Cd}^{2+}$  ions biosorption competences observed were 98.3, 96.7 and 98% for treated *A. coriaria*,

*Musa* spp. and *E. abyssinica*, respectively. Moreover the  $\text{Pb}^{2+}$  ions sorption competences were; 98.9, 96.6 and 95.2% for untreated *A. coriaria*, *Musa* spp. and *E. abyssinica* respectively. The improvement in metal biosorption was comparable to the 2–8% reported for alga spirogyra (Bishnoi et al. 2007) and the 10–20% improvement reported for waste materials (Chen et al. 2009). The reduction was similar to that of the 5–13% for Pb bioremoval by treated cork residues (Mota et al. 2006). Wan Ngah & Hanafiah (2008) documented the chemical modifications that enhance metal ions sorption to the biosorbent structural molecules as a result of NaOH treatment (Wan Ngah & Hanafiah 2008). Cadmium is known to exist to a large extent in the exchangeable fraction, whereas Pb is known to bind strongly due to different adsorption mechanisms.

### Comparison of selected biosorption efficiencies for trace metals

The biosorption efficiencies of *A. coriaria* bark, *E. abyssinica* bark and *Musa* spp. banana peels for the removal of trace metal ions has been compared with other biomasses in literature in Table 1. The biosorbents under study showed high biosorption efficiency values comparable to those for other

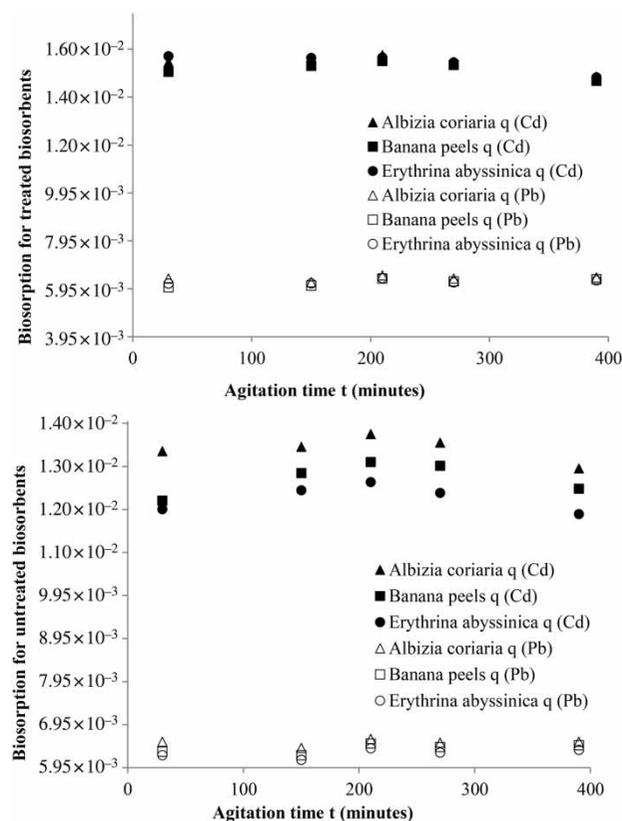


Figure 3 | Variation of biosorption capacities  $q$  (mmol  $M^{2+}$ /g) with agitation time.

biomasses in the literature and therefore, have potential for the removal of  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  ions from aqueous solution.

### Effect of pH on biosorption

The effect of the initial pH on the biosorption capacities of untreated and treated biosorbents were studied and are presented for pH 2.0–9.0 in Figure 2.

Biosorption capacities for Cd (II) ions increased between pH 2.0 and 5, followed by a gradual decrease in biosorption an with increase in initial pH. The biosorption performance for  $\text{Cd}^{2+}$  ions was in the order of *A. coriaria* >

*E. abyssinica* > *Musa* spp. peels. The biosorption capacities for Pb (II) ions increased between pH 2.0 and 4.0, then decreased sharply with an increase in pH. Biosorption of  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  ions was pH dependent and the optimal pH was 4.0 for Pb (II) whereas it was pH 5.0 for Cd (II) ions. The optimal pH values concurred with those reported in the literature as pH 5.0 for Cd and pH 4.0 for Pb (Kaewsam et al. 2008; Dekhil et al. 2011). The electrostatic attraction between the negative biomass surface and the positive metal ions increased with pH, although it reduced above pH 5.0, probably due to complexation with  $\text{OH}^-$  ions and chemical precipitation.

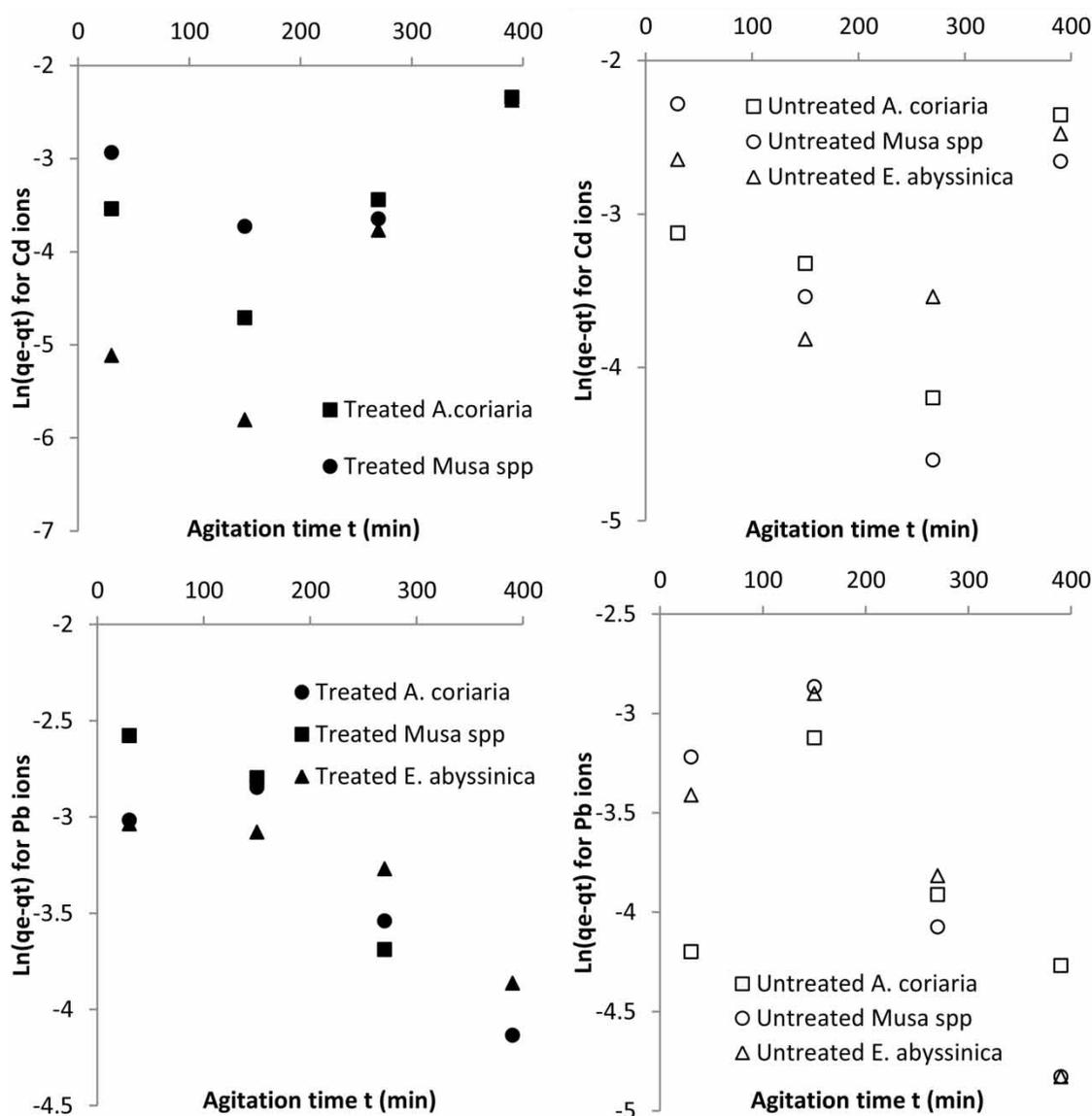


Figure 4 | Plots of Lagergren kinetic model fitting of the sorption data for Cd and Pb ions.

### Effect of agitation time on biosorption

The results of the effect of agitation time on biosorption are presented in Figures 3.

The biosorption capacities of both treated and untreated biosorbents increased gradually for Cd<sup>2+</sup> and Pb<sup>2+</sup> ions to peak values at 210 min and then reduced for longer agitation times. The Pb<sup>2+</sup> ions biosorption trends for treated and untreated biosorbents were similar, although the treated materials showed higher values. The biosorption capacities increased with agitation time for treated and untreated biosorbents up to 3.5 hours at 24 ± 1 °C. Therefore, the optimum agitation time was selected as 3.5 hours for Cd<sup>2+</sup>

and Pb<sup>2+</sup> ions biosorption at 24 ± 1 °C for 10 mg/L biosorbent dosage ('Biosorption experiments' section).

### Kinetic modelling of biosorption

The plots for the Lagergren and Ho kinetic models fitting to the sorption data are presented in Figures 4 and 5.

The pseudo first-order (Lagergren) model did not fit all the experimental data for Cd<sup>2+</sup> ions, although part of the data for Pb<sup>2+</sup> ions sorption gave good regression coefficient ( $R^2$ ) values; 0.8183–0.9084. The Lagergren model could not explain the Cd<sup>2+</sup> ions sorption mechanisms but could describe Pb<sup>2+</sup> ions sorption for short durations of 30

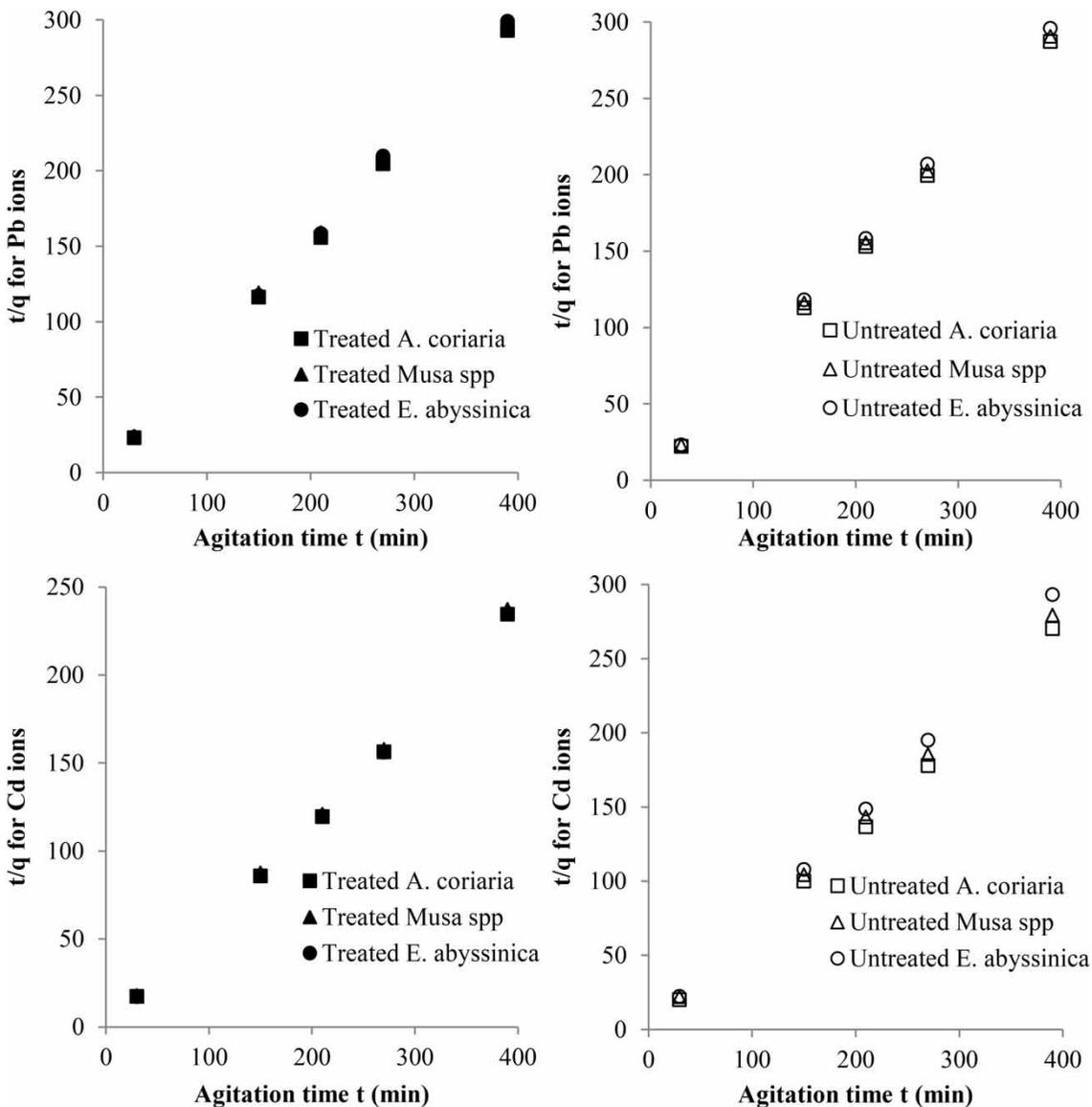


Figure 5 | Plots of Ho kinetic model fitting of the sorption data for Cd and Pb ions.

minutes. The Ho model parameters give very satisfactory fits for both Cd<sup>2+</sup> and Pb<sup>2+</sup> biosorption data for all biosorbents with regression coefficient ( $R^2$ ) values; 0.9978–0.9999 for Cd<sup>2+</sup> ions and 0.9995–0.9998 for Pb<sup>2+</sup> ions. The  $q_e$  values were; 1.334–1.728 mg/g for Cd<sup>2+</sup> ions and 1.306–1.360 mg/g for Pb<sup>2+</sup> ions. The Ho model parameters for all the biosorbents were a very good representation of the sorption process. Since the Ho model fits all the Cd<sup>2+</sup> and Pb<sup>2+</sup> ions experimental data, the biosorption mechanism predicted was chemisorption. The Ho model fitting of sorption data was in agreement with other studies (Kalmykova 2009; Sari & Tuzen 2009; Dekhil et al. 2011).

## CONCLUSIONS

Chemical treatment of biosorbents enhanced Cd<sup>2+</sup> ions removal but had a reductive effect on Pb<sup>2+</sup> ions biosorption efficiencies. Maximum biosorption was achieved at pH 4 for Pb<sup>2+</sup> ions and pH 5 for Cd<sup>2+</sup> ions for 3.5 hours of contact time at 24 ± 1 °C. The biosorption data were adequately described by the Ho model with regression coefficient ( $R^2$ ) values; 0.9978–0.9999 for Cd<sup>2+</sup> ions and 0.9995–0.9998 for Pb<sup>2+</sup> ions, which indicated that the chemisorption reaction mechanism governed the sorption process. The treated biosorbents were more appropriate for Cd<sup>2+</sup> ions removal, whereas the untreated materials were more suitable for Pb<sup>2+</sup> ions sorption. Biosorption performance for trace metal removal was in the order of *A. coriaria*, *Musa* spp. and *E. abyssinica*. The plant wastes; *A. coriaria*, *E. abyssinica* and *Musa* spp. have been found to be potential biosorbents for the removal of Cd<sup>2+</sup> and Pb<sup>2+</sup> ions from aqueous solutions.

## ACKNOWLEDGEMENTS

This study was funded by the Royal Swedish Government through the Swedish International Development Cooperation Agency (Sida). The authors are grateful to the sponsors, Kungliga Tekniska Högskolan and Makerere University.

## REFERENCES

- Abdel-Ghani, N. T. & Elchaghaby, G. A. 2007 Influence of operating conditions on the removal of Cu, Zn, Cd and Pb ions from wastewater by adsorption. *Int. J. Environ. Sci. Technol.* **4** (4), 451–456.
- Bailey, S. E., Olin, T. J., Bricka, R. M. & Adrian, D. D. 1999 A review of potentially low-cost sorbents for heavy metals. *Water Res.* **33** (11), 2469–2479.
- Bishnoi, N., Kumar, R., Kumar, S. & Rani, S. 2007 Biosorption of Cd(II) from aqueous solution using algal biomass *spirogyra* spp. *J. Hazard. Mater.* **145**, 142–147.
- Chen, J. & Wu, P. 2004 Acid/base-treated ACs: characterization of functional groups and metal adsorptive properties. *Langmuir* **20**, 2233–2242.
- Chen, Y., Nie, J., Chen, M. & Zhang, D. 2009 Biosorption Removal of Lead and Cadmium from Water by Waste Materials. IEEE, Ganzhou Jiangxi.
- Dekhil, A., Hannachi, Y., Ghorbel, A. & Boubaker, T. 2011 Removal of lead and cadmium ions from aqueous solutions using dried marine green macroalga (*Caulerpa racemosa*). *Int. J. Environ. Res.* **5** (3), 725–732.
- Ho, Y. & McKay, G. 1998 A comparison of chemisorption kinetic models applied to pollutant removal on various sorbents. *Process Saf. Environ. Prot.* **76**, 332–340.
- Kaewsam, P., Saikaew, W. & Wongcharee, S. 2008 Dried Biosorbent Derived from Banana Peel: A Potential Biosorbent for Removal of Cadmium Ions from Aqueous Solutions. Ubon Ratchathane University, Pattaya.
- Kalmykova, Y. 2009 *Alternative Sorption Materials for Contaminated Water Treatment*. Chalmers University of Technology, Göteborg.
- Kishe, M. & Machiwa, J. 2003 Distribution of heavy metals in sediments of Mwanza Gulf of Lake Victoria, Tanzania. *Environ. Int.* **28**, 619–625.
- Krishnani, K. & Ayyapan, S. 2006 Heavy metals remediation of water using plants and lignocellulosic agrowastes. *Rev. Environ. Contam. Toxicol.* **188**, 59–84.
- Lagergren, S. 1898 Zur theorie der sogenannten adsorption geloster stoffe. *K. Sven. Vetenskapsakad Handl* **24**, 1–39.
- Mota, D., Marques, P., Pereira, C., Gil, L. & Rosa, M. F. 2006 Lead Bioremoval by Cork Residues as Biosorbent. Fernando Pessoa University, Oporto, Portugal, pp. 251–264.
- Rowell, R. 2006 *Removal of Metal Ions from Contaminated Water Using Agricultural Residues*. ECOWOOD 2006: Fernando Pessoa University, Oporto, Portugal, pp. 241–250.
- Sari, A. & Tuzen, M. 2009 Kinetic and equilibrium studies of biosorption of Pb(II) and Cd(II) from aqueous solution by macrofungus (*Amanita rubescens*) biomass. *J. Hazard. Mater.* **164**, 1004–1011.
- Taty-Costodes, V., Fauduet, H., Porte, C. & Delacroix, A. 2003 Removal of Cd(II) and Pb(II) ions from aqueous solutions by adsorption onto sawdust of *Pinus sylvestris*. *J. Hazard. Mater. B* **105**, 121–142.
- Wan Ngah, W. S. & Hanafiah, M. A. K. M. 2008 Removal of heavy metal ions from wastewater by chemically modified plant wastes as adsorbents: a review. *Bioresour. Technol.* **99**, 3935–3948.
- Zhao, N., Wei, N., Li, J., Qiao, Z., Cui, J. & He, F. 2005 Surface properties of chemically modified ACs for adsorption rate of Cr (VI). *Chem. Eng. J.* **115**, 133–138.

First received 3 December 2013; accepted in revised form 5 March 2014. Available online 19 March 2014