

# Competitive biosorption of Pb(II) and Cd(II) ions from aqueous solutions using chemically modified moss biomass (*Barbula lambarenensis*)

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Received: 26 January 2016 / Accepted: 23 December 2016  
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**Abstract** Treatment of biosorbents to add functional groups that increase toxic metal biosorption is an important way to improve its effective application. Hence, different portions of pristine *Barbula lambarenensis* (RBL) were treated separately with sodium tripolyphosphate (TPP) and ethylene glycol. The pristine and treated RBL biomasses were used to evaluate the simultaneous removal of Pb(II) and Cd(II) from aqueous solutions. Equilibrium, kinetics and adsorption isotherms were studied. Results revealed that biosorption of Pb(II) and Cd(II) metal ions were spontaneous and described by the pseudo-second-order kinetics. TPP-treated RBL showed higher biosorption capacity for Pb(II), while the ethylene glycol-treated adsorbent was more efficient for Cd(II) biosorption. The simultaneous presence of Pb(II) and Cd(II) in solution did not affect Pb(II) biosorption. However, Cd(II) biosorption dropped 44, 42 and 19% for the pristine, ethylene glycol and TPP-treated adsorbents, respectively, in the competitive adsorption. Both treatments enhanced Pb(II) and Cd(II) biosorption by RBL.

**Keywords** Lead · Cadmium · *Barbula lambarenensis* · Biosorption · Chemical treatment

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## Introduction

Over 2.3 billion people of the global population live in water-stressed areas, a number that will increase by 52% in 2025 (Hejazi et al. 2011). The situation is not ameliorating because recent anthropogenic activities have greatly contributed to toxic chemicals in water bodies leading to unprecedented pollution (Mokwenye et al. 2016; Olu-Owolabi et al. 2016; Okoli et al. 2014). Lead and cadmium are particularly notorious due to their high level of toxicity. Hence, the search for cheap, efficient, and accessible water treatment technologies cannot be overemphasized. Several techniques have been studied for the treatment of contaminated water, but biosorption is a technique of choice because it is cheap, easy to perform, fast, environmentally friendly and less limited by other techno-economic considerations that plague other techniques (Vimala and Das 2009; Meitei and Prasad 2013; Maurya et al. 2006; Chakravarty et al. 2010). However, a major challenge for the industrial application of most biosorbents for cleanup of toxic metals in wastewater is their low biosorption capacities (Deng and Ting 2005), thus limiting the application of most biosorbents reported in the literature.

The treatment of biosorbents of plant origin in order to improve biosorption capacity has become the subject of most recent studies. Different treatments have been investigated including acids (Montazer-Rahmati et al. 2011), bases, acetone and ethanol (Feng et al. 2011; Bulgariu and Bulgariu 2011), formaldehyde (Montazer-Rahmati et al. 2011; Feng et al. 2011), glutaraldehyde and polyethylene imine (Deng and Ting 2005; Montazer-Rahmati et al. 2011). Treatment of biosorbents such as cross-linking and functionalization can enhance biosorption capacity and stability of the components present in the biomass (Feng et al. 2011; Olu-Owolabi et al. 2016). Majorly these treatments either increase cation

exchange capacity by impregnating new functional groups onto the biosorbent, or react with the biosorbent to expose hidden functional groups on the biomass surfaces. Ultimately, biosorbents treatments aim to enhance biosorption capacity in order to remove high metal ions concentrations in wastewater such as reported in the Lalupon, Ibadan, Nigeria (Ogundiran and Osibanjo 2008). A preliminary study (not reported here) and other studies (Ogundiran and Osibanjo 2008) have shown that aquifer water and underground water storage facilities around Lalupon have Pb(II) and Cd(II) concentrations in excess of 700 and 400 mg/L, respectively. The soils and sediments within the area have even higher concentrations in excess of 10,000 mg/L. Lalupon was used as untreated waste dump site by a defunct lead–acid battery manufacturing factory between 1996 and 1998, hence, the high metals concentrations found within its environment.

The use of various adsorbents have been reported for the removal of Cd(II) (AlSaadi et al. 2016; Boparai et al. 2011), Pb(II) and other metals (Amosa 2015; Olu-Owolabi et al. 2016; Diagboya et al. 2015a) from water. However, some major drawbacks of these adsorbents include non-availability of the adsorbents or their precursors, the cost of procurement or synthesis, and their adsorption efficiencies. *Barbula lambarenensis* (RBL) is an ubiquitous moss species that can survive extreme weather conditions (Ogunfowokan et al. 2004) and has been reported to be a good biosorbent for the removal of toxic metal ions from aqueous solution with good biosorption efficiency (Olu-Owolabi et al. 2012). Despite the reported acceptable adsorption performance, RBL suffer similar limitation associated with most biosorbent. Hence, suitable chemical modification may improve its adsorption for toxic metals (Feng et al. 2011). For instance, it is expected that treatment of pristine RBL with sodium tripolyphosphate (TPP) could result in phosphate groups being attached on RBL surfaces, thus improving its metal chelating ability and adsorption capacity (Unuabonah et al. 2007). On the other hand, ethylene glycol treatment could present more surface hydroxyl groups for metal removal. Therefore, the objective of this study was to modify RBL with sodium tripolyphosphate (TPP) and ethylene glycol separately. The resulting adsorbents were used to study the simultaneous removal of Pb(II) and Cd(II) ions from aqueous solutions, while the experimental data were explained using different adsorption models.

## Methodology

### Sampling, pretreatment and characterization of biosorbent material

The pretreatment, physical and chemical characterization (specific surface area (SSA), bulk density, specific gravity, pH at the point zero charge (pH PZC), Fourier

transform infrared (FTIR) spectra and scanning electron microscope (SEM) image) of the RBL and treated sorbents used in the present study was described in Olu-Owolabi et al. (2012). After pretreatment, the surfaces of two separate portions of RBL were treated separately with either sodium tripolyphosphate (Unuabonah et al. 2007) or ethylene glycol. This was achieved by placing a 100 g of RBL sample in 200 mL of 2 M sodium tripolyphosphate or ethylene glycol solution which was then stirred using a magnetic stirrer for a period of 48 h at room temperature. The treated RBL samples were then washed several times under pressure with deionized water to remove excess tripolyphosphate or ethylene glycol. The tripolyphosphate (PPB) and ethylene glycol-treated RBL (EGB) were air-dried and re-sieved prior to the biosorption experiment.

### Biosorption technique

In establishing the usefulness of a new adsorbent for water treatment, it is vital to determine the best operating parameters for the adsorbent. These parameters (such as pH, adsorption time, concentration of adsorbents and temperature) affect differently the individual adsorbent's surface chemistry and adsorption efficiency (Okoli et al. 2014). Hence, batch equilibrium biosorption procedure was used to determine the best operating conditions for RBL, PPB and EGP. The effects of pH (3–7), time (5–720 min), temperature (298 and 323 K), Pb(II) and Cd(II) concentrations (50–700 mg/L), as well as the effect of the simultaneous presence of both metals on biosorption were investigated on the pristine and treated RBL. Analytical grade chloride salts of Pb(II) and Cd(II) were used for preparation of the salts. The concentrations of Pb(II) and Cd(II) used for the experiments were 700 and 400 mg/L, respectively, except where otherwise stated. Equal concentrations of Pb(II) and Cd(II) were used for the competitive adsorption (50, 100, 150, 200, 300 and 400 mg/L). The biosorbent (0.5 g each) and 20 mL of the metal solution were shaken on a thermostated mechanical shaker at 100 rpm during the course of the experiment. At the end of each experiment, the mixtures were centrifuged at 4500 rpm followed by determination of metals left in solution using the Buck Scientific 205 Atomic Absorption Spectrometer (AAS). All experiments were carried out in duplicate. The extents of metal biosorption on the sorbents were calculated (Eq. 1).

$$q_e = \frac{(C_o - C_e)V}{M} \quad (1)$$

where  $q_e$ ,  $C_o$  and  $C_e$  are the amount of metal ion adsorbed (mg/g), the initial and final metal concentrations in the solution (mg/L), respectively, and  $V$  (mL) and  $M$  (g) are,

respectively, the volume of solution and mass of adsorbent (Olu-Owolabi et al. 2015).

Equilibrium biosorption data were fit to and explained by the following equilibrium isotherm model—Langmuir (Langmuir 1916)—Eq. 2, Freundlich (Freundlich 1906)—Eq. 3 and Dubinin–Radushkevich (Dubinin and Radushkevich 1947)—Eq. 4. The biosorption kinetics data were explained using the Lagergren (Lagergren 1898) pseudo-first (Eq. 6) and pseudo-second-order (Eq. 7) equations, and intra-particle diffusion (Eq. 8) models (Di-agboya et al. 2016).

$$\text{Langmuir: } \frac{C_e}{q_e} = \frac{1}{Q_o b} + \frac{C_e}{Q_o} \quad (\text{Linear form}) \quad (2)$$

$$\text{Freundlich: } \log q_e = \log K_f + n \log C_e \quad (\text{Linear form}) \quad (3)$$

where  $Q_o$  (mg/g) and  $q_e$  is the maximum adsorption and amount of solute adsorbed per unit weight of adsorbent (mg/g), respectively.  $C_e$  is same as above;  $b$ ,  $K_f$ , and  $n$  are isotherm constants obtained from the slopes and intercepts.

$$\text{Dubinin – Radushkevich } \ln q_e = \ln X_m - \beta \varepsilon^2 \quad (4)$$

where  $X_m$  and  $\beta$  are the Dubinin–Radushkevich monolayer adsorption capacity (mg/g) and the constant related to sorption energy, respectively, and  $\varepsilon$  is the Polanyi potential which is related to the equilibrium concentration (Eq. 5).

$$\varepsilon = RT \ln \frac{1}{C_e} \quad (5)$$

$$\text{Pseudo – first – order (PFO)} \\ \log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (6)$$

$$\text{Pseudo – second – order (PSO)} \quad \frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (7)$$

$$\text{Intra – particle diffusion (IPD)} \quad q_t = K_d(t^{1/2}) + C \quad (8)$$

where  $q_e$  and  $q_t$  are the amounts of metals sorbed (mg/g) at equilibrium and at time  $t$ , respectively, and  $k_1$  and  $k_2$  are the rate constants ( $\text{min}^{-1}$ ). The  $q_e$  and rate constants,  $k$ , were calculated from the slopes and intercepts of the plots of  $\log(q_e - q_t)$  versus  $t$  and  $t/q$  versus  $t$ , respectively, for both equations.

## Results and discussion

### Solution pH

The pH of highest metal biosorption is an important parameter to be determined when establishing a new metal biosorbent for water treatment. This is imperative in biosorption because pH affects the ionization of functional

groups present on the surface of the biosorbents which are responsible for biosorption as well as the charge on the pollutant in solution (Okoli et al. 2014). Since various biosorbents have various surface functional groups, it is assumed that each will have different pH values of best biosorption for the different metals, thus the need to determine the pH values of best biosorption of the sorbents used in this study. Effect of pH on the biosorption of Pb(II) and Cd(II) ions from solutions has been determined by equilibrating the sorbent for 1440 min in simulated aqueous metal solutions at varying pH.

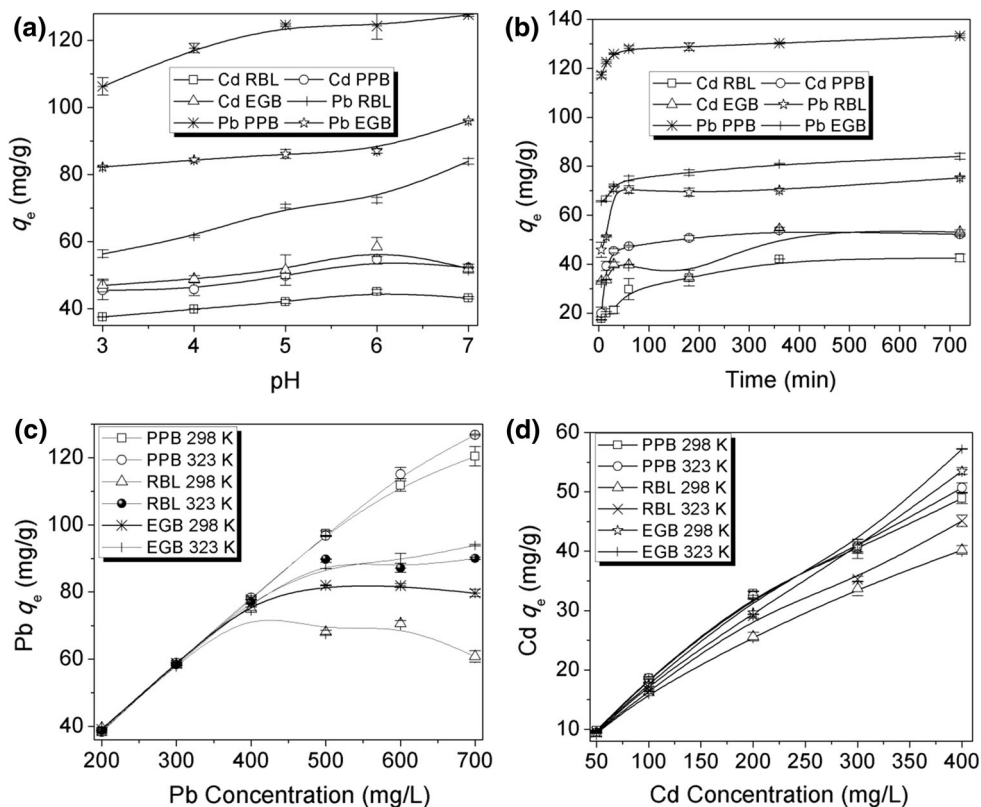
Figure 1a showed that the biosorption of Pb(II) and Cd(II) ions from the simulated aqueous solutions was pH dependent; amount of metal adsorbed increased with the increase in pH. At pH values less than 4.0, there is reduced polarity of the charged surfaces and the amount of functional groups ionized on the biosorbent surfaces was low due to effective competition between the cations and protons in solution (Olu-Owolabi et al. 2014). This results in few charged surfaces available for biosorption, hence the low amounts of metals adsorbed. However, as pH increased, the amount of protons in solution reduced, and there is less effective competition from protons for adsorption sites resulting in ionization of protonated functional groups, this is what brought about the enhanced biosorption observed. Increase in biosorption of the metals ions was observed until the pH values of 5 and 6 for Pb(II) and Cd(II), respectively. No significant Pb(II) biosorption was recorded after pH of 5.0 though lower equilibrium Pb(II) concentrations was recorded in solution above pH 6; this has been attributed mainly to solvation and formation of Pb(II) precipitates in solution above that pH (Olu-Owolabi et al. 2012). Further experiments on the operating variables for biosorption were carried out at pH 5 for Pb(II) and pH 6 for Cd(II), while experiments on the competitive biosorption of aqueous metal ions were done at a pH  $5.5 \pm 0.2$ .

Table 1 summarizes the quantity of each metal adsorbed by the RBL and the treated biosorbents. It was observed that while the PPB adsorbent was better for Pb(II) biosorption, the EGP adsorbent had better biosorption for Cd(II). At best pH values for biosorption, the metal sorption trend for Cd(II) ions was  $\text{EGP} > \text{PPB} > \text{RBL}$ , while it was  $\text{PPB} > \text{EGP} > \text{RBL}$  for Pb(II) ions.

### Biosorption kinetics

Metal removal rate is another important parameter that needs to be determined in order to ascertain the efficiency of any biosorbent to be used for wastewater treatment. The rates of Pb(II) and Cd(II) ions removal from the aqueous solutions have been determined in the time range of 5–720 min (Fig. 1b). The time for any biosorbent to be

**Fig. 1** Effects of **a** pH on Pb(II) and Cd(II) biosorption, **b** time on Pb(II) and Cd(II) biosorption, **c** temperature on Pb(II) biosorption, **d** temperature on Cd(II) biosorption



**Table 1** Quantity of metals adsorbed by various biosorbent modifications at best biosorption pH

Adsorbent	Metal ion	Best biosorption pH	Amount metal adsorbed (mg/g)
RBL	Cd(II)	6.0	45.1
PPB	Cd(II)	6.0	54.7
EGP	Cd(II)	6.0	58.4
RBL	Pb(II)	5.0	70.6
PPB	Pb(II)	5.0	124.6
EGP	Pb(II)	5.0	86.2

saturated by a metal sorbate can be determined by the time taken by 1.0 g of such biosorbent to reach maximum biosorption. Adsorption results showed that the biosorption of Pb(II) by all three biosorbents was faster than those of Cd(II); it took <60 min to obtain maximum Pb(II) biosorption, while it was 360 min for Cd(II) biosorption. After these points, there were no significant increases in adsorption for any of the metals. Increase in biosorption with time follows from the fact that at the beginning of the process, there were numerous vacant biosorption sites with very high affinity for metal sorption, hence the initial rapid increase in biosorption. As these vacant sites become filled up with the metals in solution, their high affinity for metals reduces, and at equilibrium, the remaining vacant surface sites become very difficult to occupy due to the repulsive forces between the solute molecules on the solid and bulk

phase. Olu-Owolabi et al. (2012) had stated that the breaking of some of the barrier of these repulsive forces and further biosorption is time dependent. It is suggested that chemisorption, a subsequent slow, often irreversible uptake, is responsible for much of the later biosorption which is specific and involves forces much stronger than physical biosorption.

The fits of the biosorption data to various kinetics models have been studied using the pseudo-first-order, pseudo-second-order and intra-particle diffusion models (Table 2). These were used to evaluate the metals biosorption mechanisms involved in the uptake of Pb(II) and Cd(II) ions from aqueous solutions by all three biosorbents, and the models showed that the data fit the pseudo-second-order kinetics better than for pseudo-first-order kinetics for both Pb(II) and Cd(II) biosorption in all

**Table 2** Kinetics parameters for Pb(II) and Cd(II) biosorption

Model	Model parameters	RBL		PPB		EGP	
		Pb(II)	Cd(II)	Pb(II)	Cd(II)	Pb(II)	Cd(II)
PFO	$q_e$ (mg/g)	19.6	23.0	13.3	9.6	16.3	20.5
	$k_1 \times 10^{-3}$ (min)	7.0	7.0	7.0	2.0	2.0	2.0
	$r^2$	0.83	0.95	0.92	0.40	0.98	0.68
PSO	$q_e$ (mg/g)	76.9	45.5	500	55.6	90.9	55.6
	$k_2 \times 10^{-3}$ (g/mg/min)	2.0	1.0	0.1	3.0	2.0	1.0
	$r^2$	0.99	0.99	0.74	1.00	1.00	0.98
IPD	$C$ (mg/g)	62.5	40.22	126.7	55.53	74.1	48.18
	$K_d$	1.65	1.10	1.92	1.33	1.78	1.44
	$r^2$	0.70	0.965	0.97	0.680	0.98	0.658
Experimental $q_e$ (mg/g)		75.3	42.7	133.3	53.8	85.0	54.2

three biosorbents. The values of correlation coefficients ( $r^2$ ) of the predicted and experimental values of the entire data set for the pseudo-second-order kinetics were closer to unity (0.98–1.00) than those of the pseudo-first-order kinetics (0.40–0.98). Thus, the pseudo-second-order kinetics adequately described the biosorption of Pb(II) and Cd(II) onto the surfaces of both the untreated and modified biosorbents, indicating that the rate controlling mechanism for the biosorption was chemisorption involving valence forces through sharing or exchange of electrons between the biosorbent and metal sorbates (Feng et al. 2011).

The effect of time data has also been evaluated by the intra-particle diffusion model in order to elucidate whether the biosorption process was surface phenomenon or a partitioning process. The values of intra-particle diffusion model parameter,  $C$  (mg/g), indicated the thickness of the surface adsorbed metal species and gave insight into the relationship between  $q_e$  and  $C$  values. According to the model, if the  $C$  value equals the experimental  $q_e$  values, then surface adsorption accounted for the bulk of the metal species removal from solution; if otherwise, then partitioning of metal species within the adsorbent was responsible for the sorption process (Weber and Morris 1963; Diagboya et al. 2014a). Comparing the  $C$  values to the experimental  $q_e$  (mg/g) values, it was observed that these metal ions adsorption were mainly surface phenomena on all sorbents.

**Equilibrium and isotherms studies**

Biosorption isotherms have been evaluated in this study at 298 and 323 K for Pb(II) and Cd(II) ions. The metal concentrations used for Pb(II) and Cd(II) ions were from 200 to 700 mg/L, and 50 to 400 mg/L, respectively. Figure 1c showed that for both Pb(II) and Cd(II) ions, temperature had an effect on the quantity of metal adsorbed. Higher temperature resulted in higher degree of metal adsorption.

This was more pronounced for Pb(II) than for Cd(II) ions. The increase in metal biosorption has been attributed to the fact that temperature is required to reduce the effect of the repulsive forces on the sorbents surfaces close to equilibrium (Olu-Owolabi et al. 2012). It was also observed in this study that for Pb(II) biosorption, PPB adsorbent had higher biosorption capacity than the other adsorbents; the biosorption trend is PPB > EGP > RBL. Thus, treatment of the biosorbent increased Pb(II) biosorption onto the RBL surfaces. Tripolyphosphate group is a well-known chelating agent, and on treatment of the RBL, the numerous phosphate of the tripolyphosphate group provided extra biosorption surfaces compared to ethylene glycol, hence the higher biosorption in PPB. Similar result has been reported by Unuabonah et al. (2007). However, Cd(II) biosorption followed a different trend with EGP having a higher adsorption value than the other biosorbents. The Cd(II) biosorption trend is EGP > PPB > RBL. The presence of the hydroxyl groups from ethylene glycol on the RBL surfaces provided additional biosorption sites for Cd(II) ions. Comparison of metal biosorption by the three biosorbents showed a higher preference for Pb(II) than Cd(II). This may be attributed to Pb(II)'s smaller hydrated radius when compared to Cd; the greater affinity of Pb for most functional groups; and its higher electronegativity, making it a better candidate for electrostatic and inner-sphere surface complexation reactions (Diagboya et al. 2015b).

Biosorption data obtained from this study have been fit to the Langmuir, Freundlich and Dubinin–Radushkevich adsorption isotherms (Table 3). It was observed that both the Langmuir and Freundlich adsorption isotherms could be used in describing the biosorption data;  $r^2$  close to unity and  $q_e$  and  $Q_o$  values close to experimental values. The Langmuir adsorption isotherm assumes that the adsorption sites possess equal affinity for the adsorbates and forms an adsorbate monolayer on the biosorbent surface at

saturation; the Freundlich isotherm assumes adsorption on heterogeneous surfaces with possible interactions between the adsorbate on the biomass surfaces and those in solution. The good fits of the data to both the Langmuir and Freundlich adsorption isotherms suggests that the final isotherm is made up of several Langmuir-type isotherms (Weber et al. 1992; Diagboya et al. 2015b; Olu-Owolabi et al. 2016); it has been shown that a combination of several Langmuir-type adsorption isotherm models occurring simultaneously can give a good approximation to the Freundlich-type isotherm model. The Dubinin–Radushkevich adsorption isotherm combines the assumptions of Langmuir and Freundlich isotherms; Table 3 shows that though the  $r^2$  values were close to unity, the  $X_m$  were not close to experimental values. Zhang et al. (2012) have suggested that the reason for the differences in experimental and  $X_m$  values may be caused by the time lag possibly due to a boundary layer or external resistance at play at the beginning of the biosorption. This time lag is difficult to quantify; thus, a trial and error method may be used to obtain the equilibrium metal uptake.

### Competitive biosorption of Pb(II) and Cd(II)

The effect of the simultaneous biosorption of Pb(II) and Cd(II) onto the surfaces of the various biosorbents has been studied within the concentration range of 50 and 400 mg/L (Fig. 2a–c). Both metals were observed to have identical biosorption trends as in the single metal solution experiments. The presence of Cd(II) ions in solution seem not to affect the biosorption of Pb(II) ions in solution; however, the presence of Pb(II) ions in solution affected to a significant extent the biosorption of Cd(II) ions from solution. For instance, the maximum biosorption capacity,  $Q_o$ , of Pb(II) ions was nearly unaffected in all biosorbents, but were reduced for Cd(II) ions by 44, 19 and 42% for RBL, PPB and EGP, respectively, following the trend PPB > EGP > RBL. Thus, Cd(II) ions biosorption in PPB was least affected by the presence of Pb(II) ions in solution. This result shows that though Cd(II) and Pb(II) ions may be adsorbed on similar adsorption sites, most biosorption of Cd(II) and Pb(II) ions onto the biosorbent surfaces occurs at sites with varying sorption affinity for Cd(II) and Pb(II) ions, and these sites are occupied

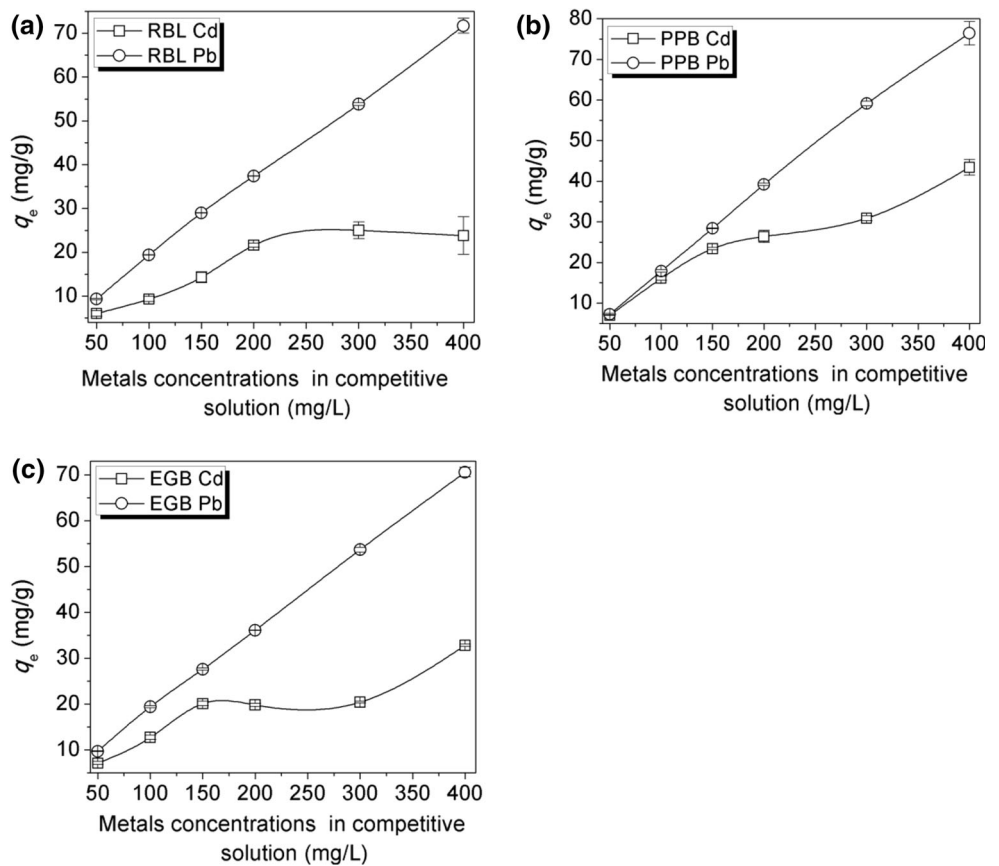
**Table 3** Biosorption isotherms

Model	Cd(II) parameters			Pb(II) parameters		
	RBL <sup>a</sup>	PPB	EGP	RBL <sup>a</sup>	PPB	EGP
Langmuir at 298 K						
$Q_o$ (mg/g)	43.48	50.0	58.8	62.5	125	83.3
$\beta$	0.04	0.09	0.04	0.19	0.50	4.00
$r^2$	0.97	0.98	0.91	0.99	1.00	1.00
Langmuir at 323 K						
$Q_o$ (mg/g)	50.0	52.6	58.8	90.9	143	100
$\beta$	0.04	0.07	0.05	0.69	0.47	0.50
$r^2$	0.96	0.98	0.91	1.00	1.00	1.00
Freundlich at 298 K						
$q_e$ (mg/g)	38.3	47.9	47.7	67.9	142	77.8
$K_f$	6.37	11.5	6.58	49.7	51.5	50.7
$r^2$	1.00	1.00	0.99	0.59	0.82	0.70
Freundlich at 323 K						
$q_e$ (mg/g)	41.7	50.1	48.9	78.1	157	94.3
$K_f$	7.19	9.23	8.24	47.86	49.66	51.64
$r^2$	0.98	0.99	0.98	0.72	0.80	0.75
D–R at 298 K						
$X_m$ (mg/g)	9.57	12.7	10.0	53.5	61.0	55.4
$r^2$	0.97	0.89	0.98	0.24	0.56	0.48
D–R at 323 K						
$X_m$ (mg/g)	10.0	12.4	10.8	55.5	63.2	56.4
$r^2$	0.98	0.91	0.97	0.55	0.51	0.58
Exp. value at 298 K						
$Q_o$ (mg/g)	42.7	53.9	57.0	63.6	129	84.2

D–R Dubinin–Radushkevich, Exp. value experimental value

<sup>a</sup> Olu-Owolabi et al. (2012)

**Fig. 2** Effect of competitive metal ions concentrations on Pb(II) and Cd(II) biosorption for **a** RBL, **b** PPB and **c** EGP

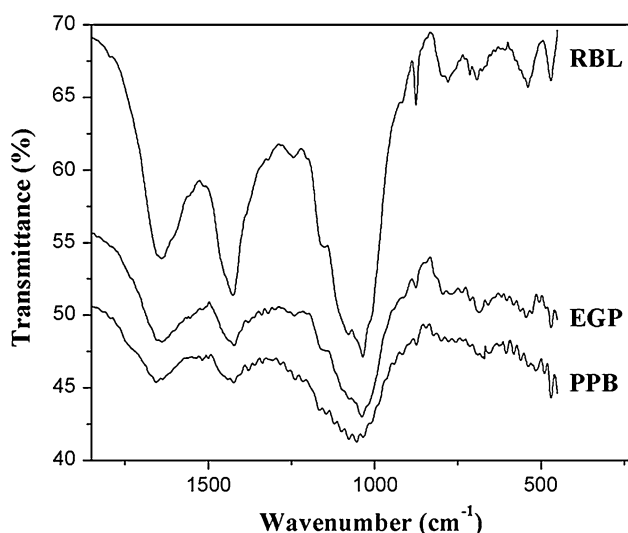


**Table 4** Review of sorption capacity ( $q_e$ ) of some sorbents for Pb(II) and Cd(II) sorption

Biomass	Cd(II) $q_e$ (mg/g)	References	Biomass	Pb(II) $q_e$ (mg/g)	References
EGP	54.2	Present study	PPB	133.30	Present study
PPB	53.8	Present study	Lignin	102.40	Guo et al. (2008)
RBL	42.5	Present study	Gracilaria sp	93.2	Sheng et al. (2004)
Gracilaria sp	33.7	Sheng et al. (2004)	EGP	85.0	Present study
Juniper fiber (treated)	29.5	Min et al. (2004)	Tea leaves	78.87	Tan and Abd Rahman (1998)
Rice husk (modified)	20.2	Kumar and Bandyopadhyay (2006)	RBL	75.3	Present study
Papaya wood	17.4	Saeed et al. (2005)	Tree fern	40.00	Ho et al. (2004)
Palm Petiolar-felth sheath	10.8	Iqbal et al. (2002)	Groundnut husks	39.40	Okieimen et al. (1991)
Juniper fiber (untreated)	9.2	Min et al. (2004)	Sphagnum moss peat	30.70	Ho et al. (2004)
Rice husk (raw)	8.6	Kumar and Bandyopadhyay (2006)	hazelnut shell	28.18	Pehlivan et al. (2009)
Corncob	5.1	Leyva-Ramos et al. (2005)	Sawdust	21.05	Li et al. (2007)

independent of the presence of the other metal ions in solution. At saturation of these sites, the common biosorption sites shared by both metals will then be filled. However, Pb(II) ions

are favored for biosorption onto these sites due to their smaller hydrated radius, and higher affinity for most functional groups (Diagboya et al. 2015b).



**Fig. 3** FTIR spectra of RBL, PPB and EGP

Figure 2a–c also shows a comparison of the  $q_e$  values of Cd(II) and Pb(II) ions as concentration of each metal increased in solution. For all three biosorbents, higher metal biosorption were recorded for Pb(II) than for Cd(II) ions, indicating that the effect of competition on the simultaneous biosorption of both metals was more pronounced on Cd(II) biosorption than on Pb(II).

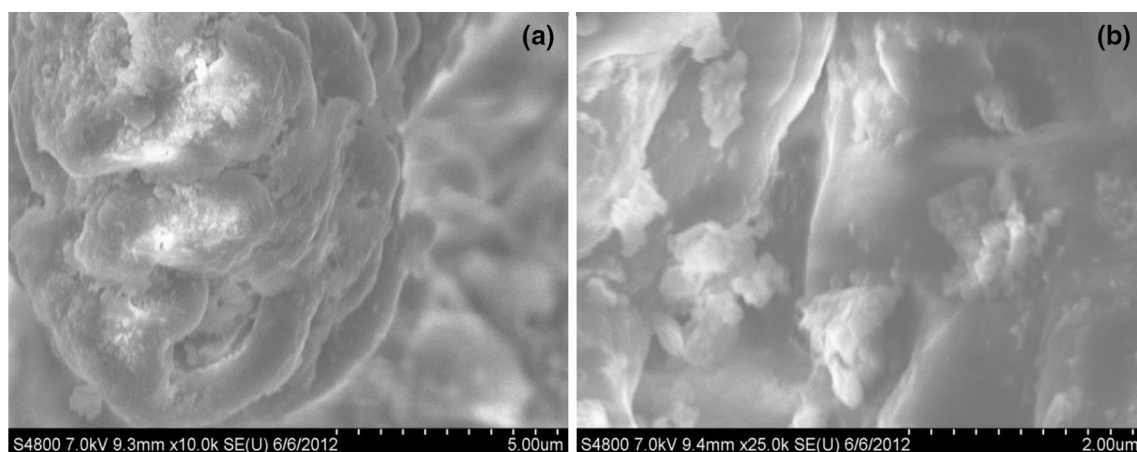
The adsorption capacities of the considered biosorbents have been compared to some alternative biosorbents reported in the literature (Table 4). The table shows that RBL, EGP and PPB were better than most of the biosorbents reported in the literature and that appropriate modification of the RBL can lead to cost-effective and enhanced treatment of wastewater.

### Physicochemical properties of the biosorbents

A description of the physicochemical parameters of biosorbents is necessary because the biosorbent particles

are usually not identical in physical and chemical properties such as size, shape, specific density, surface functional group. The physical and chemical parameters are important in estimating the biosorbent metal binding capacity. These parameters have been determined following methods described in Olu-Owolabi et al. (2012). Figures 3 and 4 and Table 5 show some of the major physicochemical parameters of the biosorbents studied. Treatment with tripolyphosphate caused an increase in the specific surface area of RBL from 11.4 m<sup>2</sup>/g to 17.6 m<sup>2</sup>/g in PPB. However, modification with ethylene glycol reduced the surface to 10.0 m<sup>2</sup>/g in EGP. The bulk density and specific gravity showed no changes upon modification. The pH<sub>PZC</sub> values which mark the pH where the surface functional groups do not contribute to the pH of the solution were relatively high when compared to those recorded in the literature for most biosorbents (Ibrahim et al. 2010; Malkoc 2006; Leyva-Ramos et al. 2005; Meena et al. 2007). RBL, PPB and EGP have pH<sub>PZC</sub> values in the range of 6.0–7.0. These high values may be an indication of a high amount of basic groups available on the surface of the biomass.

The FTIR spectra of RBL and the modified biomasses are shown in Fig. 3. The various functional groups attached to the biosorbent surface of RBL have been discussed extensively in Olu-Owolabi et al. (2012). These groups include carboxyl, carbonyl, thioesters, amides and hydroxyl. The FTIR spectra of the modified biomasses (EGP and PPB) were compared with that of the pristine biomass (RBL). PPB-modified biosorbent showed appearance of new peaks at 1081, 1102 and 1128 cm<sup>-1</sup>, indicating the presence of the phosphate, phosphonate and phosphate esters. However, the EGP-modified biosorbent showed no significant changes in its spectra except for the peaks' intensity changes around 1640 and 3400 cm<sup>-1</sup>, indicating the presence of O–H and amine-I band vibrations. Diagbaya et al. (2014b), Lee et al. (2001), Sureshkumar et al. (2010), Unuabonah et al. (2007), Yu et al. (2012) and Zeng



**Fig. 4** SEM images of the RBL showing surface morphology at a 5.00 μm, b 2.00 μm



**Table 5** Physico-chemical parameters of RBL, PPB, and EGP

	SG (g/cm <sup>3</sup> )	BD (g/cm <sup>3</sup> )	SSA (m <sup>2</sup> /g)	PZC
RBL	0.2	0.4	11.4	7.0
PPB	0.2	0.4	17.6	6.4
EGP	0.2	0.4	10.0	6.4

SSA specific surface area, BD bulk density, SG specific gravity

et al. (2011) had also shown that modification of sorbents by tripolyphosphate produced similar peaks, as well as enhanced adsorption. The enhanced adsorption performances of the modified biosurfaces were attributed to the presence of the above bands (Amosa et al. 2016; Cui et al. 2011; Zhou et al. 2010). Further insight into the nature of the RBL surface and as well as the biosorption process was obtained by the scanning electron microscopy (SEM) images (Fig. 4), and it was observed that the surface morphology was irregular and spongy in nature.

### Conclusion

*B. lambarenensis* was treated with sodium tripolyphosphate and ethylene glycol to improve its adsorption of aqueous Pb(II) and Cd(II) ions. These treatments enhanced physicochemical parameters such as surface area and the active functional moieties responsible for the cations adsorption. Biosorption of Pb(II) and Cd(II) ions was spontaneous. Tripolyphosphate and ethylene glycol treatments resulted in higher Pb(II) ions adsorption than the pristine RBL (74.9 and 14.4%, respectively) for individual metal ions, while the same treatments also resulted in higher Cd(II) ions adsorption than the pristine RBL (26.2 and 33.6%, respectively). Simultaneous adsorption data showed that tripolyphosphate treatment resulted in higher adsorption for both metals than in the pristine RBL and EGP treatment. Tripolyphosphate and ethylene glycol may be used to effectively treat *B. lambarenensis* to improve Pb(II) and Cd(II) ions adsorption from aqueous solutions.

**Acknowledgements** We acknowledge the supports of the World Academy of Sciences (TWAS), Trieste Italy and the Chinese Academy of Sciences (CAS), China, for the award of CAS-TWAS Post-graduate Fellowship (FR Number: 3240255024) to P. N. Diagboya; the Chief S.L. Edu/Chevron research grant; late Mrs. Rebecca A. Okoh and Mr. Victor P.O. Okoh, Department of Estate Management, School of Environmental Sciences, Yaba College of Technology, Lagos Nigeria.

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