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Biosorption of Pb(II) from aqueous solution using Rooibos shoot powder (RSP)

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ABSTRACT

Rooibos (*Aspalathus linearis*) plants are cultivated for the production of the Rooibos tea. In this work, biosorption process of Pb(II) from aqueous solution on Rooibos shoot powder (RSP) was studied in a batch process. The effect of experimental parameters such as solution pH (2–9), contact time (30–180 min) and initial Pb(II) concentration (25–400 mg L^{-1}), adsorbent dosage (0.2–2.1 g), and temperature (25–80˚C) on biosorption process was examined. In an attempt to determine the biosorption capacity and rate of Pb(II) removal, isotherm and kinetic data were modeled using different equations. To this end, the biosorption process by RSP followed the Langmuir model for Pb(II) ions ($R^2 = 0.9907$), with maximum monolayer adsorption capacity of 18.90 mg g^{-1}. Kinetic data were properly fitted with the pseudo-second order kinetic model, and it can be seen that the calculated q_e (cal) value (11.31 mg g^{-1}) agrees with the experimental value (12.80 mg g^{-1}). Furthermore, the biosorbent showed good removal of Pb(II) from industrial wastewaters.

Keywords: Biosorption; Rooibos shoot powder; Isotherm; Kinetics; Wastewater

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1. Introduction

In recent years, the drive for industrial development has led to the discharge of heavy metals into environmental wastewaters. The heavy metals cannot be biodegraded and the pollution tends to have accumulating characteristics in nature. These metals tend to exist in wastewater from many industries such as battery manufacturing, pigments, lead mining, printing, metallurgical alloying, photography, explosives, ceramics, leaded glass making, and metal plating [1]. Lead (Pb) is regarded as one of "the big three" of the heavy metals (others are Cd and Hg) due to its toxicity and potential hazard to the environment and organisms [2]. Lead can exist in organic and inorganic forms causing its bio-accumulation in plants, animals, and humans, which can ultimately result in serious environmental and human health related problems. The bio-accumulation of relatively low Pb(II) levels has been reported to damage the brain in children resulting in mental-related problems [1,3]. At high Pb(II)-level exposures, damage to the kidney, liver, nervous system, cardiovascular and reproductive systems in adults has been reported [4]. The permissible maximum concentration of Pb(II) in drinking water is fixed as 0.05 mg L^{-1} according to the US Environmental

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Protection Agency [5]. Consequently, the search of alternative methods for removing and reducing the concentration of Pb(II) ions in industrial wastewaters so that water quality standards are achieved is particularly significant.

Among the several methods to treat Pb(II)-contaminated industrial wastewaters are chemical precipitation, ion exchange, electrolysis, reverse osmosis, oxidation and reduction, fixation, cementation, and adsorption with activated carbon [1,6]. However, due to drawbacks such as the high cost, disposal of resulting sludge, and environmental concerns, associated with these methods, there is a dire need for cheaper and eco-friendly alternatives to remove Pb(II) ions from industrial wastewater. Biosorption is a recent technology that is gaining popularity as it is perceived to be relatively rapid, reversible, economical, and environmentally friendly [7]. The technology utilizes naturally occurring waste materials (biomaterials and agricultural products) for the removal of heavy metals from aqueous solutions [8–11]. The use of many low-cost biomaterials or agricultural waste (algae, sea weed, moss peat, peanut hull, plant biomass, sago waste, rice hull, coconut husk, and egg shell) has been reviewed [12–18]. Most of these have been reported as good biosorbents for removal of heavy metals from aqueous solutions [3,19,20].

Rooibos (*Aspalathus linearis*) plant is one of the few economic recognized plants that have transcended from a local wild resource to a cultivated crop. The shoot (stem and leaves) of this plant is used to produce an herbal infusion (Rooibos tea) internationally ascribed with important health promoting properties [21], including the potential to lower glucose levels in animals [22]. The plant is a member of the legume family and indigenous to the Cederberg region, in the northwest of Cape Town, South Africa, where the local communities have been using it to brew tea for centuries. This is the only place in the world where Rooibos grows naturally. The Rooibos bush is a small and shrubby bush, with thin needle-like leaves. The bush only grows between 1 meter to one and half tall. On the bush, the leaves are green, but once processed, they turn a deep red from the oxidization of the Rooibos leaves. The processing of the tea produces agro-wastes such as coarse shoot materials, fine dust, and rejected grades. Interestingly, large quantities of unique flavonoids, aspalathin (2′,3,4,4′,6′-pentahydroxy-3′-C-β-D-glucopyranosyldihydrochalcone) have been reported to be present in dried aerial parts of the plant [23]. The use of Rooibos plant waste in biosorption has not been reported. Hence, it is important to extend the investigation on the waste to fill a much-needed niche in the overall carbon market which is extremely high for the removal of Pb(II) from aqueous solution. Therefore, the focus of this study was to assess the potentiality of Rooibos shoot powder (RSP) biosorbent for the removal of Pb(II) from aqueous solution and wastewaters. The effects of pH, adsorbent dosage, contact time, and initial Pb(II) concentration were investigated. The biosorption isotherm and sorption kinetics of Pb(II) onto RSP are presented. Furthermore, application of the RSP for the removal of Pb (II) from environmental wastewater samples is presented.

2. Materials and methods

2.1. Preparation of biosorbent

The shoots (stem and leaves) were obtained from Rooibos (*A. linearis*) plants which were harvested from farmers' fields in the Cederberg region, northwest of Cape Town, South Africa. The fresh shoots collected were hand-washed with tap water followed by distilled water and sun dried. Drying at 60°C in an oven for 72 h removed most of the moisture. The dried material was crushed to powder, and the fine powder was further fractionated into different particle sizes. The size fractions ranging from 150 to 300 μm were used for adsorption studies.

2.2. Preparation of metal ion solution

A stock solution of Pb(II) was prepared from pure analytical grade (>97%) lead nitrate ($Pb(NO_3)_2$) obtained from Merck (Pretoria, South Africa). About 1.6 g of lead nitrate was weighed and dissolved in a 1,000-mL volumetric flask and topped up to the mark with distilled water. The solution was stirred to obtain a homogeneous stock solution. The used concentrations were obtained by dilution of the stock solution. A pH meter (Crison 2001 micropH, Spain) was employed for measuring pH values in the aqueous phase after adding either 1 M HNO_3 or 1 M NaOH. All the necessary chemicals used in the study were of analytical grade.

2.3. Biosorption experiments

The biosorption capacity of RSP for Pb(II) ions, with respect to pH, was carried in the range of 2–9. Briefly, 100 mg L^{-1} of Pb(II) was placed in 100-mL flasks, followed by 0.2 g of RSP. The mixtures were stirred using a mechanical shaker at 100 rpm for 60 min at 25°C.

For studying, the effect of dosage, 100 mg L^{-1} of Pb(II) was placed in twelve different flasks. Different dosages of RSP, ranging from 0.2 to 2.1 g were added. The mixtures were placed on the shaker and stirred at 100 rpm for 60 min at 25°C.

To study the effect of contact time, 100 mg L^{-1} of Pb(II) was placed in different flasks at pH 6.7 and 0.2 g of RSP was added to each flask. The solutions were stirred at 100 rpm at different durations of time: 30, 60, 90, 120, 150, and 180 min at 25°C.

For initial metal concentration, different Pb(II) ion concentrations; 25, 100, 150, 180, 200, 250, 300, and 400 mg L^{-1} were placed in 100-mL Erlenmeyer flasks at pH of 6.7. Then, 0.2 g of RSP was added into each flask followed by mechanical shaking at 100 rpm for 60 min at 25°C.

The temperature was investigated in the range 25–80°C. Briefly, 100 mg L^{-1} of Pb(II) was placed in different flasks at pH 6.7 and 0.2 g of RSP was added. The solutions were stirred at 100 rpm for duration 60 min at different temperatures.

After mechanical shaking during investigation of each parameter, the solutions were centrifuged for 3 min and filtered with a 0.45-μm membrane filter immediately. Blank solutions (without biosorbent) were also processed. The supernatant liquid was analyzed by atomic absorption spectrometer (Shimadzu AA-140, Japan) linked to a HP Compaq with an HPL1906 at a wavelength of 217.0 nm. The percentage removal of Pb(II) was calculated according to the following equation:

$$R = \frac{(C_o - C_e)}{C_o} \times 100\% \tag{1}$$

The amount of Pb(II) adsorbed by the biosorbent was calculated using the following equation:

$$q_e = \frac{(C_o - C_e)V}{M} \tag{2}$$

where q_e is the amount (mg g^{-1}) of Pb(II) adsorbed by RSP, C_o, and C_e are the metal concentrations (mg L^{-1}) in the solution initially and after biosorption, respectively, V is the volume (L) of the solution, and m is the mass (g) of biosorbent used in the experiment.

3. Results and discussion

3.1. Effect of sorption parameters

3.1.1. Effect of pH

The solution pH is an important factor affecting metal biosorption onto the biosorbent [7]. This might be due to H^+ ions themselves strongly competing with the biosorbate. The batch biosorption experiments were conducted within a range of pH 2.0–9.0. The results obtained are presented in Fig. 1. The biosorption was found to be minimum (11%) at pH 2.0. At low pH values, the removal of Pb(II) ions from solution was low possibly due to electrostatic repulsion forces between positively charged H^+ and Pb^{2+} ions. The functional groups available on the surface of the adsorbent are protonated, which means the majority of the binding sites for the Pb(II) ions are occupied by the protons. The biosorption removal increased from 11 to 90% at pH 2.0–6.7, respectively. On the other hand, a slight decrease in biosorption of Pb(II) ions after pH 6.7, was observed perhaps due to the formation of $Pb(OH)_2$ and soluble hydroxyl complexes such as $PbOH^+$, aqueous $Pb(OH)_2$, and $Pb(OH)^{3-}$ and the biosorbent deteriorating with accumulation of Pb(II) ions making binding to sites impossible. Similar results were reported in literature for wheat bran [24] and spent grain [25]. Hence, further biosorption experiments were carried at an optimum pH 6.7.

3.1.2. Effect of biosorbent dosage

The dosage of an biosorbent strongly influences the extent of sorption. The results obtained from varying biosorbent dosages from 0.2 to 2.1 g are presented in Fig. 2.

As shown in Fig. 2, the biosorption capacity decreased from 15.09 to 0.73 mg g^{-1} with an increase in RSP biosorbent dosage. On increasing biomass concentration further, the biosorption capacity of Pb(II) decreased perhaps due to overlapping or aggregation of biosorption sites resulting in a decrease in the total adsorbent area [7]. A biosorbent dose of 0.2 g was used in further experiments since it was sufficient for optimum biosorption of Pb(II).

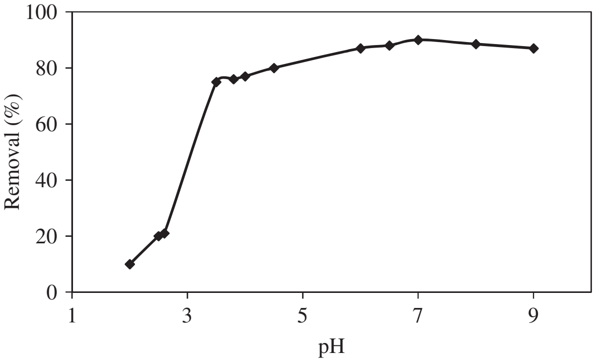

Fig. 1. Effect of pH on Pb(II) biosorption (C_o = 100 mg L^{-1}, biosorbent dosage = 0.2 g, T = 25°C, t = 60 min).

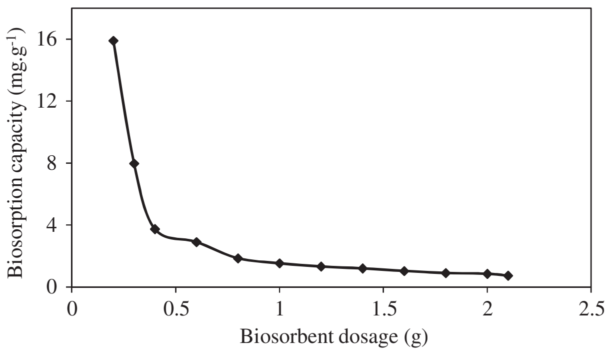

Fig. 2. Effect of biosorbent dosage on Pb(II) biosorption (pH 6.7, $T = 25^\circ$C, $C_o = 100$ mg L^{-1}, $t = 60$ min).

3.1.3. Effect of contact time

Contact time is one of the factors required when selecting wastewater treatment systems. The amount of Pb(II) biosorbed at definite intervals of time (30–180 min) was monitored for a fixed amount of RSP as shown in Fig. 3.

It is obvious that with the increase in time (Fig. 3), the biosorption rate of the Pb(II) over the RSP increases, and almost 60 min was required to bring complete saturation of the active sites. The maximum biosorption capacity was 12.80 mg g^{-1}. The high sorption rate with increasing time is due to attraction of active functional groups toward Pb(II) which led to stronger surface binding. As the surface sites of the RSP became exhausted, the uptake rate is controlled by the rate at which the Pb(II) ions are transported from the exterior to the interior sites. Therefore, 60 min was seen as sufficient for biosorption to attain equilibrium and adopted in further experiments.

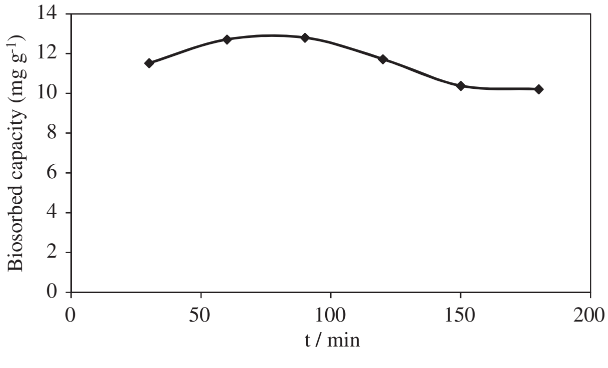

Fig. 3. Effect of contact time on Pb(II) biosorption (pH 6.7, biosorbent dosage = 0.2 g, $C_o = 100$ mg L^{-1}, $T = 25^\circ$C).

3.1.4. Effect of initial metal concentration

The effect of initial metal concentration on the biosorption rate was analyzed within the range 25–400 mg L^{-1} for Pb(II) ions (Fig. 4). As shown in Fig. 4, an increase in the biosorption capacity of the Pb(II) with increasing initial concentrations was observed. The Pb(II) biosorption capacity went up from 1.77 to 15.53 mg g^{-1}. The initial rapid increase in the biosorption capacity of Pb(II) can be attributed to the availability and interaction of active sites of the RSP. At higher concentration, more Pb(II) ions are left unadsorbed in the solution due to the saturation of the RSP binding sites.

3.1.5. Effect of temperature

The biosorption of Pb(II) on RSP was investigated as a function of temperature in the range of 25–80°C (Fig. 5). As shown in Fig. 5, the biosorption capacity of RSP for Pb(II) increased with up to 45°C indicating that the sorption process was endothermic. The small increase in biosorption may be due to the desolvation of the sorbing species and change in the size of the pores [26]. However, above 45°C, the sorption of Pb(II) slowly decreased. The main reason might be that at high temperatures, the thickness of the boundary layer decreases, due to the increased tendency of the Pb(II) ion to escape from the RSP biomass surface to the solution phase. For further studies, a temperature of 25°C was selected.

3.2. Biosorption isotherms

Biosorption equilibrium is established when the amount of solute being biosorbed onto the biosorbent is equal to the amount being desorbed [27]. An

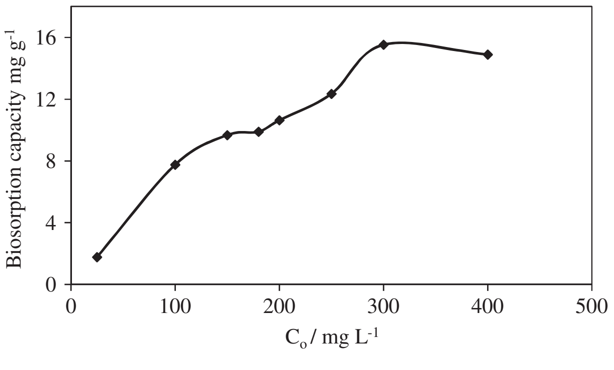

Fig. 4. Effect of initial concentration on Pb(II) biosorption (pH 6.7, biosorbent dosage = 0.2 g, $T = 25^\circ$C, $t = 60$ min).

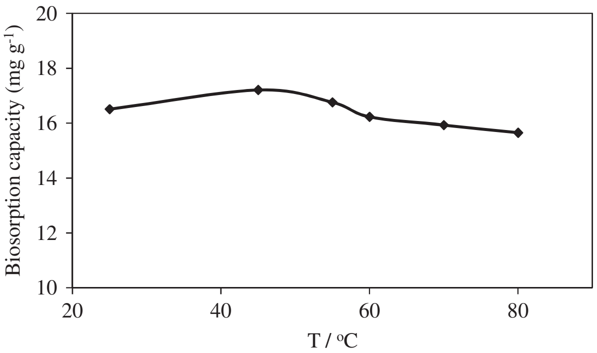

Fig. 5. Effect of temperature on Pb(II) biosorption (pH 6.7, biosorbent dosage = 0.2 g, $C_o = 100$ mg L^{-1}, $t = 60$ min).

equilibrium biosorption isotherm is predicted when the solid phase concentration is plotted against liquid phase concentration graphically. In this study, two models, namely Langmuir and Freundlich, were used to interpret the equilibrium data [28,29].

The Langmuir model assumes that biosorption occurs on a homogenous surface by monolayer sorption without interaction between biosorbed molecules. The linear form of the Langmuir isotherm model can be represented by:

$$\frac{C_e}{q_e} = \frac{C_e}{q_{\max}} + \frac{1}{bq_{\max}} \tag{3}$$

where Langmuir constants $q_{\max}$ (mg g^{-1}) and b (g L^{-1}) can be determined from the linear plot of C_e/q_e vs. C_e, which has a slope of $1/q_{\max}$ and an intercept of $1/q_{\max}b$.

The Freundlich model assumes a monolayer sorption with heterogeneous energetic distribution of active sites and with interaction between biosorbed molecules. It is expressed as:

$$q_e = K_F C_e^{\frac{1}{n}} \tag{4}$$

The parameters can be linearized by taking logarithms to determine the parameters K_F and n:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \tag{5}$$

where q_e (mg g^{-1}) is the amount of metal ion adsorbed at equilibrium by the biosorbent, C_e (mg L^{-1}) is the equilibrium concentration, and K_F (mg g^{-1}) and n are constants representing the biosorption capacity and intensity of absorption. A plot of $\ln q_e$ vs. $\ln C_e$ gives a straight line, and K_F and n can be calculated from the intercept and slope, respectively.

Fig. 6(a) and (b) shows the Langmuir and Freundlich biosorption isotherm, respectively. The Langmuir constants b and $q_{\max}$, Freundlich constants n and K_F, and their corresponding correlation coefficients, R^2 are given in Table 1. The calculated value of $q_{\max}$ from the Langmuir isotherm plot was 18.90 mg g^{-1} and the coefficient of determination, $R^2 = 0.9907$ was obtained. It can be concluded that the equilibrium data fitted well with the Langmuir isotherm model. The calculated value of Freundlich constant n was 2.96 and represented beneficial biosorption since it falls between 1 and 10. However, the linearized equation did not give good correlation ($R^2 = 0.9272$) indicating that the Freundlich model was not so adequate to describe the equilibrium relationship. The adsorption capacity ($q_{\max}$) of Pb(II) onto RSP was compared with other adsorbents reported in the literature [30–35] and is shown in Table 2. It can be seen from the table that RSP shows good biosorption capacity revealing that it can be considered as a viable biosorbent for the removal of Pb(II) from aqueous solutions.

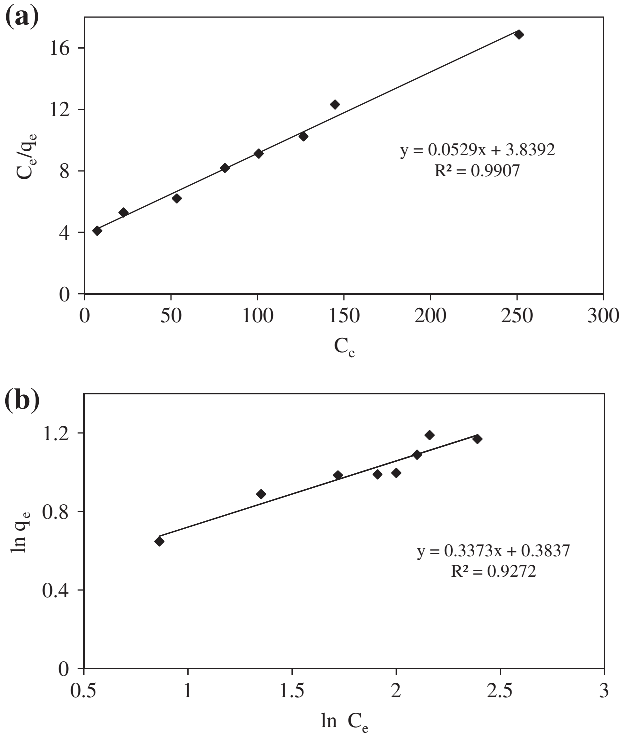

Fig. 6. (a) Langmuir isotherm (b) Freundlich isotherm for Pb(II) biosorption (biosorbent dosage = 0.2 g, $t = 60$ min, $T = 25$°C, pH 6.7).

Table 1
Langmuir and Freundlich constants for Pb(II) biosorption onto RSP

Adsorption isotherm	Parameter	RSP
Langmuir	$q_{\max}$ (mg g^{-1})	18.90
	b (L mg^{-1})	0.014
	R^2	0.9907
Freundlich	K_F (mg g^{-1})	1.47
	n	2.96
	R^2	0.9272

Table 2
Comparison of biosorption capacity with other biosorbents

Biosorbent	$q_{\max}$ (mg g^{-1})	References
Groundnut hull	31.54	[30]
Hazelnut husks	13.05	[31]
Paper mill waste	14.1	[32]
Portulaca plant	17.24	[33]
Barley straw	23.20	[34]
Baobab fruit shells biomass	7.65	[35]
RSP	18.90	This study

3.3. Biosorption kinetics

The biosorption kinetics of Pb(II) onto RSP was investigated with the aid of three kinetic models, Lagergren's pseudo-first-order model [36], Ho and Mckey's pseudo-second-order model [37] and intra-particle diffusion model [38] to analyze experimental data.

3.3.1. Pseudo-first-order kinetic model

The pseudo-first-order model which assumes that the rate of biosorption site occupation is proportional to the number of unoccupied sites is expressed linearly as follows:

$$\log(q_e - q_t) = \log q_e - \frac{t \cdot k_1}{2.303} \tag{6}$$

where q_e and q_t are the amount of Pb(II) biosorbed (mg g^{-1}) onto RSP at equilibrium and at any time t, k_1 (min^{-1}) is the rate constant of pseudo-first-order model and t is the time (min). Plotting log ($q_e - q_t$) vs. t, the values of k_1 and q_e are determined from the slope and the intercept, respectively.

3.3.2. Pseudo-second-order kinetic model

The pseudo-second-order model assumes that the rate of occupation of biosorption sites is proportional to the square of the number of unoccupied sites [26]. The integrated linear equation is expressed as:

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{k_2 (q_e)^2} \tag{7}$$

where k_2 is the equilibrium rate constant of pseudo-second-order kinetic model (g mg^{-1} min^{-1}). The values of q_e and k_2 are determined from the slope and intercept of the plot of (t/q_t) vs. t, respectively. The plots of pseudo-first-order and pseudo-second-order models for Pb(II) adsorption on RSP are shown in Fig. 7(a) and (b), and the biosorption kinetic parameters are presented in Table 3.

The coefficient of determination for the pseudo-first-order model was $R^2 = 0.893$, indicating that it could not be used to describe the entire adsorption process well. The correlation coefficient (R^2) value of the pseudo-second-order kinetic model was 0.9992 and the q_e (cal) value agrees well with the experimental value. The results suggest that the pseudo-second-order model describes the biosorption kinetics of the present system.

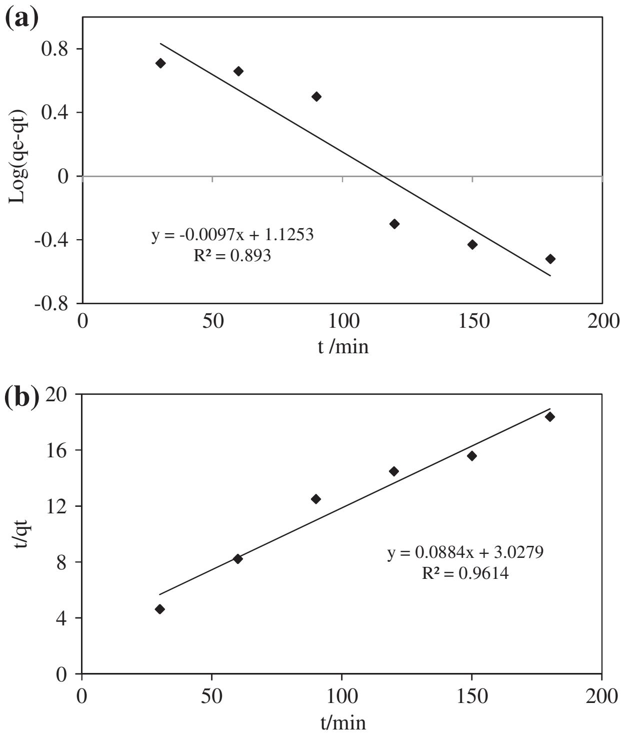

Fig. 7. (a) Pseudo-first-order plot (b) pseudo-second-order plot for biosorption of Pb(II) ions onto RSP (C_o = 100 mg L^{-1}, biosorbent dosage = 0.2 g, T = 25°C, pH 6.7).

Table 3
Rate constants for Pb(II) biosorption on RSP

Adsorbent	Experimental value q_e (mg g^{-1})	Pseudo-first-order kinetic model			Pseudo-second-order kinetic model		
		q_e (mg g^{-1})	k_1 (min^{-1})	R^2	q_e (mg g^{-1})	k_1 (g mg^{-1} min^{-1})	R^2
RSP	12.80	3.08	2.58 × 10^{-2}	0.8752	11.31	2.58 × 10^{-3}	0.9614

3.3.3. Intra-particle diffusion model

The intra-particle diffusion plays an important role in order to gain insight into the mechanisms and rate controlling steps affecting the kinetics of biosorption. The linear form can be expressed as:

$$\log R = \log\ K_s + b \log\ t \tag{8}$$

where R is the percent Pb(II) biosorbed, t is the contact time (min), b is the gradient of linear plots, and K_s is the intra-particle diffusion constant. The plot of log R vs. log t shown in Fig. 8 is linear showing that intra-particle diffusion was involved in the biosorption process. The kinetic constants for intra-particle diffusion were K_s (13.84), b (0.23), and R^2 (0.8578). However, the plot does not pass through the origin indicating some degree of boundary layer control and further showing that the intra-particle diffusion is not the only rate-limiting step, but also other kinetic models may control the rate of biosorption, all of which may be operating simultaneously.

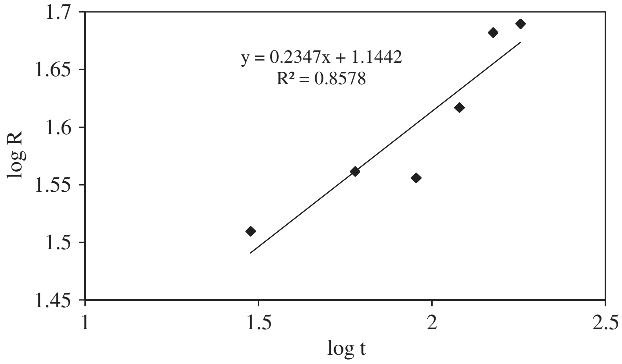

Fig. 8. Intra-particle diffusion plot (log$R$ vs. log$t$) (C_o = 100 mg L^{-1}, biosorbent dosage = 0.2 g, t = 60 min, T = 25°C, pH 6.7).

3.4. Application of RSP in the treatment of industrial effluents

Raw industrial effluents without treatment were collected from local industries into plastic containers and taken to the laboratory for analysis. After filtration, the initial concentrations of Pb(II) and pH were measured and recorded (Table 4). Batch experiments were carried out under optimized conditions such as pH 6.7, temperature 25°C, dosage concentration 0.2 g/100 mL, and contact time 60 min to evaluate the performance of RSP for the removal of Pb(II). The results are shown in Table 4. About 67 and 78% of Pb (II) were removed from effluents of Namakwa Sands and Rand Uranium, respectively. Table 4 shows the efficacy of RSP biosorbent for the removal of Pb(II) from environmental wastewaters.

4. Conclusions

The biosorption of Pb(II) onto RSP was found to be dependent on factors such as pH, adsorbent dosage, temperature, contact time, and concentration of Pb(II). The results obtained are as follows:

1. pH 6.7 was deduced as optimum for the removal of Pb(II).
2. Biosorption uptake decreased with increasing biosorbent dosage and increased with increasing Pb(II) concentration.

Table 4
Composition of the effluent from industrial sites

Parameter	Namakwa Sands effluent		Rand Uranium effluent	
	Before biosorption	After biosorption	Before biosorption	After biosorption
pH	1.99	6.71	2.88	6.70
Pb (mg L^{-1})	0.09	0.03	0.52	0.11

(3) The equilibrium time for RSP was 60 min.
(4) Biosorption followed the pseudo-second order model.
(5) Langmuir isotherm model best described the biosorption mechanism.

The results from this study show that RSP may be used as a low-cost, eco-friendly, and effective biosorbent to remove Pb(II) from environmental wastewaters.

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